

# Study on Recycling of the Food Wastes Considering Environmental Load

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## Abstract

In modern society, it is essential to reuse waste in all fields based on the SDGs, and waste recycling has improved rapidly since around 1996. Many recycling methods have been proposed to further increase the recycling rate. Among them, some industries have very few types of recycling methods, which are food waste. In the recycling of food waste, highly efficient resource recycling technology is not necessarily advanced because the composition of the waste is unstable. The amount of recycled food waste is about 50 percent of the amount generated, and most of it is used as fertilizer or feed. The recycling rate has been flat for a long time because there are few other resource utilization methods. Therefore, in this study, the food waste is recycled by methods other than feed and fertilizer. Also, the cost needs to be reduced as much as possible due to the large amount of waste. From these facts, the recycling method is examined for three food wastes. The three food wastes are rice husk, fishbone, and sugar syrup, respectively. Rice husks are discarded from agriculture, fishbones are discarded from fisheries, and sugar syrups are discarded in large quantities from households due to expiration. Rice husk and fishbone are reused as adsorbents for harmful substances, and waste syrup is reused as a concrete admixture. Alternatively, as for fish bone, a new functional adsorbent using fishbone is developed. As a result of each test, it is possible to achieve both environmental purification and volume reduction of waste by recycling waste.

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# 1 . Introduction

## 1.1 Framework of this thesis

The effort of the SDGs worldwide is attracting attention, and development to form a sustainable society around the world is conducted mainly by developed countries. The SDGs set targets for 17 items such as poverty, education, energy and resources. In Japan, where land is small and resources are scarce, recycling of waste is an important factor. It is necessary to reduce the volume of waste and consider safe disposal methods for sustainable development and the continuity of society. Since the idea of a recycling-oriented society was advocated in 2001, the amount of waste generated in Japan has been greatly improved. However, the amount has not changed in recent years. This is because the recycling of waste has not progressed depending on the type of industry. The recycling rate of food waste from agriculture and fisheries in the primary industry or households have not been improved because new methods of recycling other than fertilizer and feed have not been established. Disposal of food waste by landfill or incineration has a negative impact on the environment. In addition, it has led to a shortage of disposal sites, which is one of the factors that hinder the formation of a circulating society. Therefore, in this study, the aim is to achieve both volume reduction of food waste and environmental purification. This thesis is summarized these studies, and consisted of the following six chapters. In Chapter 1, the food waste treatment methods and status, the guidelines for recycling, past studies, and issues are discussed. Then, the significance and purpose of this study are shown based on issues. In Chapter 2, the results of test and analysis on rice husk are described. The adsorption performance of harmful substances such as cesium and heavy metals is verified by using the aromatic properties of rice husks. For the cesium, an extraction test for simulated contaminated soil is performed with the aid of the concept of electrophoresis, and the immersion test is performed for heavy metals. The adsorption concentration for each ion is shown and the adsorption performance is discussed. In Chapter 3, the results of test and analysis on the waste fish bone are described. A porous adsorbent based on calcium phosphate, FbA (Fishbone Absorber, or if powdered, FbP (Fishbone Powder)) is produced by boiling and firing the discarded fish bone. Then, the adsorption performance of the FbA and the FbP to heavy metals and strontium is verified by immersion or shaking test. In Chapter 4, the results of test and analysis on FFP (Functional Fishbone Powder) are described. The rice husk and fishbone described in the previous chapter did not show an adsorption effect on anions, especially arsenic, which is highly dangerous to the human body. Therefore, the FFP, a

new adsorbent based on the FbP, is prepared and a shaking test is performed to analyze the adsorption performance. Furthermore, an adsorption isotherm is created from the results of the shaking test, and the adsorption mechanism is examined. In Chapter 5, the results of test and analysis on waste syrup are described. Hexavalent chromium is contained in cement in a large amount. Hexavalent chromium may be eluted into the environment from ground improvement materials using cement solidification materials and recycled materials such as recycled roadbed materials. The effect of suppressing elution is verified using waste syrup as an admixture for concrete in order to prevent eluting the hexavalent chromium. A uniaxial compression test and a dissolution test are conducted on the specimens to which waste syrup is added, and their results are shown. In Chapter 6, this thesis is summarized.

## 1.2 Background and object of study

Japan rapidly achieved economic growth after the postwar high economic growth. The basic factors due to high economic growth are the introduction of technological innovation, the increased investment and the securing of a young workforce. Companies invested in capital to make production facilities in line with the introduction of European and American technological innovations. That prompted other companies to invest in capital, and the investment generated next investments, which lead to a rapid expansion of capital investments. As the results, business investments led to the increase both employment and productivity. The high economic growth made Japan the second largest economy in nations, and the people's income and living standards raise. On the other hand, environment disruption was caused by factory wastewater and exhaust gas because mass production and mass consumption were repeated in the whole society. In addition, the environmental destruction and the shortage of disposal sites are caused by an increase in industrial waste from companies and general waste from households <sup>1)</sup>. Change in general waste emissions is shown in Fig. 1.1, and change in industrial waste is shown in Fig. 1.2 <sup>2)</sup>. In the trend of general waste emissions, the total amount of waste and the amount per person per day has slightly decreased since the second oil crisis in 1979. After that, it has increased rapidly from around 1985, and has flat or slightly increased since 1990. The amount of emissions has decreased since 2001 and has reached 43.98 million tons in 2015. The total amount of resources recycled in 2015 is 9 million tons, and the recycling rate for the total amount of waste is greatly increased from 5.3 percent in 1990 to 20.4 percent. Additionally, focusing on the status of industrial waste emissions since 1990, there is no significant change at around 400 million tons, and it is almost flat. Alternatively, the changes in the residual capacity and the remaining years of final disposal sites for general waste are shown in Fig. 1.3, and those of industrial waste are shown in Fig.

1.4 <sup>2)</sup>. As at the end of 2015, the final disposal site for general waste has 1,677, the remaining capacity is 104.04 million m<sup>3</sup> and the remaining years are 20.4 years for the national average. The remaining capacity has been decreasing, and the remaining years has been increasing. As at the end of 2014, the remaining capacity of the final disposal site for industrial waste is 166.44 million m<sup>3</sup>, which is about 5.76 million m<sup>3</sup> less than the previous year. Also, the remaining years are 16.0 years for the national average. The remaining years in the metropolitan area is 5.4 years although the remaining years are gradually improving. Especially, the remaining capacity in metropolitan areas is decreasing. Therefore, urgent reduction of waste volume and elimination of disposal site shortage are required.

In recent years, the society of mass production and the mass consumption turned into a recycling society in order to eliminate environmental destruction, resource shortage and disposal site shortage. In modern society, it is essential to reuse waste in all fields based on the three R concepts (see Fig. 1.5). Waste recycling has improved rapidly since around 1996. The recycling

rate of general waste and the recycling rate of industrial waste are shown in Fig. 1.6 and Fig. 1.7<sup>3)</sup>, respectively. The recycling rate of general waste has increased until around 2007 and has been around 20 percent ever since. Also, the recycling rate of industrial waste has increased until around 2004 and has been around 53 percent since then. Many recycling methods have been proposed to further improve the recycling rate. Among them, some industries have very few types of recycling methods, which is food waste. The classification of food waste is shown in Fig. 1.8<sup>4)</sup>. Food wastes include both industrial wastes and general wastes, each of which is mixed with various types of foods. In the recycling of food waste, highly efficient resource recycling technology is not necessarily advanced because the composition of the waste is unstable. The status of food waste generation and treatment are shown in Table 1.1<sup>5)</sup>. The amount of recycled food waste is about 50 percent of the amount generated, and most of it is used as fertilizer or feed. Many wastes cannot be recycled, and about 50 percent of the generated amount is incinerated or landfilled. It is considered that the recycling rate can be improved by establishing a recycling method other than using fertilizer and feed. Therefore, the purpose of this study is to propose and establish a new method of recycling food waste.

In 2000, a law on the recycling of food waste is enacted, and resources are recycled<sup>6) 7)</sup>. There are various proposed methods of recycling existing food waste. For example, both study using high-pressure fluid and using methane gas fermentation are conducted as past research on fertilizer and feed conversion<sup>8) 9)</sup>. In both studies, the process for recycling is complicated and expensive. Besides, the studies using food waste for the cultivation of brown beech mushroom have revealed that the fertilizer derived from vegetable waste promotes hyphal growth<sup>10)</sup>. However, the waste cannot be consumed in large quantities, and it cannot be said that it contributes to the improvement of the recycling rate. Therefore, in this study, the recycling method which considers the following two points is examined. One is to devise a recycling method other than feed and fertilizer to improve the recycling rate. The other is to consider low-cost recycling methods. The cost should be reduced as much as possible due to the large amount of waste. From these facts, three food wastes are selected, and the recycling method is examined for each waste. The three food wastes are rice husk, fish bone, and sugar syrup. Rice husks are discarded from agriculture, fish bones are discarded from fisheries, and sugar syrups are discarded in large quantities from households due to expiration. They have few effective recycling methods and are discarded. In this study, the recycling methods focusing the characteristics of each waste are examined. Each study outcome is shown in each chapter.

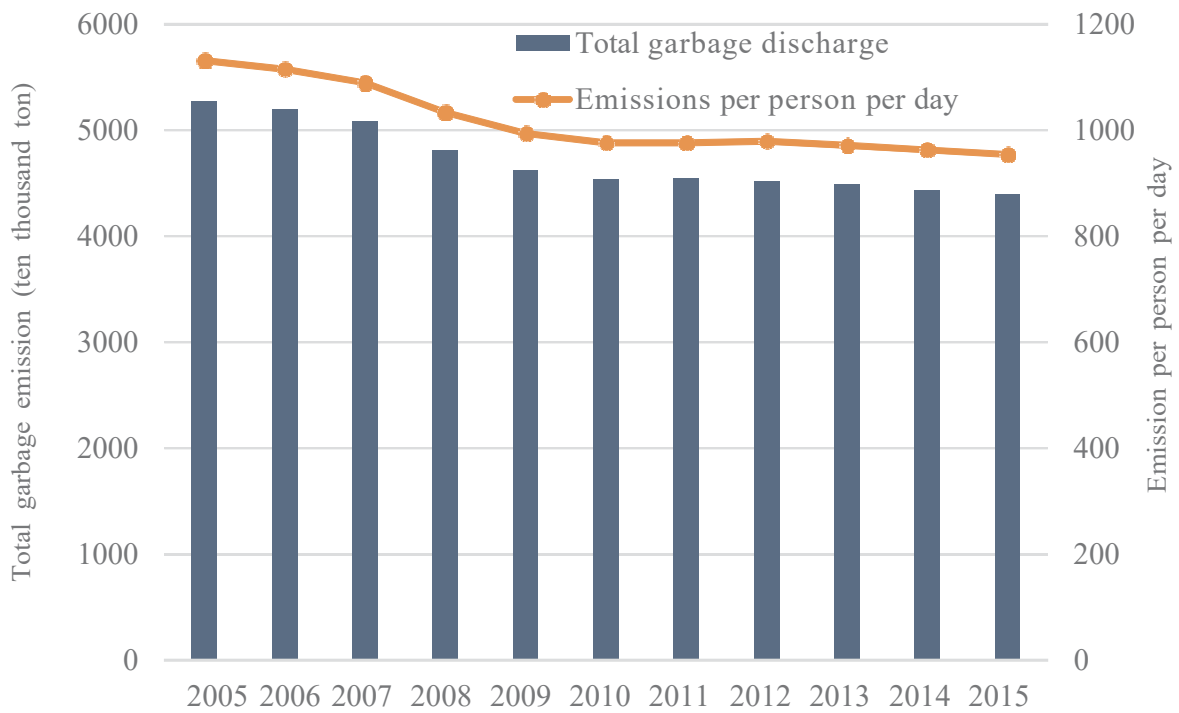


Fig. 1.1 Changes in total garbage emissions and garbage emissions per person per day

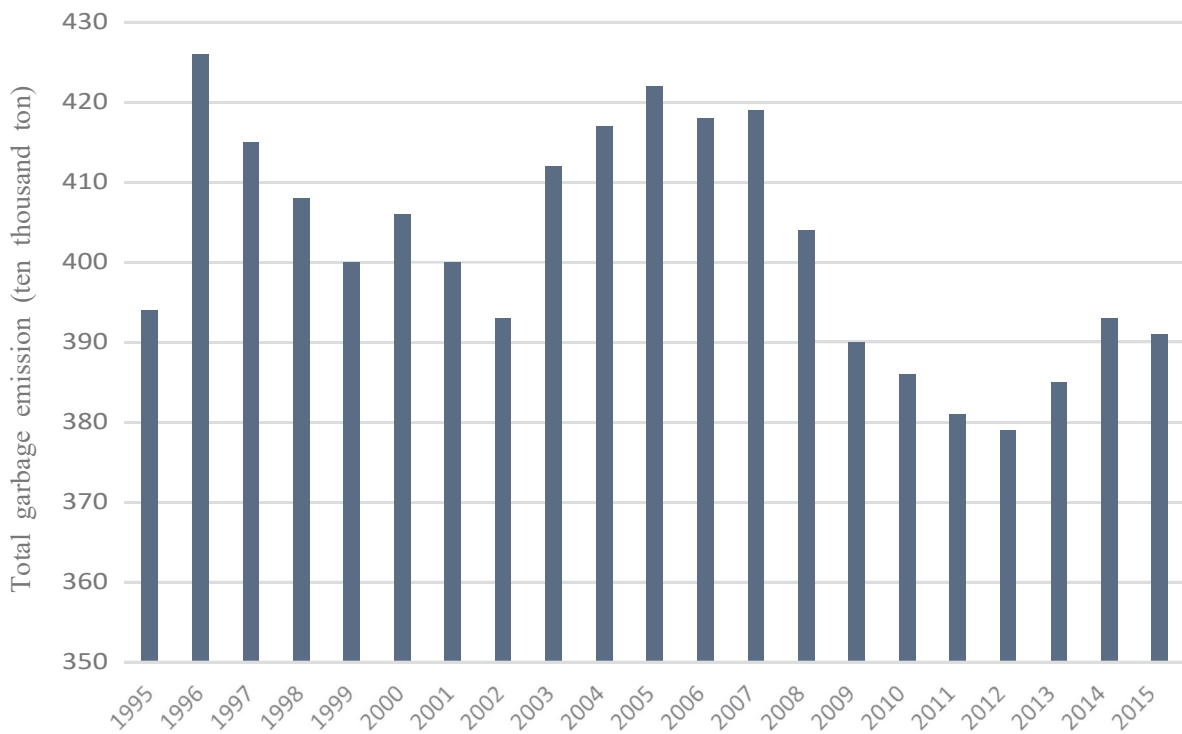


Fig. 1.2 Changes in industrial waste emissions

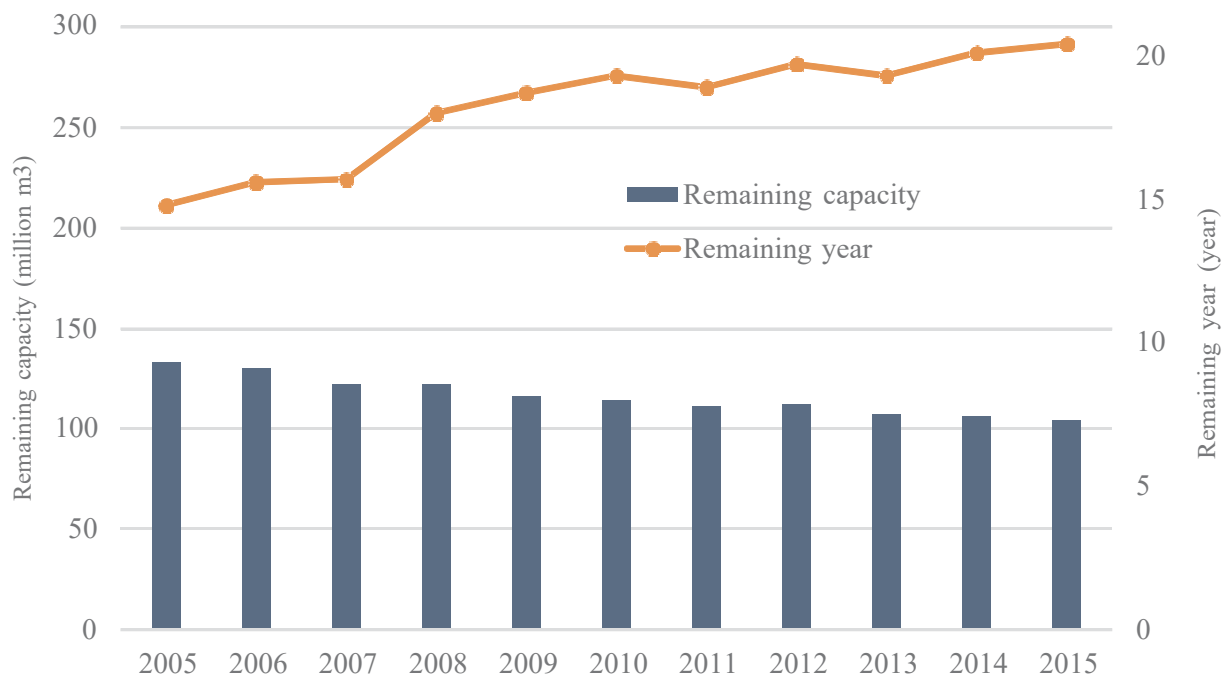


Fig. 1.3 Changes in residual capacity and remaining years at final disposal sites (general waste)

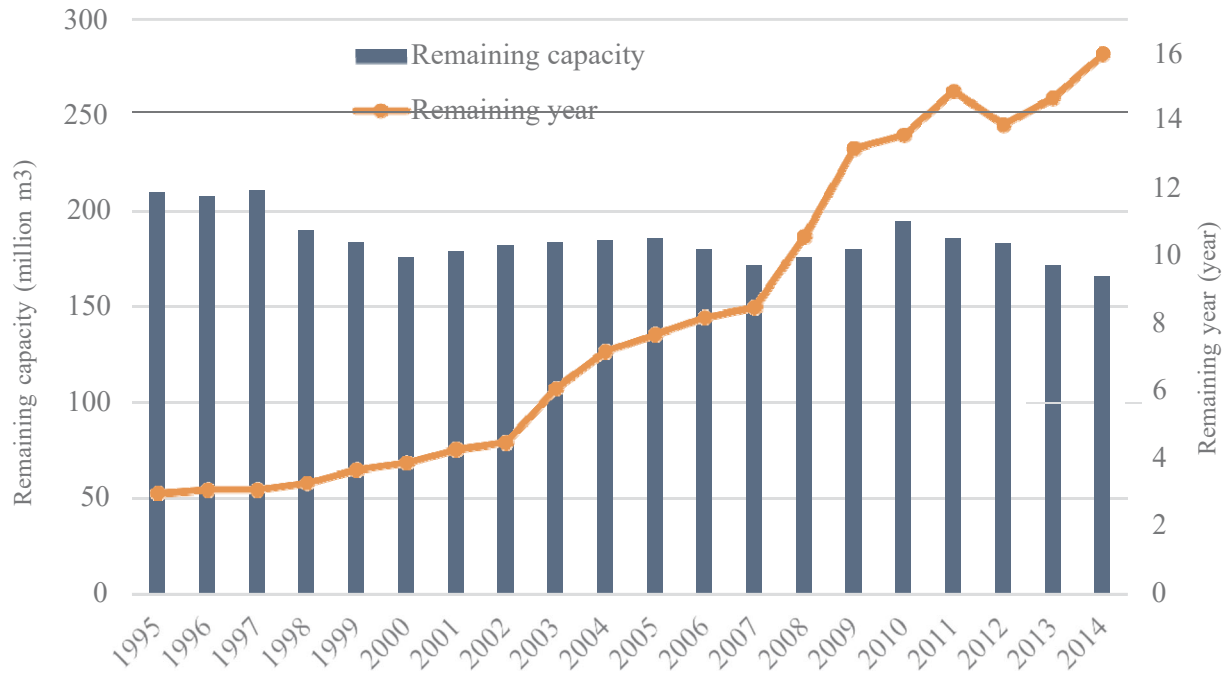


Fig. 1.4 Changes in residual capacity and remaining years at final disposal sites (industrial waste)



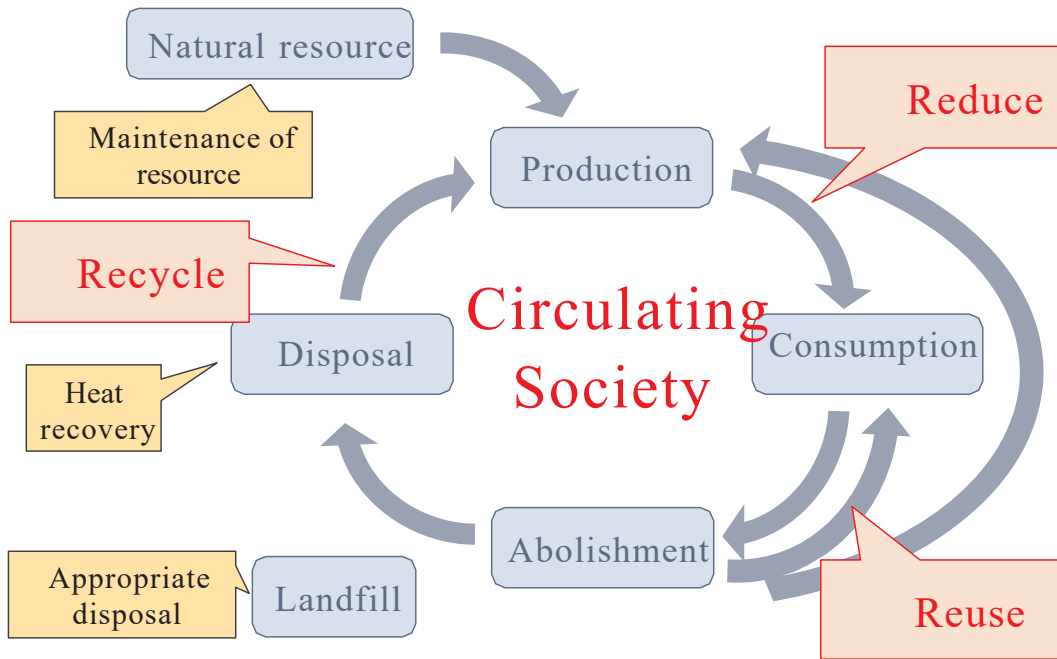


Fig. 1.5 Three R

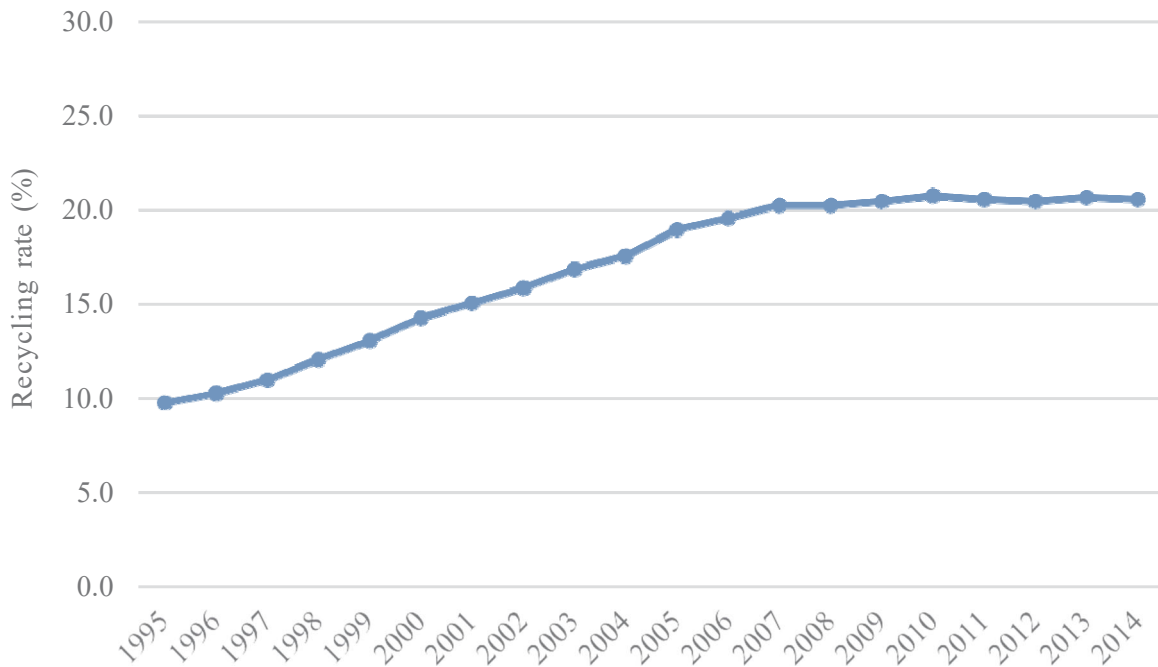


Fig. 1.6 Recycling rate of general waste

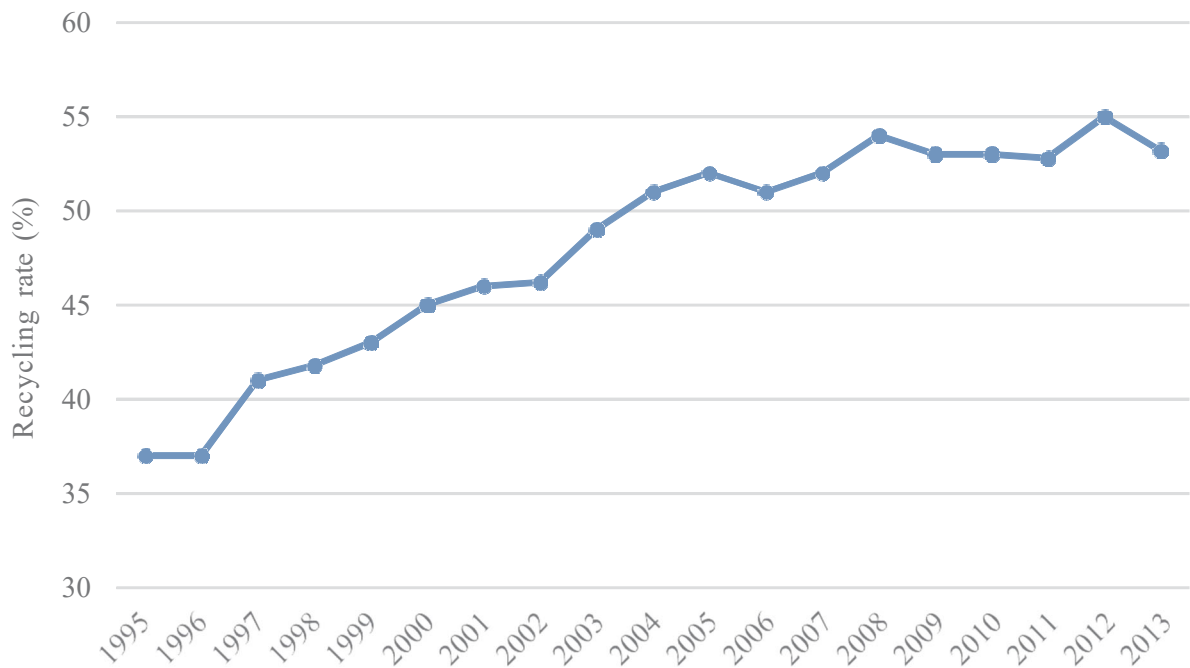


Fig. 1.7 Recycling rate of industrial waste

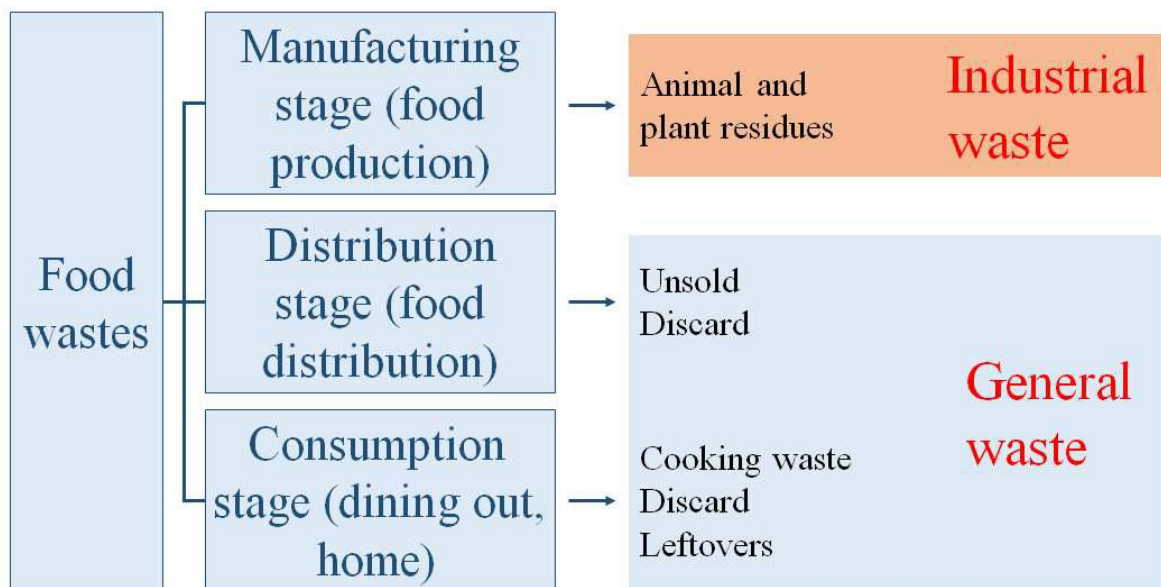


Fig. 1.8 Classification of food waste

Table 1.1 Food waste generation and treatment status

<i>million ton</i>	<i>Amount generated</i>	<i>Disposal amount</i>					<i>Weight loss</i>
		<i>Incineration and landfill disposal amount</i>	<i>Recycled amount</i>			<i>subtotal</i>	
			<i>Fertilizer</i>	<i>Feed conversion</i>	<i>Other</i>		
Business waste and valuables	1953	334	249	983	162	1394	225
Business waste	839	-	-	-	-	-	-
Valuables	889	-	-	-	-	-	-
Household waste	822	767	-	-		54	-
total	2775	1101	-	-		1449	-

## 2. Rice husk (RH) and rice husk powder (RHP)

### 2.1 Physical property of RH

The rice husk (RH) is the shell of berry taken from the spike of rice. The RH is covered with a wax component which protects the surface of the organism called the cuticle. The RH is hard to decompose since the wax component shed the water. The RH is shown in Photo 2.1, and has the feature that about 20 percent of silica is contained <sup>13)</sup>. Bamboo is also said to have a lot of silica, but even it is less than 0.1 percent in the case of raw bamboo. The silica is the silicon dioxide or the generic name of substances which constituted by silicon dioxide. The RH is very hard and difficult to process due to the properties of silicic acid which is the raw material of glass contained in chaff. The amount of RH emissions is about 2 million tons annually nationwide, and most of them are discarded as the industrial waste since the usage of unprocessed RH is limited. The unprocessed RH has been used for packing or seedling cover materials, but the usage as plastics material has been increasing in recent years. Various researches on the adsorption ability for cesium of rice husk have been studied <sup>14)</sup>, <sup>15)</sup>. For example, the research by Shozugawa et al. states that radioactive cesium is trapped by viscous fungi on the rice husks <sup>16)</sup>. Although it is considered that the optimum processing and utilization method of unprocessed RH are few, the rice husk ash made by burning rice husk has been studied for many uses. In Thailand, the RH is used as a heat source to generate steam and power. The rice husk ash (RHA) given off from these generation is used for material of cement. As a similar technology, the researches for making building materials for houses from RH, which were developed by the National Institute of Advanced Industrial Science and Technology Kyushu Industrial Technology Laboratory (now Kyushu Center for Industrial Science and Technology) is conducted. After using RH as a heat source, the RHA, caustic lime and glass fiber are mixed and solidified to produce boards that can be widely used as lightweight building materials for general houses such as insulation materials. Furthermore, a study that the RHA is mixed in concrete are also conducted <sup>17)</sup>. In addition, it is confirmed by the studies of Nakanoku University of Chukyo University that RHA has high adsorption rate for radioactive materials such as the cesium and strontium. As noted above, various usage methods are studied for the RHA, but it is necessary to control the temperature at 400 - 600 degrees and burn in order to produce the high quality RHA <sup>18)</sup>. Crystallized silicic acid

and dioxin may be generated when the burning temperature falls below 400 degrees. Practical realization has not progressed much due to the difficulty of such processing. In order to propose a new method of utilizing raw RH and to reduce the cost of processing, in this study, an adsorption performance of dried RH for heavy metals without processing is examined (see Photo 2.2). Alternatively, a powdered rice husk (RHP) is prepared separately from the dried rice husk to understand the effect of specific surface area and particle size on the adsorption performance for cesium and heavy metals. Commercialized powdered rice husk is used in order to reduce the variation in particle size of the powdered rice husk.

### 2.1.1 XRD (RH)

XRD and SEM-EDS are used to analyze the components of RH used in the tests. This is because the sample is a suitability as the material for the tests when the content of the sample is significantly different from that of general rice husk. Also, it is necessary to confirm that RH does not contain substances such as the heavy metal or strontium that affects the test. Alternatively, elemental analysis for FbP and FFP (described later) is conducted by XRD and SEM-EDS for the same reason.

### XRD

The XRD (see Photo 2.3) used in the tests is described in detail. X-rays are scattered by each atom in the crystal when the crystal is irradiated with the X-rays. The scattered X-rays interfere with each other if the X-rays are monochromatic. Additionally, a strong scattered X-ray is generated in a specific direction. In the case of interference of scattered X-rays from a large number of lattice planes, the direction in which scattered X-rays strengthen depends on the path difference due to the spacing between adjacent surfaces. The distance between atomic arrangements is determined by the type of atoms and ions. Therefore, the types of substances constituting the sample can be specified if the distance between the atomic planes is known.

### XRD of RH

The analysis of RH is conducted by XRD. The analysis method is shown in Fig. 2.1. From the Fig. 2.1, an intensity peak appears when the value of  $2\theta$  is around 23. This peak appears when silicon dioxide is included in the crystal<sup>19)</sup>. The peak is similar to that of general RH, and it is confirmed that the material is suitable for use in the test.



Photo 2.1 Rice husk (RH)

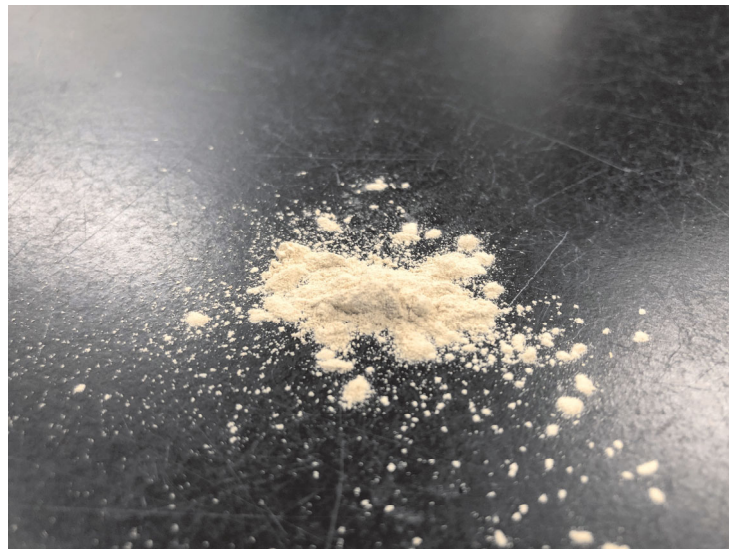


Photo 2.2 Rice husk powder (RHP)



Photo 2.3 XRD device

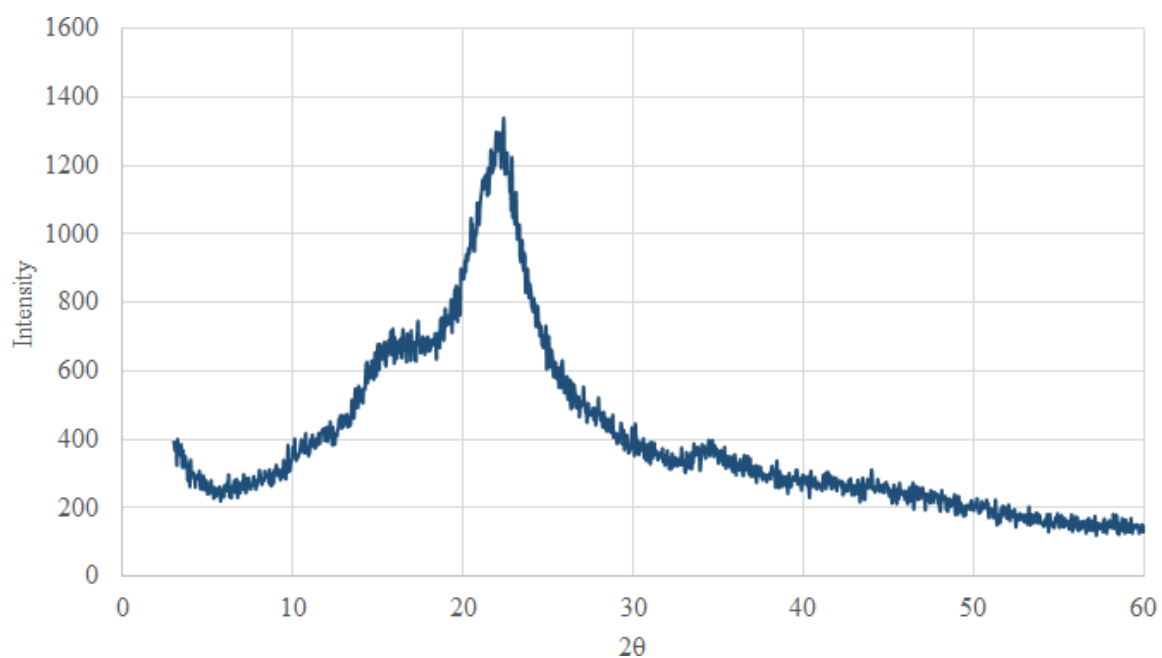


Fig. 2.1 Spectrum of RH by XRD

## 2.1.2 SEM-EDS

### (RH)SEM-EDS

SEM-EDS (SEM is scanning electron microscope, EDS is energy dispersive X-ray analysis) is a combination of SEM and EDS analyzers (see Photo 2.4). An optical microscope (OM) applies light to a sample, and the shape of the sample is observed by the reflected light. On the other hand, in the SEM, the shape of sample is observed by using a detector to detect secondary electrons or reflected electrons generated when a thin electron beam is applied to the sample. Furthermore, the generation intensity of secondary electrons varies depending on the angle of the electron probe incident on the sample surface. Therefore, the sample surface structure with minute irregularities that cannot be observed with OM can be magnified and observed clearly. The EDS is a device that identifies the elements contained in the sample surface from the characteristic X-rays generated by the electron beam irradiated to the target area. The generated characteristic X-ray is converted into a pulse signal by the detection element, and the characteristic X-ray energy and the number of occurrences are measured. The number of pulse signals generated with a certain energy has a correlation with the content of a specific element. The elements contained in the sample surface and their contents can be determined by the characteristic X-ray energy obtained from the pulse and the number of occurrences per unit time. The feature of SEM-EDS is that multielements can be measured simultaneously in a short time. The SEM-EDS is suitable for analysis of unknown samples because of its excellent detection efficiency and measurement with a small current. Besides, All samples used for SEM analysis are powdered.

### SEM image of RH

Fig. 2.2 is the SEM image of RH. The sample is adhered to the carbon tape and observed. Therefore, the carbon tape in the back is reflected in the screen. The peak of carbon tends to be large. Also, the SEM image becomes unclear when the magnification is increased too much. Therefore, there are two conditions for the observation of magnification; one is that the carbon tape is not visible, and the other is that the image is as clear as possible. Based on these conditions, the observation magnification for RH is set to 3300 times. The observation of magnification is relatively low because the surface of dried rice husk is very noisy. This is due to the large amount of static electricity on the surface. Also, only the center part is focused because the surface irregularities are large. The surface is covered with a vitreous material, and it can be confirmed that a lot of silicon exists.

### Spectrum of RH

Fig. 2.3 is the spectrum of RH with EDS. It is revealed that the elements contained in rice husks are carbon, oxygen, silicon and potassium. The analysis results are valid because most





Photo 2.4 SEM-EDS device

of the components of rice husk are cellulose and silicon dioxide. Potassium may be a nutrient absorbed by rice from the soil. It is confirmed that the cesium and heavy metals used in the test are not included by the analysis results.

## 2.2 Study on Electrophoresis test

### Background and object

The huge tsunami caused by the Great East Japan Earthquake brought devastating damage to the Pacific coast of the Tohoku and Kanto regions, Japan. Even now, about nine years have passed since the tsunami disaster, and the reconstruction of Fukushima Prefecture has not been completed due to the serious nuclear accident of the diffusion of a large amount of radioactive materials at the Fukushima Daiichi Nuclear Power Plant of Tokyo Electric Power Company. Among the released radioactive materials, the radioactive cesium is still detected in a wide range in Fukushima Prefecture since it is released in large quantities and has a long half-life<sup>20)</sup>. In addition, it is known that it is difficult to extract cesium due to the elective fixation of cesium in the clay mineral<sup>21)</sup>. The soil distribution map in Fukushima prefecture is shown in Fig. 2.4

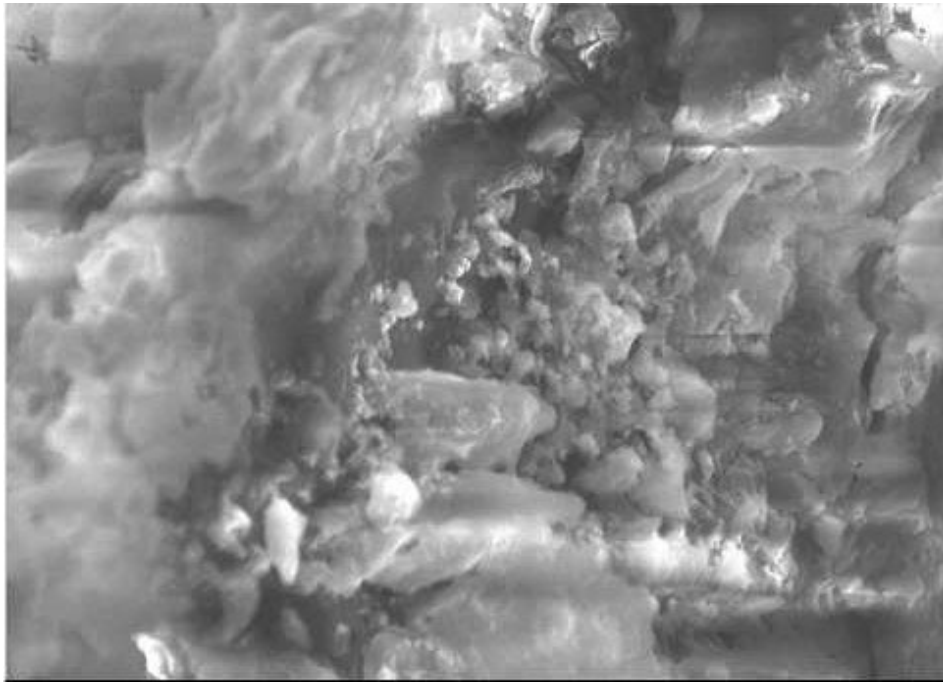


Fig. 2.2 SEM image of RH

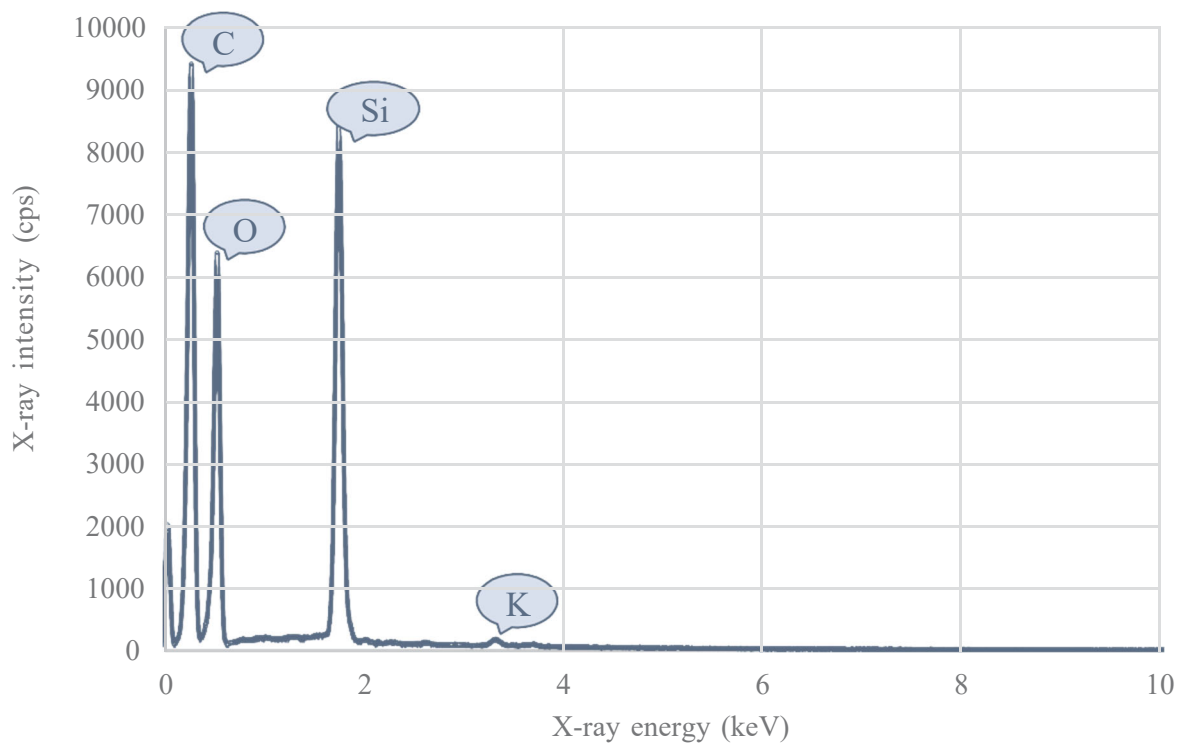


Fig. 2.3 Spectrum of RH by EDS

<sup>22)</sup>, <sup>23)</sup>. From Fig. 2.4, the soil in Fukushima prefecture has a relatively large amount of clay soil, and cesium is likely to be incorporated into the soil under the circumstance. Fig. 2.5 shows the abundance of radioactive cesium in multiple soils when one year has passed since the nuclear accident <sup>24)</sup>. It can be seen that almost all of the radioactive cesium is fixed in the soil as a "fixation". It has been confirmed that a large amount of fixed radioactive cesium is fixed between the layers, called as Frayed Edge, in which mineral particles such as vermiculite are involved. The vermiculite is broadly distributed in the soil of Fukushima prefecture. Therefore, the development of effective removal technology of cesium from vermiculite is an urgent issue. The biggest issue in the decontamination project in Fukushima prefecture is how to treat the contaminated soil generated by decontamination. Since much of the deposited radioactive cesium exists in the surface layer of about 10 cm of the contaminated soil, the radiation dose has been reduced by the surface decontamination such as the peeling of the topsoil. Large amounts of collected contaminated soil are temporarily stored in flexible container bags in temporary storage areas in Fukushima prefecture. The contaminated soil enclosed in the flexible container bags is scheduled to be sequentially delivered to intermediate storage facilities in Fukushima prefecture in the future. However, it is not easy to carry out a large amount of contaminated soil from the temporary storage place to the intermediate storage facility, in fact, about 2.18 million m<sup>3</sup>, which is about 15.6 percent of about 14 million m<sup>3</sup> of the transported objects. Also, it should be transported to the intermediate storage facility, has been carried out of the temporary storage place. Furthermore, the contaminated soil transported to intermediate storage facility will be sorted by a sieve, and incinerated at a high temperature of 800 degrees or higher <sup>25)</sup>. However, not only the transportation cost of a large amount of contaminated soil but also the incineration cost has not been clarified. Therefore, it is necessary to establish a technology for reducing the volume of contaminated soil by removing cesium from the contaminated soil in the flexible container bags at a temporary storage place. The technology should reduce the radiation dose of the contaminated soil without transporting it to an intermediate storage facility. Thus, in this study, the simulated flexible container bag is produced on the assumption of the removal of cesium in the flexible bag at the temporary storage place, and the test is conducted with the sand in which vermiculite and Toyoura standard sand are mixed as a simulated contaminated soil. For the removal method of a cesium in the contaminated soil, it is verified whether cesium in the soil can be moved and adsorbed to adsorbents by means of the electrophoresis method. The purpose of this study is to examine the effective cesium extraction conditions and to discuss the possibility of volume reduction of contaminated soil through the obtained results of various tests.

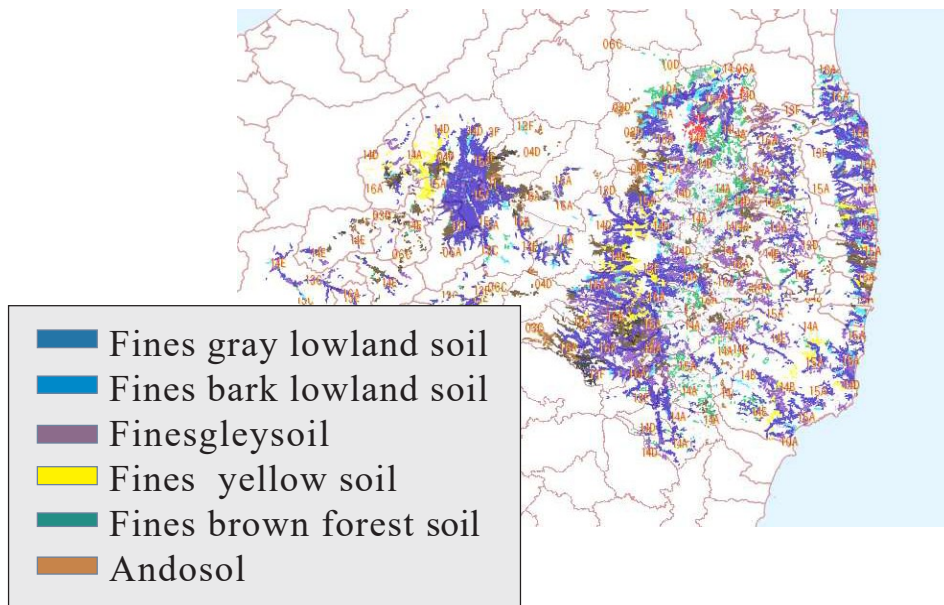


Fig. 2.4 Soil distribution map in Fukushima prefecture <sup>22)</sup>

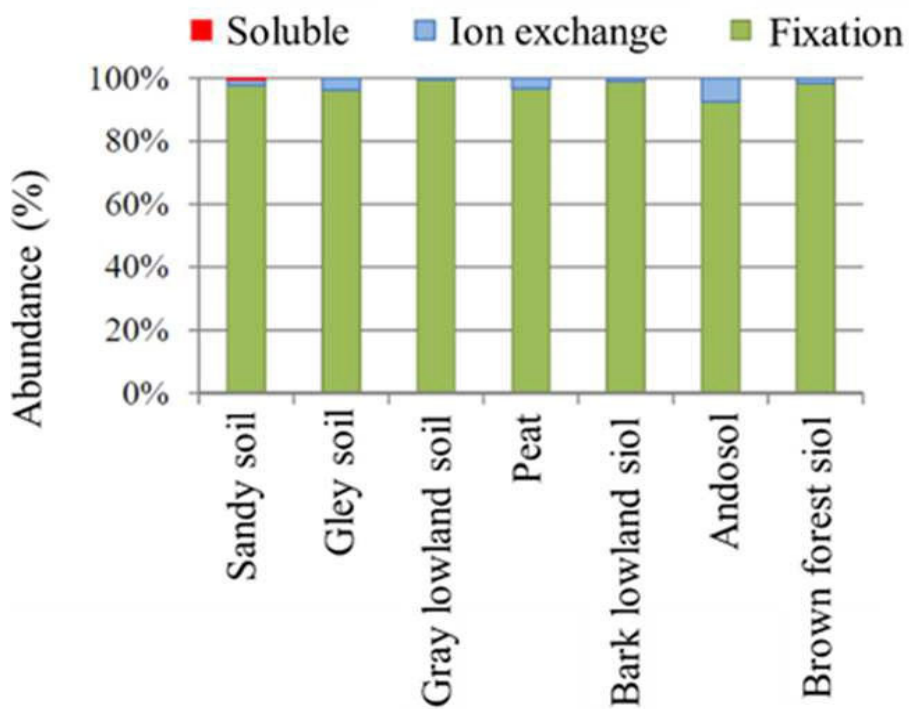


Fig. 2.5 Abundance of cesium in the soils <sup>24)</sup>

## Cesium in soil

Cesium exists as a monovalent cation in soil and is adsorbed to the soil particles which is charged with a negative in soil. Additionally, cesium is easily adsorbed in and on the clay particles whose size is small. It is the 2:1 layered silicate constituting a clay mineral that cesium adheres to the soil. The 2:1 layered silicate is a generic term of the minerals in which the relation between the thickness of silicon tetrahedral sheet and those of aluminum octahedral sheet is 2:1. In a silicon tetrahedron sheet and an aluminum octahedron sheet, either sheet or both of the sheets become insufficient in positive charge when a part of silicon or aluminum is replaced with another element having a small amount of positive charge. After that, the negative charge is appeared by the lack of positive charges in the sheet, and the cations are adsorbed to neutralize the interlayers of the sheet. The layer charge shows high selectivity to cesium ions<sup>26)</sup>. This is because the size of cavity called a six-membered ring formed by oxygen atoms on the basic plane of a silicon tetrahedral sheet is approximately equal to the ionic radius of cesium ion. In addition, the bonding strength to the six-membered ring increases as the hydration energy decreases, which means that cesium ion has the highest bonding strength. However, the potassium ion occupies the six-membered ring because the abundance of potassium ion is decisively large in the soil (see the top of Fig. 2.6). The end of the clay mineral layer is frayed by weathering of soil, and the potassium ion is released. As a result, the region into which other cations can penetrate is formed and called as frayed edge site (see bottom of Fig. 2.6). It is difficult to replace cesium ions fixed to the frayed edge site with other cations<sup>27)</sup>.

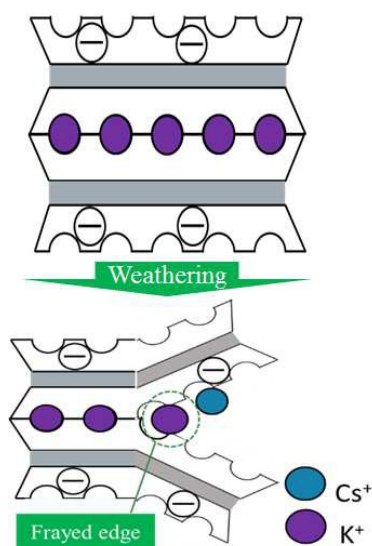


Fig. 2.6 Top part of 2:1 type of lamellar silicate and bottom part of the Frayed edge

### 2.2.1 Electrophoresis

In this study, the electrophoretic method is employed in order to transfer cesium ions extracted from clay minerals in soil. The cesium ions transferred to the cathode are adsorbed by an adsorbent placed in front of the cathode. An electrophoretic phenomenon is the movement of charged particles in a liquid medium under an electric field. Cesium ions are transferred to the cathode side by using the electrophoretic phenomenon, and are adsorbed in or on the zeolite or rice husk which are placed in front of the cathode side.

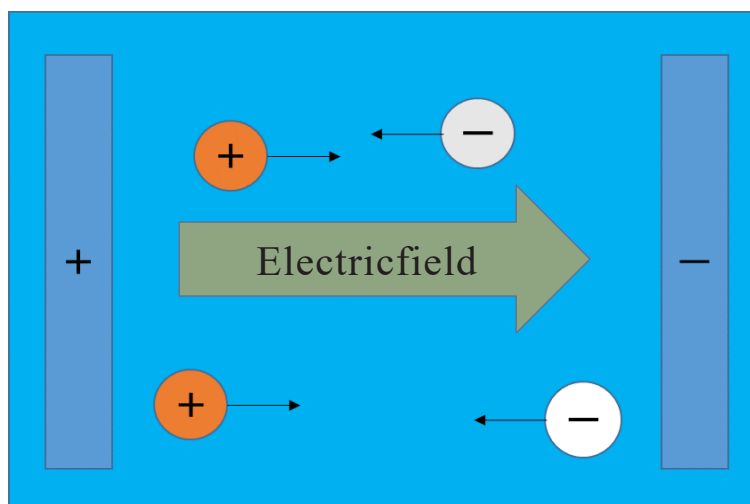


Fig. 2.7 Mechanism of electrophoresis

### 2.2.2 Electrophoresis test and analysis method

1. Simulated soil is added to the acrylic container bag
2. Cesium standard solution is added to the soil and the sand is soaked for 168 hours
3. Electrophoresis is conducted for 48 hours
4. The soil is collected and washed out by stirring
5. Analyzing by AAS

The experiment device by which the flexible bag packing the soil contaminated by radioactive cesium is simulated is produced in the course of conducting the electrophoresis test. First, a simulated contaminated soil is prepared by adding 1 mL of the cesium standard solution so as to assume a real contaminated soil. The simulated soil consists of vermiculite and standard sand.

Next, the simulated contaminated soil is placed in an acrylic container bag, and a carbon rod (diameter of 15 mm and length of 40 mm) serving as an anode is placed vertically in the center of the soil. Additionally, the simulated contaminated soil is placed in a simple container that combines filter paper and bolding cloth (mesh size 37  $\mu\text{m}$ ) to prevent mixing with the adsorbents. Moreover, the simulated contaminated soil is immersed in ammonium acetate aqueous solution (3.0 percent of concentration, 60 - 70 mL) and the adsorbent is placed in front of an aluminum plate so as to enclose the simulated contaminated soil (see Fig. 2.8). After an energization for a specified time, the soil is collected and washed out by stirring. The extracted amount of cesium contained in the solution and soil after the test is quantified by an atomic absorption spectrophotometer (AAS) for the solution separated through filtration. The AAS is the device that the concentration of ion in the solution is analyzed by atomic absorption method. Atomic absorption is a phenomenon in which each element exhibits a specific narrow absorption spectrum when it is irradiated with light by being heated to a high temperature and atomized. An analytical method that uses this phenomenon to qualify and quantify elements contained in a sample is called atomic absorption spectrometry. The photo of AAS is shown in Photo 2.5 The extraction rate is determined by the following Eq. (2.1).

$$\text{Extractionratio} = \frac{\text{extractedamount}}{\text{addedamount}} \times 100 \dots \dots \dots (2.1)$$

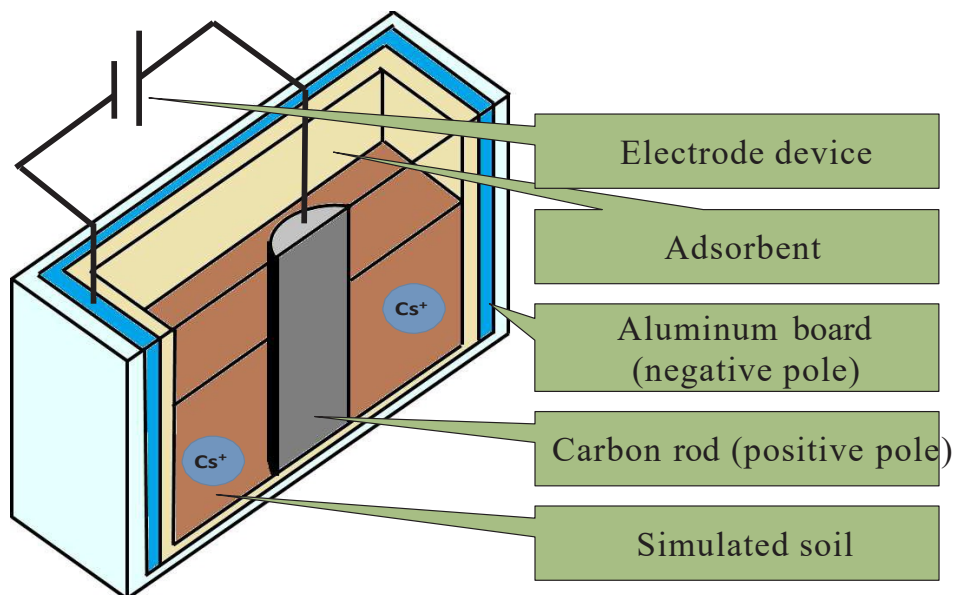


Fig. 2.8 Electrophoresis test device



Photo 2.5 Atomic absorption spectrophotometer (AAS)

### 2.2.3 Test results using zeolite

#### Zeolite

Zeolite is a clay mineral with regular tubular pores and cavities. Zeolite crystals have adsorption properties and ion exchange properties because they have many pores. In particular, it is known that the zeolite has high ion exchange properties against cesium. Thus, the zeolite is selected so as to exam the adsorption ability of the rice husk through the results of adsorption tests as a comparative material for RH. In the test, powdered zeolite is used (see Photo 2.6).

#### Test condition

The volume ratio of standard sand to vermiculite contained in simulated contaminated soil is 1 1, and the mass of simulated contaminated soil is 120 g. The current values during the electrophoresis test are 25, 50, and 100 mA, and the energizing time is 48 hours. The results of tests using three types of adsorbents are shown in graphs, respectively. Each test is conducted three times to ensure a reproducibility, and the average value for three batches is listed in the graphs. The test conditions are shown in Table 2.1.





Photo 2.6 Powdered zeolite

Table 2.1 Electrophoresis test conditions

Soil	Standard sand 114 g, Vermiculite 6 g	
Electrolyte	Ammonium acetate aqueous solution (3.0 ) 60-70	
Sample	mL	
Adsorbents	Zeolit	Cesium standard solution 1mL
	e	10 g
	RH	3 g
	RHP	10 g
Curing time	168 hours	
Energizing time	48 hours	
Current value	25, 50, 100 mA (under 40 V)	

## Test results

Fig. 2.9 shows the test results when zeolite is used as the adsorbent. The vertical and horizontal axes of the graph represent the extraction ratio of cesium and the current value, respectively. The results of the test with and without zeolite are compared. As a result of the test, the extraction rate of cesium decreases with increasing of the current value regardless of the presence or absence of the adsorbent. It is found that about 20 percent of the added cesium is extracted, which can help the volume reduction of the contaminated soil. On the other hand, about 80 percent of the added cesium remains in the soil. These facts indicate the difficulty of extracting cesium from the soil. Before the electrophoretic test is carried out, the curing period of 168 hours is set to fix the cesium sufficiently to the soil. Most of the cesium is adsorbed to the vermiculite during the curing period, which makes it difficult to extract the cesium from the vermiculite. Alternatively, the most effective extraction of the cesium from the soil appears when the current value is 25 mA in the electrophoresis test. It is found that the extraction of cesium is inhibited if the current value becomes enough high. This is caused by the re-adsorption of cesium, temperature rise, the promotion of evaporation of electrolyte, etc. The investigation of the cause should be examined in the future. Considering the practical operation, it can be said that the low current value is advantageous from the viewpoint of running cost. Suppose the difference between the extraction ratios of specimens with and without zeolite is the adsorption ability of zeolite for cesium, the adsorption ability hardly changes with increasing or decreasing current value. In other words, it is found that the current value has little significant influence on the adsorption ability.

### 2.2.4 Test results using

#### RH Test results

Fig. 2.10 shows the test results when the RH is used as the adsorbent. The test results are very similar to those of zeolite. The smaller the current value, the larger the extraction ratio. The current value has little significant influence on the adsorption ability of RH. It is clarified that the RH has almost the same adsorption capacity for cesium as the zeolite. It is noted that the used amount of adsorbents are 10g of zeolite and 3g of RH. The unification of the volumes of both materials caused a difference in the mass of the materials. Thus, from the viewpoints of mass, the RH has higher adsorption capacity per unit volume than the zeolite. As these results, it may be most useful to use raw rice husk as adsorbent from the viewpoint of both volume reduction of radioactive material and processing cost of rice husks when the amount of adsorbent and adsorption performance are focused.

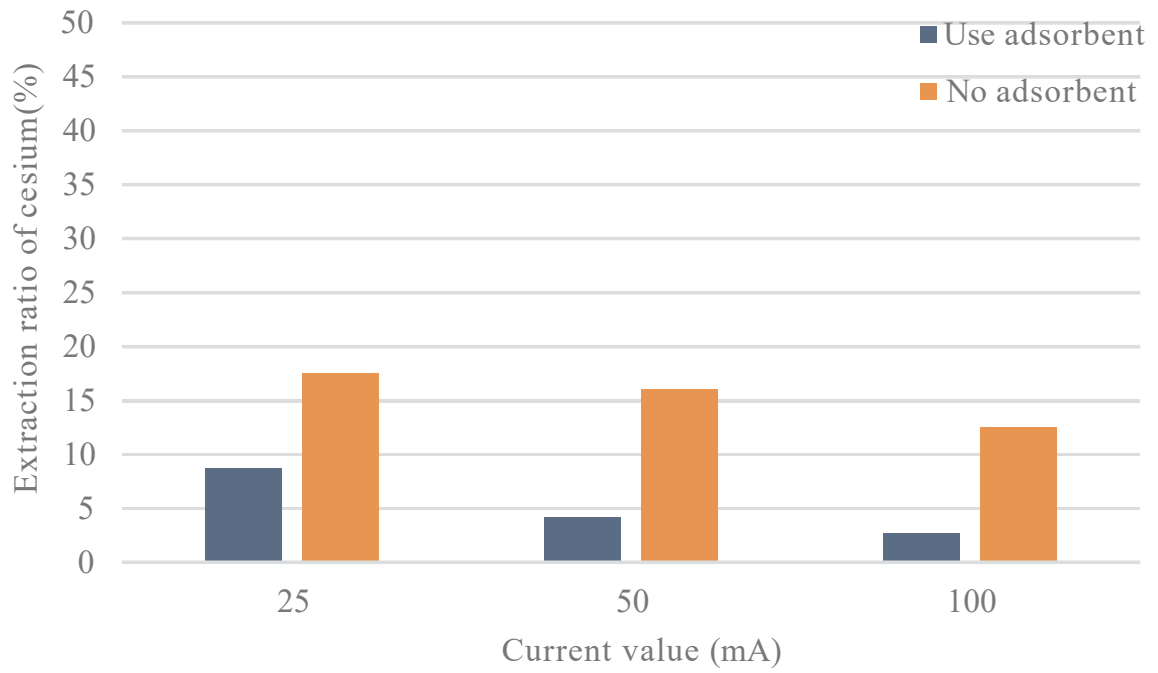


Fig. 2.9 Extraction ratio of Cs using zeolite

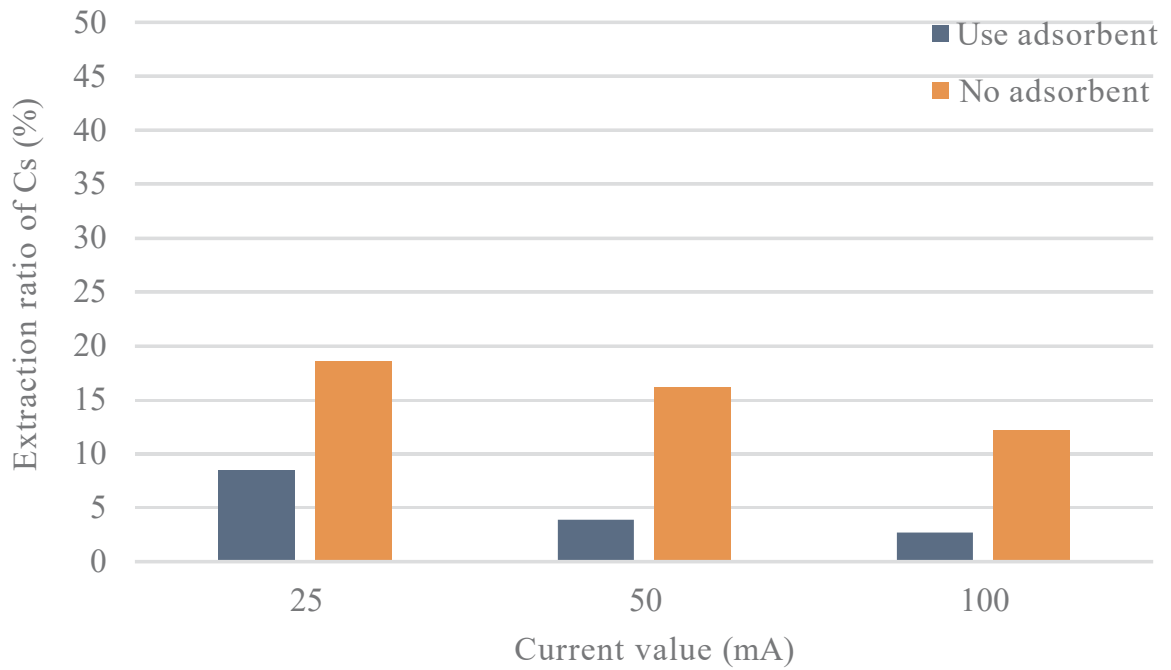


Fig. 2.10 Extraction ratio of Cs using RH

### 2.2.5 Test results using RHP

#### Test results

Fig. 2.11 shows the test results when the RHP is used as the adsorbent. The test results are similar to those of zeolite and rice husk. The mass of the adsorbent is 10g of RHP as well as zeolite, and the RHP has the more or less same adsorption ability as zeolite. The adsorption for cesium is largely due to the micropore distribution of the adsorbent and the constituent elements. In the future, it is necessary to investigate the cause by comparing the micropore distributions with using a facility such as a BET specific surface area measurement device.

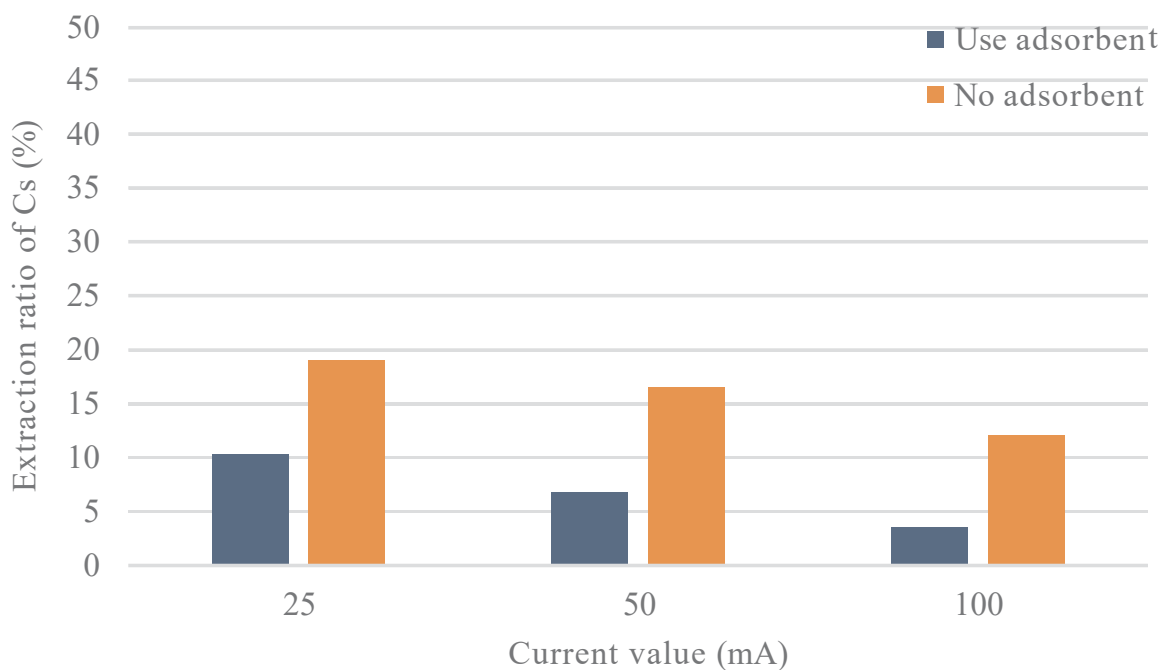


Fig. 2.11 Extraction ratio of Cs using RHP

### 2.2.6 Consideration of electrophoresis test

In this study, the experiment device which simulates the flexible container bag packing the soil contaminated by radioactive cesium is produced, and the electrophoresis tests are conducted

under various conditions in order to investigate appropriate transfer conditions of cesium to the adsorbents (zeolite, rice husk and rice husk powder).

The extraction rate of cesium is the highest at the minimum current values (25 mA) when the cesium is extracted by electrophoresis without an adsorbents. The adsorption rate of cesium at 50 mA of current value shows the maximum value to compare with the other current values (25, 100 mA) when the zeolite is used as the adsorbent. However, the difference due to the current is not so large.

The adsorption rate of cesium at 50 mA of current value also shows the maximum value to compare with the other current value (25, 100 mA) when the rice husk or the rice husk powder are used as the adsorbent.

The test results with zeolite, rice husk and rice husk powder as an adsorber for cesium are similar, which shows that their adsorption properties for cesium are more or less same.

It is not clear whether there is a clear correlation between the mass and the amount adsorbed, but it is venture to discuss them here. It can be seen that the rice husk adsorbs the cesium in a smaller amount. It is considered that the adsorption principle of rice husk is one of the factors that enable rice husk to adsorb cesium in a smaller amount than rice husk powder.

Some of the cesium can be trapped by viscous fungi that attaches to the rice husk surface. The reason why the adsorbent performance of rice husk powder is inferior to that of rice husk can be that the adsorption property mentioned above is lost during the powder processing from rice husk to powder form. It is identified that a rice husk is an excellent adsorbent for cesium because the powder processing is not necessary and the required amount to adsorb the cesium is small.

## 2.3 Immersion test of RH

### Background and object

In recent years, the soil and groundwater contamination cause harmful materials come to a head through the redevelopment in empty lots. According to the reports of each prefecture's soil and groundwater pollution case released by the Ministry of the Environment <sup>11)</sup>, <sup>12)</sup>, the number of bath cases has increased since 1991, when the soil environmental standards were enacted. In particular, the number of both cases has rapidly increased in 2002 by executing the Soil Contamination Countermeasures Act, and the cases have increased again in 2010 when executing the revision Soil Contamination Countermeasures Act. The researched cumulative number of cases is 19,927, and the cumulative number of cases that exceeds the environmental standard value is about 9,733 in the case of soil contamination cases grasped by prefectures by the end of 2014. The soil and groundwater contaminations are often caused by heavy metals and the volatile organic compounds (VOC). The VOC has the characteristics that it is difficult to dissolve in water and its viscosity is low. Thus, the VOC moves in the soil and easily reaches the groundwater surface. On the other hand, the soil pollution by heavy metals is difficult to spread widely because most of the heavy metals are easily adsorbed by minerals in the soil. However, the heavy metals such as hexavalent chromium and arsenic are highly soluble in groundwater, and have high mobility in soil. Therefore, there are many cases of groundwater contamination by hexavalent chromium and arsenic among heavy metals. The cleaning treatment water for the excavated soil and the contaminated water pumping is generated by digging and washing the contaminated soil. The adsorption disposal by the activated carbon is conducted as the disposal method for both contaminated water and pumped groundwater after the aeration disposal. The activated carbon is most frequently used as an adsorbent, is inexpensive compared to other adsorbents, and has an advantage of having a high specific surface area. Especially, it is known that the activated carbon has a high adsorption performance for organic substances such as a VOC. However, the activated carbon has a low adsorption performance for inorganic substances such as the heavy metals. For this reason, adsorbents such as the zeolite and the silica are used for inorganic substances, but they have the disadvantage that the manufacturing cost is higher than that of activated carbon. It is predicted that the number of soil and groundwater contamination increases with redevelopment etc. in the future. Therefore, the adsorbent which can be manufactured at a low cost is required. Thus, in this study, the RH and fish bones which are an industrial waste are focused on. The material cost is saved by using industrial waste. The unprocessed RH and only burned fishbone are used as an adsorbent in order to reduce the manufacturing cost. Also, the adsorption performance of the RH and fishbone for heavy metals are examined whether both materials can be used as a new adsorbent. The results of the immersion test using fishbone will

be described later in Chapter 3.

### 2.3.1 Heavy metals

Among various materials which are harmful to the environment and the human body, and in this study,  $\text{Cr}^{6+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Se}^{4+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$  are selected. The materials section is based on the harmful substances specified by the uniform effluent standards of the Ministry of the Environment.  $\text{Se}^{4+}$  is the cation in the solution though  $\text{Se}^{4+}$  is a non-metallic element. Furthermore,  $\text{Se}^{4+}$  is targeted in the test because  $\text{Se}^{4+}$  is comprehended in the harmful material and the cation in the solution. For chromium, trivalent and hexavalent samples are prepared because their waste water standards are different depending on the valence. The characteristics of each heavy metal are described in detail.

#### Chromium Cr

Atomic number of chromium is 24, and Cr is classified as a transition metal. It is used as an alloy with iron, pigment and chrome tanning agent in order to enhance the corrosion resistance of steel. It is also one of the essential elements that constitute the human body. Among chromium compounds, trivalent chromium exists in nature, and hexavalent chromium is an artificial substance. Hexavalent chromium is extremely toxic, and a typical poisoning symptom of the hexavalent chromium is nasal septal perforation. In addition, cancer and skin problems may be caused by the hexavalent chromium, and it is said that symptoms are due to the strong oxidizing power of hexavalent chromium.

#### Manganese Mn

Atomic number of manganese is 25, and Mn is classified as a transition metal. Mn dioxide is mainly used for the positive electrode of Mn batteries and alkaline batteries. The Mn alone is hardly used as a metal material, it is used as a raw material for Mn steel and a deoxidizer for steel. The Mn is an essential trace element for humans and has the function of promoting bone formation. Also, Mn works as a catalyst that enhances the activity of several enzymes in the body. The Mn deficiency causes osteoporosis, bone lesions, abnormal blood coagulation and active oxygen damage, and the overdose of Mn causes central nervous system disorders and Mn pneumonia.

#### Nickel Ni

Atomic number of nickel is 28, and Ni is classified as a transition metal. Ni exists in nature and is metallic element with a lustrous silver-white color. The Ni is the fifth most abundant element on the earth and is produced from the crust of many regions. It is most often used as an alloy, and both stainless steel and heat-resisting steel are especially made of alloys with metals

such as chromium. The toxicity of Ni depends on the chemical form and its physical properties, and oral toxicity is relatively low. However, in the case of inhalation, the toxicity of Ni carbonyl produced by the reaction between carbon monoxide and metallic Ni is large, and the lethal dose is estimated to be 30 ppm / 30 min.

### Zinc Zn

Atomic number of zinc is 30, and Zn is classified as a metal element. The Zn is the twenty fifth most abundant element on the earth and is an essential trace element of animals and plants. The simple substance is a silver-white metal that dissolves in both acids and alkalis. The most important use of Zn is a galvanization to protect iron and steel from corrosion. The Zn may cause abdominal pain, vomiting and diarrhea when it enters in the body.

### Arsenic As

Atomic number of arsenic is 33, and it is classified as group 15 elements. The As is widely distributed in the earth's crust, and is released to the environment by volcanic activities and artificially industrial activities. Any living organisms contain arsenic because the arsenic released to the environment circulates in the atmosphere, water, soil and biosphere. The As compounds are usually taken from the gastrointestinal tract and respiratory tract, and early symptoms of acute toxicity are vomiting, abdominal pain and diarrhea. Also, hepatic dysfunction appears several days later, and the sensory abnormalities of the extremities appear 2-3 weeks later. Besides, the main symptoms of chronic arsenic toxication include skin lesions such as keratinization of palms and soles, peripheral neuropathy and skin cancer.

### Selenium Se

Atomic number of selenium is 34, and Se is classified as group 16 elements. The selenium is used in solar cells as a material with a photoelectric effect that flows the current by exposing to light. In addition, selenium is an essential trace element with various physiological activities. Selenium deficiency may cause myocardial damage and increase the risk of cancer. On the other hand, the selenium is highly toxic, and the range between the required amount and the amount of toxication is very small. The Overdose of the selenium can cause neuropathy, myocardial infarction, acute dyspnea and renal failure. It is also widely known that the selenium is a causative agent of soilcontamination.

### Cadmium Cd

Atomic number of cadmium is 48, and Cd is classified as group 12 elements. The cadmium is a soft blue-tinged silver-white metal that is used in plating, batteries, alloys with lead and tin to prevent the rusting of iron materials. Acute toxication includes sore throat and dyspnea after several hours of inhalation. Also, chronic exication is mainly caused by emphysema and renal



dysfunction. The cadmium is a cause of Annaka pollution and Itai-itai disease. 200 patients have been identified as Itai Itai disease, including only 5 survivors.

## Mercury Hg

Atomic number of mercury is 80, and Hg is classified as group 12 elements. The mercury is a volatile metal at room temperature and is widely used in the fields of caustic soda industry, electrical products, chemicals, agricultural chemicals, etc. In addition, there are several types of mercury, such as methyl mercury, inorganic mercury and mercury vapor. Methyl mercury and inorganic mercury cause central nervous system symptoms from the brain, generalized numbness, language / psychiatric disorders and severe renal impairment. Mercury vapor may cause death by developing anemia, kidney damage and pneumonia as acute toxicity. In particular, methylmercury is a causative agent of Minamata disease and caused more than 10,000 victims.

### 2.3.2 Immersion test and analysis method

1. Pure water is poured into the cylindrical container
2. Each heavy metal standard solution is added to container
3. Adsorbent is entered into the filter bag and it is added to the container
4. Adsorbent is immersed in thermostat.
5. Concentration of heavy metal is analyzed by ICP-AES after removing of adsorbent

The test conditions are set and adsorption tests for each heavy metal are conducted in order to examine the basic adsorption performance of the rice husk and the FbA for heavy metals. The test method is shown in Fig. 2.12. First, 300 mL of pure water is put in a cylindrical container, and a standard solution of each heavy metal (analytical reagent adjusted to 1000 mg / L) is added. The standard solution of 1mL and 5 mL (about 3.3 and 16.4 ppm of initial concentration, respectively) is added in order to ascertain the adsorption amount per unit mass of the adsorbent for each heavy metal ion. Secondly, the adsorbent is put in the filter bag and it is immersed in the solution assuming the collection of adsorbent after the end of the test. The adsorbent is taken out after immersing in a thermostat set at 25 degrees for 168 hours, and the concentration of each heavy metal ion in the solution is analyzed by the ICP-AES. The elemental analysis in the ICP-AES is conducted by emitting light to the atomized or ionized sample in the plasma (see Photo 2.7). The temperature of plasma in the ICP-AES is 5000-6000 K. It is necessary that the adsorbed amount of the adsorbent for heavy metals is examined. Also, the test results is quantified. However, the examining of the adsorbed amount is very difficult because the adsorbed heavy metals to the adsorbent is difficult to be extracted. Therefore, the added

amount of heavy metals is compared with the detectable amount of heavy metals after test. The difference is defined as the adsorbed amount. As has stated, the ICP-AES is used so as to analyze the concentration of heavy metals. The adsorption performance of each adsorbent is evaluated by the adsorption ratio derived from the residual concentration of each ion in the solution to the initial concentration at the time of addition of standard solutions.

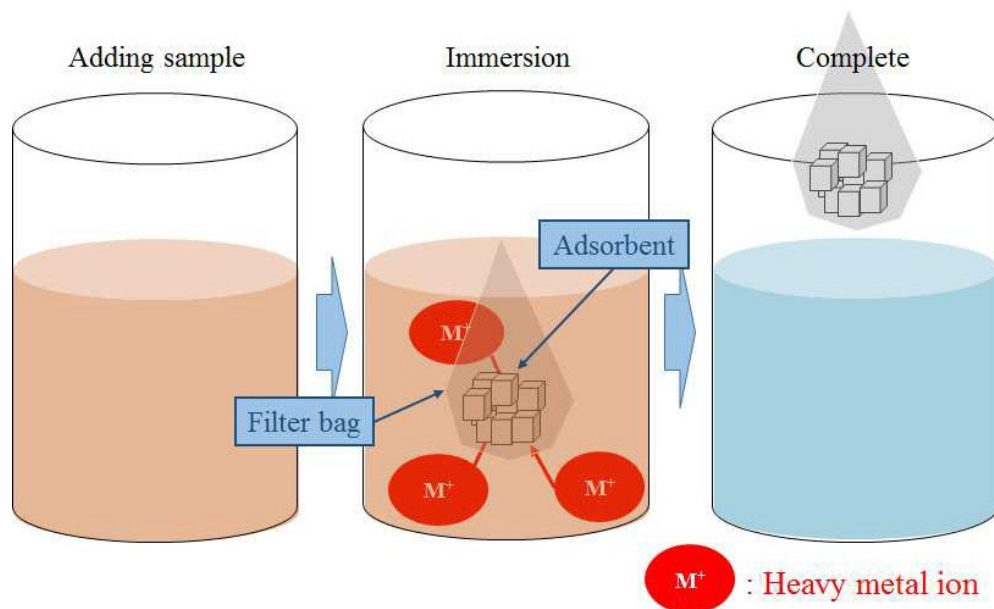


Fig. 2.12 Immersion test

### 2.3.3 Immersion test results

The adsorption ratio of heavy metal is shown in the vertical axes. The numerical value written on the top of the bar graph is the pH value which is measured immediately after taking out the adsorbent. Table 2.2 shows the pH values of each test specimen before adding the adsorbent. The pH of all test specimens indicates that the solution state is from a weak acid to strong acid before adding adsorbent because the standard solution is an acidic solution.

Table 2.2 pH value before adding adsorbent

	Cr <sup>3+</sup>	Cr <sup>6+</sup>	Mn <sup>2+</sup>	Ni <sup>2+</sup>	Zn <sup>2+</sup>	As <sup>3+</sup>	Se <sup>2+</sup>	Cd <sup>2+</sup>	Hg <sup>2+</sup>
1 mL	3.4	4.6	3.5	3.5	3.4	5.8	3.6	3.4	3.5
5 mL	2.8	3.5	2.8	2.7	2.8	4.8	2.6	2.8	2.8



Photo 2.7 ICP-AES

First, the results of the adsorption test using the RH as an adsorbent for each heavy metal are shown in Fig. 2.13 and Fig. 2.14, which correspond to the adsorption tests to 1 mL (initial concentration is about 3.3 ppm) and 5 mL (initial concentration is about 16.4 ppm) additions of the heavy metal standard solution, respectively. As shown in Fig. 2.13, 80 percent or more of  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$  are adsorbed to the RH when 1 mL of the sample is added. On the other hand,  $Cr^{6+}$  and  $As^{3+}$  are not adsorbed at all. All three types of ions with high adsorption ratio are group 12 elements. The Group 12 elements are also called zinc group elements. They are metal elements, and classified as typical elements. The Group 12 elements are considered to be closer to the adsorption mechanism of alkaline earth metal than other heavy metals classified as transition elements because the zinc group elements are a divalent cation. According to Shannon's ionic radius table, the ionic radius of the three zinc group elements is relatively close to the Ionic radius of  $Ca^{2+}$  (see Table 2.3). The high adsorption rate for ions whose ionic radii are close to suggest that RH may adsorb the ions by physical adsorption rather than chemically adsorption. It is necessary to clarify the adsorption mechanism in near future. Alternatively,  $Mn^{2+}$  and  $Ni^{2+}$  are the divalent cations in solution similarly to  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$ , and their ions are easy to be adsorbed to the adsorbent. However, the adsorption ratio remains around 50 percents. From these facts, it is considered that not only the ion valence but also the ionic radius are related to

the adsorption performance. On the other hand, there are exceptions such as  $\text{Cr}^{3+}$ , and this is probably because  $\text{Cr}^{3+}$  is in the form of anions in the solution. Focusing on pH, the pH value of  $\text{Cr}^{6+}$  and  $\text{As}^{3+}$  is higher than that of the other specimens and show the value close to neutrality. It is a possibility that the adsorption ratio may be improved by adjusting the pH value of the solution to a low value and making an acidic environment.

Table 2.3 Ionic radius ( ) (Shannon)

$\text{Cr}^{3+}$	$\text{Cr}^{6+}$	$\text{Mn}^{2+}$	$\text{Ni}^{2+}$	$\text{Zn}^{2+}$	$\text{As}^{3+}$	$\text{Se}^{2+}$	$\text{Cd}^{2+}$	$\text{Hg}^{2+}$	$\text{Si}^{2+}$	$\text{Ca}^{2+}$
0.62	0.44	0.67	0.69	0.74	0.58	0.50	0.95	1.02	0.40	1.00

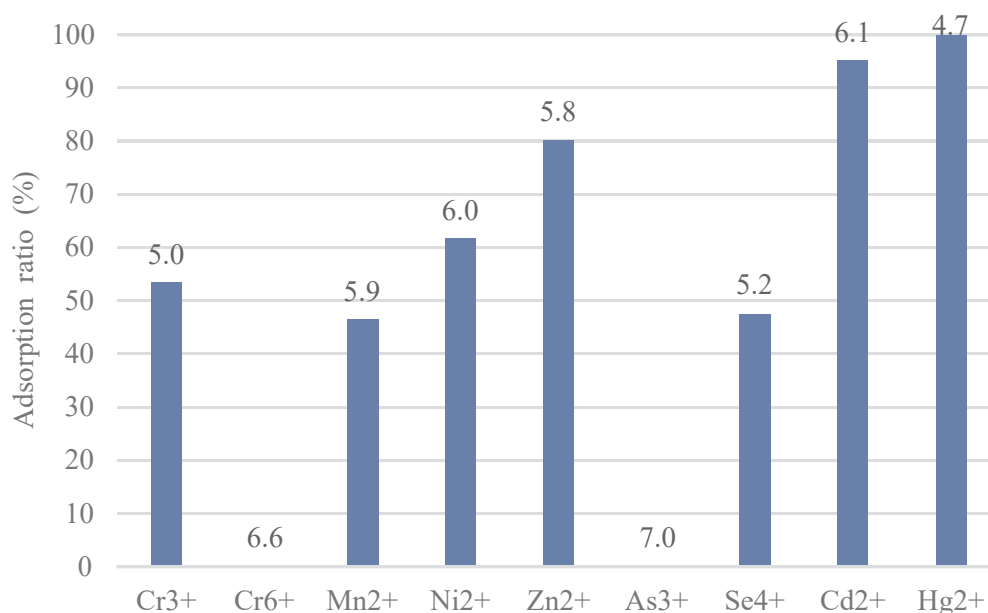


Fig. 2.13 Adsorption performance of RH (adding amount of 1 mL)

As shown in Fig. 2.14, the adsorption ratio decreases in most of the specimens to compare with using 1mL of the sample when 5 mL of the sample is added. It is considered that the amount capacity of adsorbing each ion of 0.6 g of RH may be clarified by increasing the amount of sample added. Although the adsorption ratio decreases for the most of samples, the divalent cations,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Hg}^{2+}$  tend to be relatively adsorbed. Especially, the RH for  $\text{Hg}^{2+}$  has a high adsorption ratio even if the addition amount is increased five times. The fact that 50 percents of the added amount is adsorbed suggests the adsorption amount increases. Almost all

of  $\text{Hg}^{2+}$  is adsorbed in 1 mL of addition amount and about half adsorption in 5 mL, and there is a possibility that the adsorption limit amount for  $\text{Hg}^{2+}$  is between 1 and 5 mL. The reason why the adsorption ratio decreases in most samples is considered to depend on the difference in the initial pH value (see Table 2.2). The heavy metal ion is easily adsorbed in the lower initial pH value. On the other hand, among all specimens, the adsorption ratio of the only specimen of  $\text{As}^{3+}$  and  $\text{Cr}^{6+}$  are relatively high and the pH values after the test are almost the same regardless of the amount of addition. In near future, the test should be conducted by adjusting the pH value in order to clarify the influence of the pH value on the adsorption of each heavy metal ion, and the test in which the addition amount is minutely set is conducted in order to ascertain the adsorption limit amount of RH. Consideration of immersion test using the RH is summarized in Section 3 of the next chapter, "Consideration of immersion test using FbA".

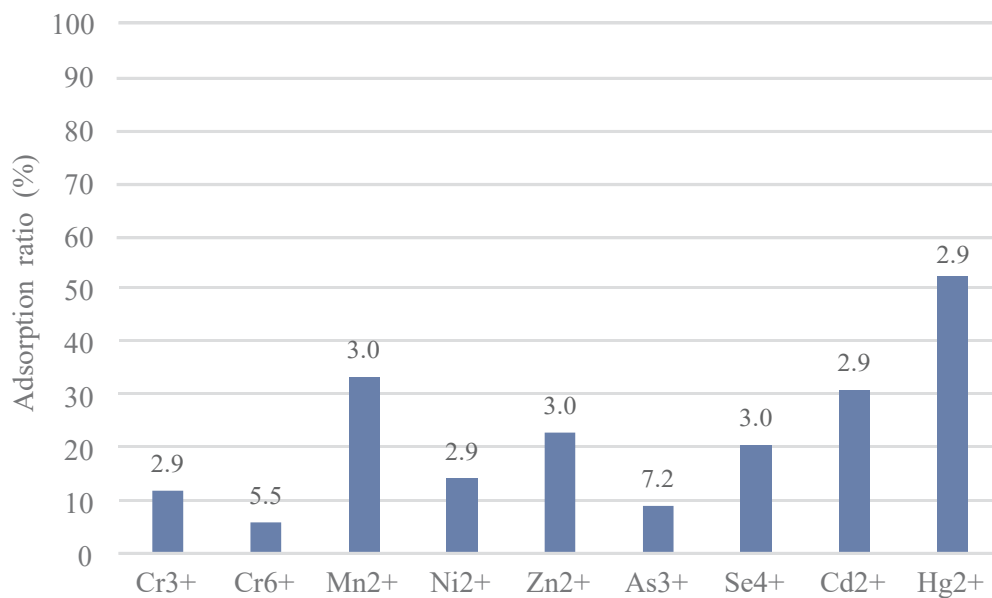


Fig. 2.14 Adsorption performance of RH (adding amount of 5 mL)

## 3. Fishbone Adsorbent (FbA) and Fishbone Powder (FbP)

### 3.1 Physical property of FbA and FbP

Hydroxyapatite is the basic calcium phosphate, and its chemical formula is  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . Hydroxyapatite is excellent in biocompatibility and used for materials such as artificial bone and implants because it is a major constituent of tooth and bones. In addition, hydroxyapatite has many functions such as high adsorptive properties (especially amino acids, proteins, lipids, sugars, etc.), ion exchange properties, catalytic properties, and ionic conduction properties<sup>30) 31) 32)</sup>. It is artificially synthesized by many methods and it is used in various fields including the biomaterials. According to the study of Nishiyama et al., it is already known that hydroxyapatite has adsorption properties not only for heavy metals but also for strontium<sup>33)</sup>. Some hydroxyapatites are derived from cattle bones or pig bones, but in this study, the adsorbent based on hydroxyapatite derived from fish bones (Fishbone Absorber, hereinafter referred to as FbA and, see Photo 3.1) is used for various tests. The size of the piece is approximately 1 cm volume and its weight is approximately

0.6 g. The FbA is produced by burning fish bone discarded at a fishing port.

Ion exchange principle of hydroxyapatite is hereby explained. The unit crystal lattice structure of hydroxyapatite consists of the hexagonal system as shown in Fig. 3.1. Two arrangement of calcium ion exists in the unit lattice. One is called the screw axis calcium (7 coordinates), and calcium ion exists at each vertex of the triangle. Another is called the columnar calcium (9 coordinates), and it has a tunnel structure. Calcium ion is easy to move the outside of structure in such a tunnel structure. Therefore, calcium ion is easy to be substituted with other positive ion within an organism<sup>34)</sup>.

Fishbone Powder (FbP) is made by powderizing FbA (see Photo 3.2). The FbP is prepared to verify the effect of particle size on an adsorption effect. Also, it is used to confirm the detailed adsorption performance of fishbone for heavy metals.

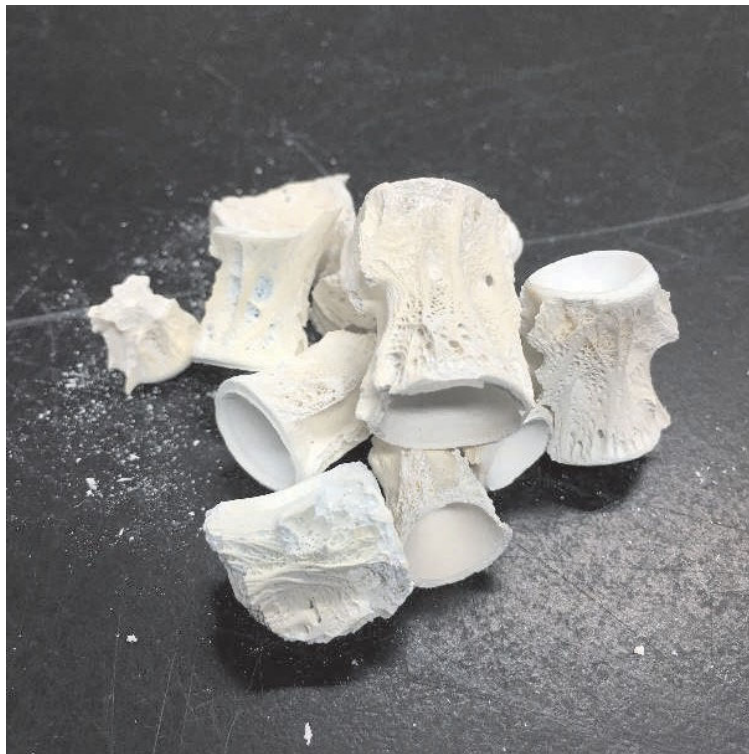


Photo 3.1 Fishbone absorber (FbA)

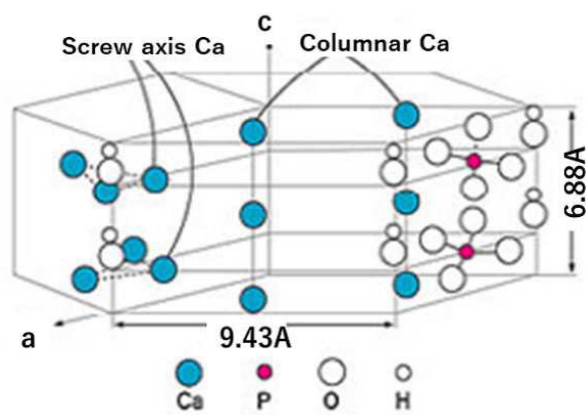


Fig. 3.1 Crystal structure of hydroxyapatite<sup>34)</sup>

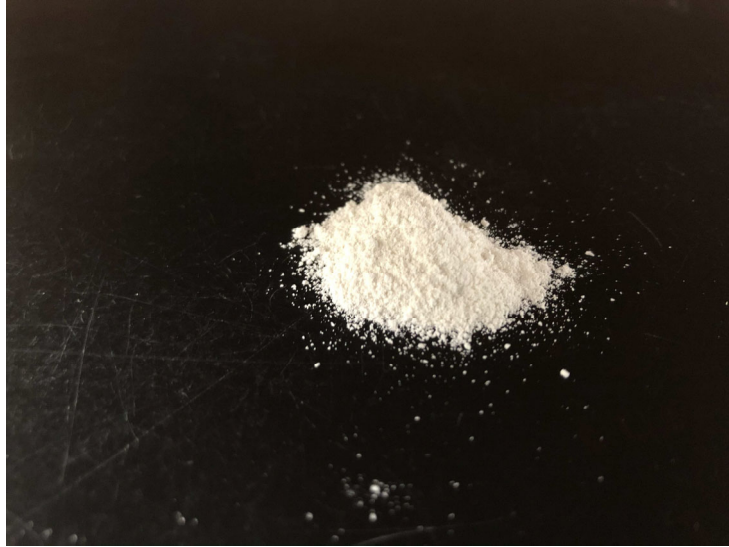


Photo 3.2 Fishbone Powder (FbP)

### 3.1.1 XRD (FbA)

XRD is used to analyzing the FbA. The analysis method is shown in Fig. 3.2. An intensity peak appears when the value of  $2\theta$  is around 30, 40 and 50. This peak appears when calcium phosphate is included in the crystal. The peak distribution is similar to that of general natural and artificial hydroxyapatite<sup>35</sup>).

### 3.1.2 SEM-EDS (FbA)

#### SEM image of FbA

Fig. 3.3 is a SEM image. The observation magnifying power for the FbA is set to 7000 times. The FbA is composed of very fine particles, and it is confirmed that the particle size is 0.1  $\mu\text{m}$  by SEM image. Thus, it is confirmed that the FbA is formed by collecting countless of fine particles with Fig. 3.3, and this high specific surface area may be due to adsorption.

#### Spectrum of FbA

Fig. 3.4 is the spectrum of the FbA with EDS. It is revealed that the elements contained in the FbA are carbon, oxygen, sodium, magnesium, phosphorus and calcium by the spectrum. It can be said that most of the FbA is composed of oxygen, phosphorus and calcium from the measure of the intensity value. The analysis results are valid because main component of the FbA are phosphate calcium. Alternatively, the FbA is originally an abandoned fish bones, and the



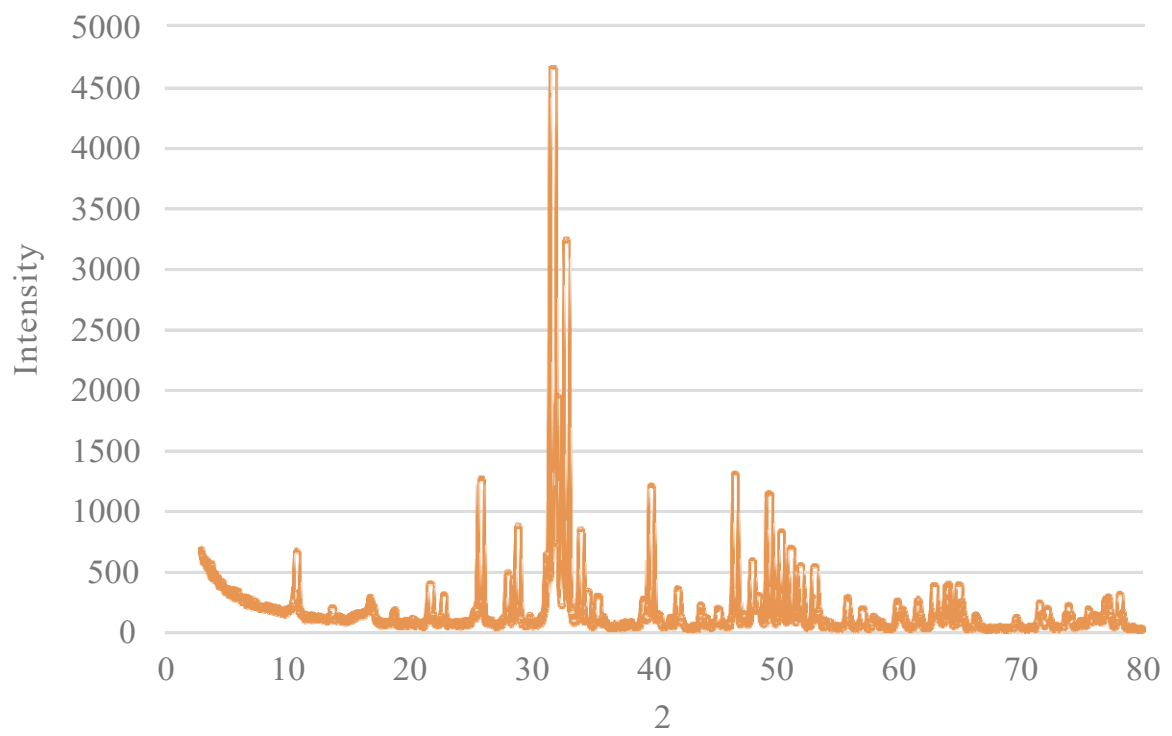


Fig. 3.2 Spectrum of FbA by XRD



Fig. 3.3 SEM image of FbA

seawater in which fish live is rich in minerals such as sodium. The intensity peaks of the sodium and the magnesium are appeared since these minerals remain in the fish bones. These components may not affect the test since the peaks are relatively small to compare with intensities of other elements.

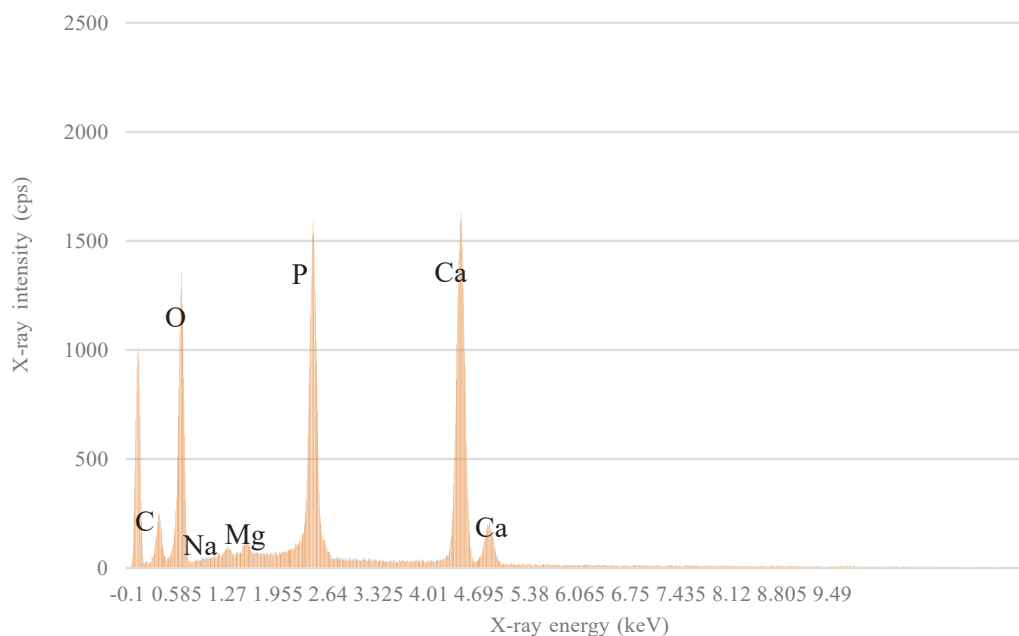


Fig. 3.4 Spectrum of FbA by EDS

## 3.2 Immersion test of FbA

In the immersion test using the FbA, the adsorption performance of the FbA on strontium and heavy metals are verified. The test method of the immersion test using heavy metals has already described in Section 3 of Chapter 2. However, the background and object of the study are anew detailed in this section because the assumed environment is different in the immersion test using strontium.

### Background and object

The nuclear disaster at the Fukushima Daiichi nuclear energy plant (1F) of the Tokyo Electric Power Company was indirectly caused by the Great East Japan Earthquake and the Tsunami on March 11, 2011. The radioactive materials discharged from the 1F due to the accident has contaminated in the surrounding land and ocean. The impact on aquatic products is of special concern as a result of the release of radioactive materials into the marine environment. Fig. 3.5 - Fig. 3.8 are developed based on the Report of Radioactivity Surveys conducted by the Hydro-graphic and Oceanographic Department Japan Coast Guard. These figures show the contaminated situations of cesium-137 ( $^{137}\text{Cs}$ ) and strontium-90 ( $^{90}\text{Sr}$ )<sup>36)</sup>. The vertical axis in the graphs is the detected value of  $^{137}\text{Cs}$  or  $^{90}\text{Sr}$ , and the horizontal is the measured year. They are surveyed in Off Otaru, Sendai bay, Tokyo bay, Ise bay and Osaka bay. The detected values of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  in the marine water are shown in Fig. 3.5 and Fig. 3.6, respectively. The detected values of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  in the marine mud are shown in Fig. 3.7 and Fig. 3.8, respectively. The radioactive concentration of strontium in Tokyo bay is almost the same as that in Sendai bay. However, the radioactive concentration of Cs in Tokyo bay is the highest. The spreading of the radioactive materials is evident from the survey results. Alternatively, it is confirmed that a large quantity of Cs and Sr were detected from marine water on 2011 and they were high in the sediment after 2012. After that, the detected of Sr did not change. On the other hand, the level of cesium remains the same until 2014. These survey results indicate that the radioactive contamination in hydrosphere is due to the cesium. It is important to take note of the matter of tainted water in the 1F. When groundwater flows into the reactor buildings, the groundwater is contaminated by radioactive materials that accumulate around the reactor buildings. Also, the securing the storage facility is a serious problem. Table 3.1 is recreated on the basis of the results, which are obtained from the analysis for groundwater in the 1F by the Tokyo Electric Power Company Holdings<sup>37)</sup>. The groundwater is collected from the thirty points which are located around the seawall of the Units 1-4 of the nuclear reactor buildings so as to investigate the contaminated situation by  $^{137}\text{Cs}$  and beta ray. The average of detected value of  $^{137}\text{Cs}$  and beta ray in the groundwater are shown in Table 3.1. Though the Tokyo Electric Power Company Holdings set out to decrease the inflow of groundwater through the nuclear reactor buildings and steps down the contamination degree of tainted water, the sign of solution is not shown. The

detected value of beta ray is very high to compare with that of  $^{137}\text{Cs}$ . It is considered that the tainted groundwater may include the major quantity of  $^{90}\text{Sr}$ , because  $^{90}\text{Sr}$  is the representative radioactive material that emits the beta ray. Therefore, the removal of Sr in the tainted water and Cs in marine mud are respectively required for remediation. Alternatively, Sr is more dangerous than Cs due to the following fact. When Cs is taken in the human body, it is mainly absorbed into muscle. After that, it is released from the body as sweat or urine. Sr, on the other hand, is absorbed into bone and is stored there for a long time. When the tainted water including the major quantity of Sr released to marine environment, it is possible that humans are exposed by ecological chain and biological concentration. Therefore, the decontamination of Sr is urgently needed. The experiments in which Sr is adsorbed to the adsorbent under the marine and tainted water so as to solve this problem were conducted in the past <sup>38)</sup>. It was confirmed that the adsorption ability of adsorbent for strontium is varied in different solutions. Thus, in this study, the adsorption ability of adsorbent is examined to maximize the performance of adsorbent for Sr under the various environmental conditions. In concrete terms, a number of water solutions are prepared, and the adsorption tests of the adsorbent for Sr in each water solution are conducted. The adsorption ability of adsorbent is understood by comparing the test results.

Table 3.1 Average of detected value of  $^{137}\text{Cs}$  and beta ray in the groundwater

	$^{137}\text{Cs}$ (Bq/L)	Sum of beta ray (Bq/L)
Around seawall of Unit 1	5.50	28.17
Around seawall of Unit 2	2931.79	92590.00
Around seawall of Unit 3	4.30	7585.11
Around seawall of Unit 4	24.90	1146.60

### 3.2.1 Strontium and heavy metals

#### Strontium Sr

The heavy metals used in the experiment are as described in Section 3 of Chapter 2. Radioactive discharged of value of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  are high, and those half-life is long. Furthermore,  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  are deeply committed to the radioactive pollution in marine because these are soluble in water. Especially,  $^{90}\text{Sr}$  is at high risk, since the property of strontium is more or less same as those of calcium that is absorbed into the bones after entering the body <sup>39)</sup>. Such internal exposure of  $^{90}\text{Sr}$  is a dangerous. Radiation exposure is divided into two categories; one is the external exposure, and the other is the internal exposure. The external exposure occurs when

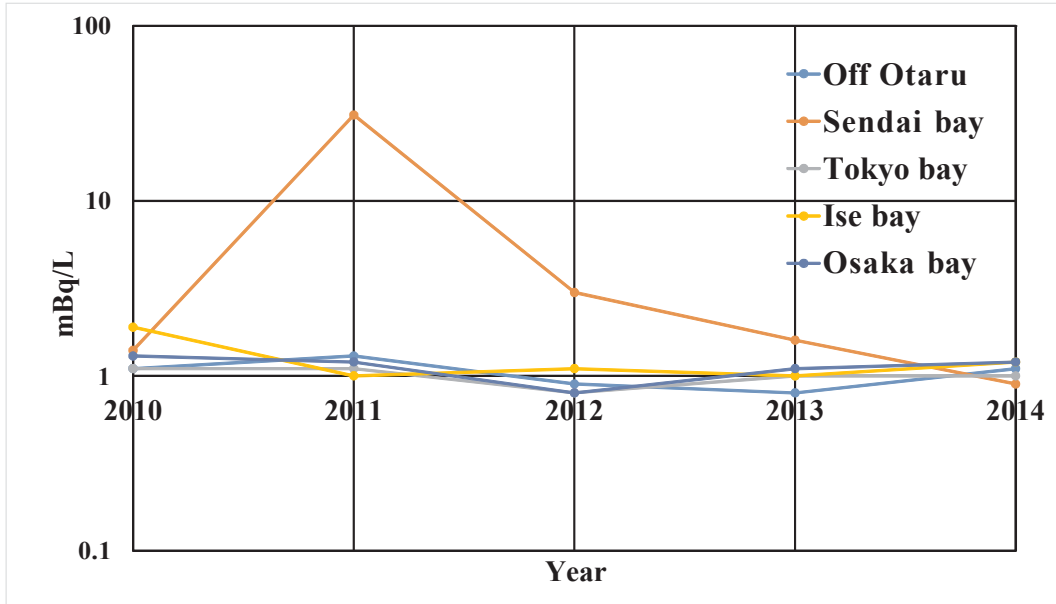


Fig. 3.5 Secular change of <sup>90</sup>Sr in marine water

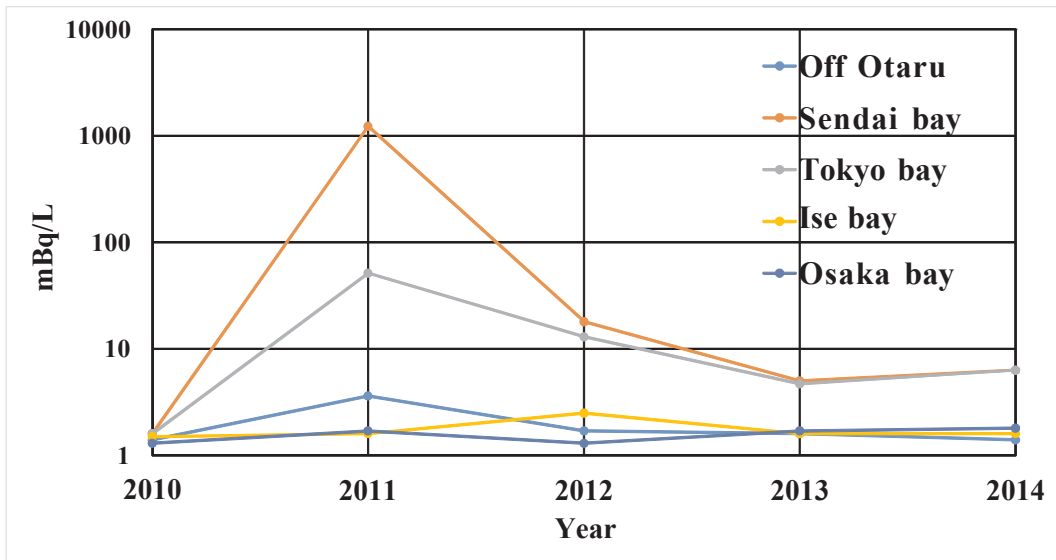


Fig. 3.6 Secular change of <sup>137</sup>Cs in marine water

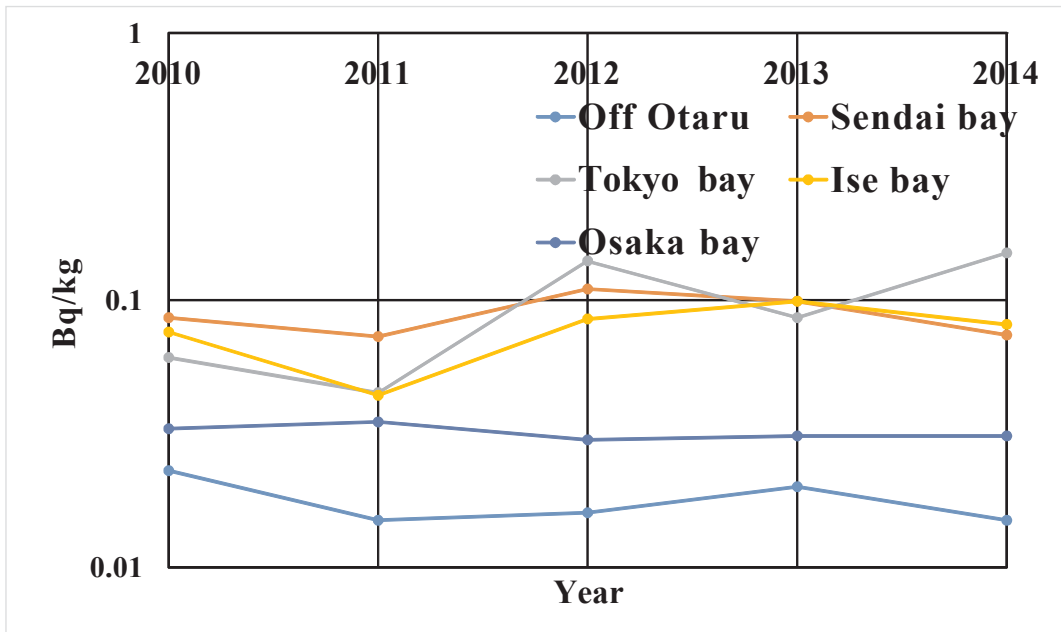


Fig. 3.7 Secular change of <sup>90</sup>Sr in marine mud

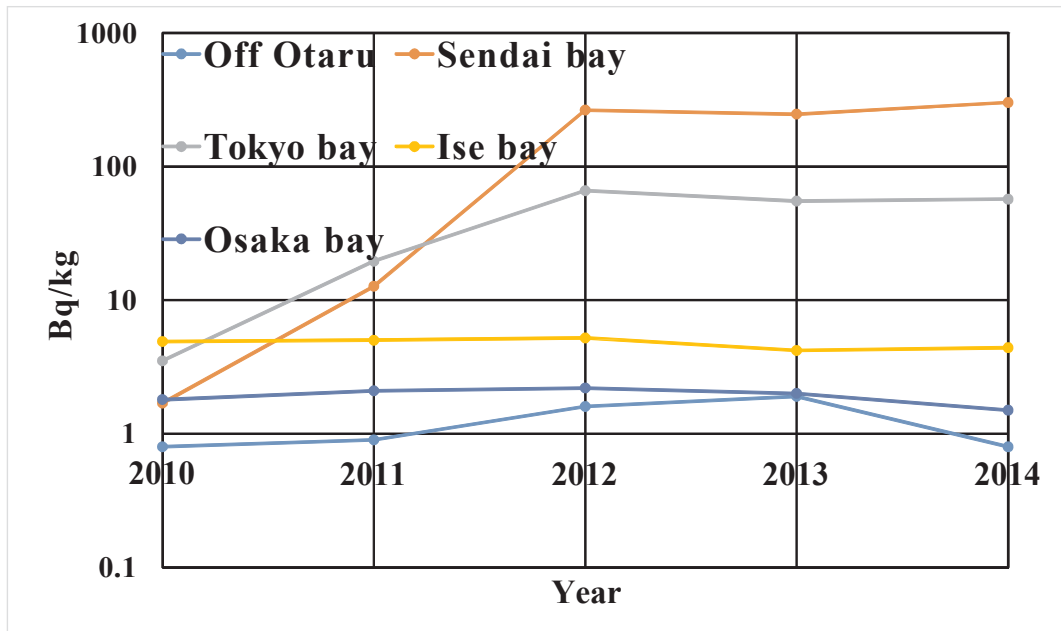


Fig. 3.8 Secular change of <sup>137</sup>Cs in marine mud

an organism receives radiation from outside the body. The internal exposure allows strontium to be substituted for calcium in the bone, and it is rare that the strontium is expelled from the body. This behavior is different from that of cesium that is absorbed into the muscles in the body. Alternatively, the nuclear power generation uses the energy generated by the reagency of atom core, and the huge energy is generated by a few fuel. The uranium and plutonium are used as the fuel of the nuclear power generation. The atom core is fissioned to the further small atom core by entering of the neutron into the uranium and plutonium from outside the atom core. The heat energy of the fission is used in the power generation (see Fig. 3.9). The burden to the environment is low because the carbon dioxide is not emitted. However, the large amount of radioactive materials exist in the using or used fission fuel because the radioactive isotope is generated by the fission <sup>40</sup>). Furthermore, the nuclear number of the radioactive isotope is often 84-105 or 129-149 <sup>41</sup>). Though the various radioactive isotopes of the nuclear number in the range exist, the radioactive isotopes of the long half-life continue to remain in the nuclear fuel rod. Therefore, the many <sup>137</sup>Cs and <sup>90</sup>Sr of the long half-life exist in the nuclear fuel rod. The above facts indicate that <sup>90</sup>Sr is the threat to humans health, and that <sup>90</sup>Sr should be decontaminated as quickly as possible.

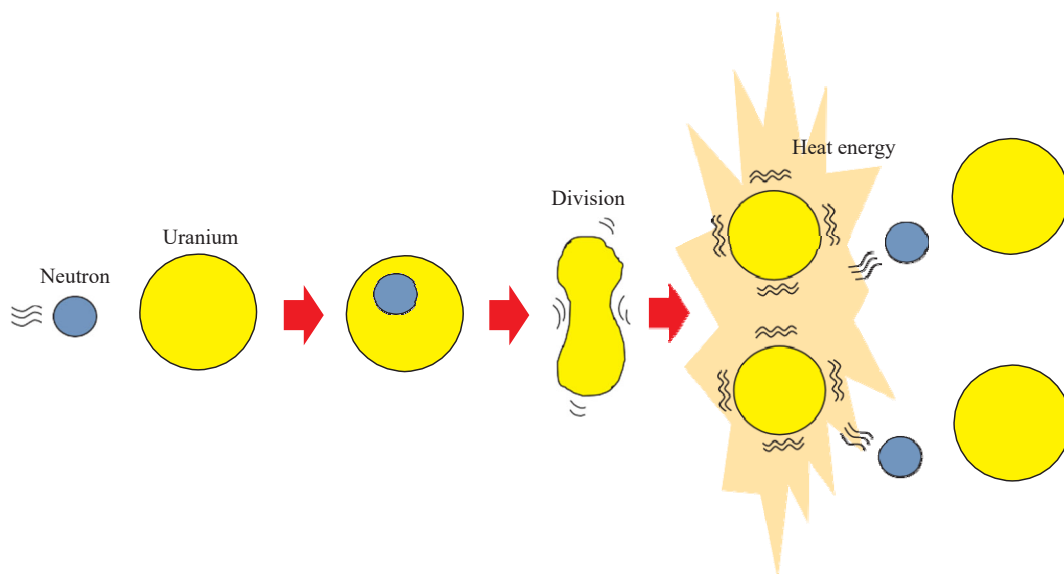


Fig. 3.9 Mechanism of fission

### 3.2.2 Immersion test and analysis method

Sr

In the experiment, the FbA and the zeolite are used as the adsorbent. The zeolite is used in order to compare the performance of the FbA due to its ability to highly adsorb cesium <sup>42</sup>). Each single size of the zeolite is about 0.2 - 0.5 cm volumes, and the weight is about 0.05 - 0.3 g (see Photo 3.3). Alternatively, five water solutions and pure water are prepared to compare the adsorption ability of the FbA or the zeolite for strontium in different environments. One specimen is prepared in terms of comparison; it is pure water, while the other contains sodium chloride, sodium acetate, potassium chloride, magnesium chloride and sodium nitrate 3 percent. The reason why the sodium chloride and etc. is 3 percents concentration in the each solution is because this is close to that in seawater. Test method is described in Section 3 of Chapter 2.

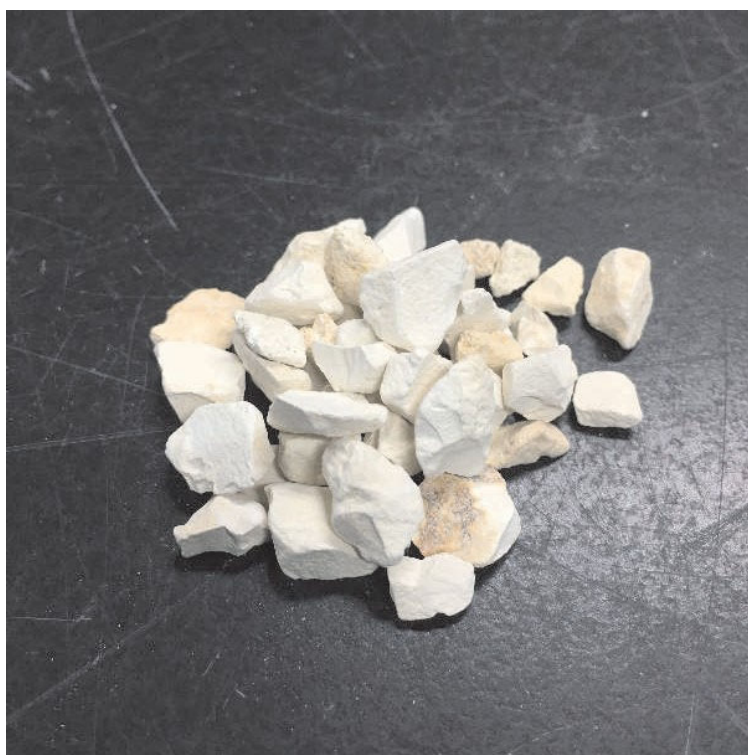


Photo 3.3 Zeolite

### 3.2.3 Test results for strontium

The residual ratio of strontium in each solution is shown in Fig. 3.10-Fig. 3.13. Also, Fig. 3.10 and Fig. 3.11 are test results when the FbA is utilized as the adsorbent, Fig. 3.12 and Fig. 3.13 are test results when the zeolite is utilized as the adsorbent. The vertical axis in the



figure is the residual ratio of strontium, and the horizontal one is the immersion time. About 10 pieces (6.0-7.0 g) of the FbA, 6.0g of the zeolite, are used in each experiment and the immersion times were 24, 72, 120 or 168 hours.

### Solutions containing chloride for FbA

The experimental results of the three solutions with involvement chloride are shown in Fig. 3.10. It is confirmed that the residual ratio of strontium in three specimens decreases with the passage of time. Especially, when potassium chloride solution or sodium chloride solution is employed as the solution, the residual ratio of strontium is almost zero percent after 168 hours, and it is the lowest in the potassium chloride solution after 24 hours. It is possible that the adsorption of the FbA for strontium is prompted by the potassium. On the other hand, when magnesium chloride solution is employed, almost thirty percent of strontium remained in the solution even after 168 hours. Furthermore, the adsorption ability of the FbA for strontium is clearly influenced by divalent cationic magnesium.

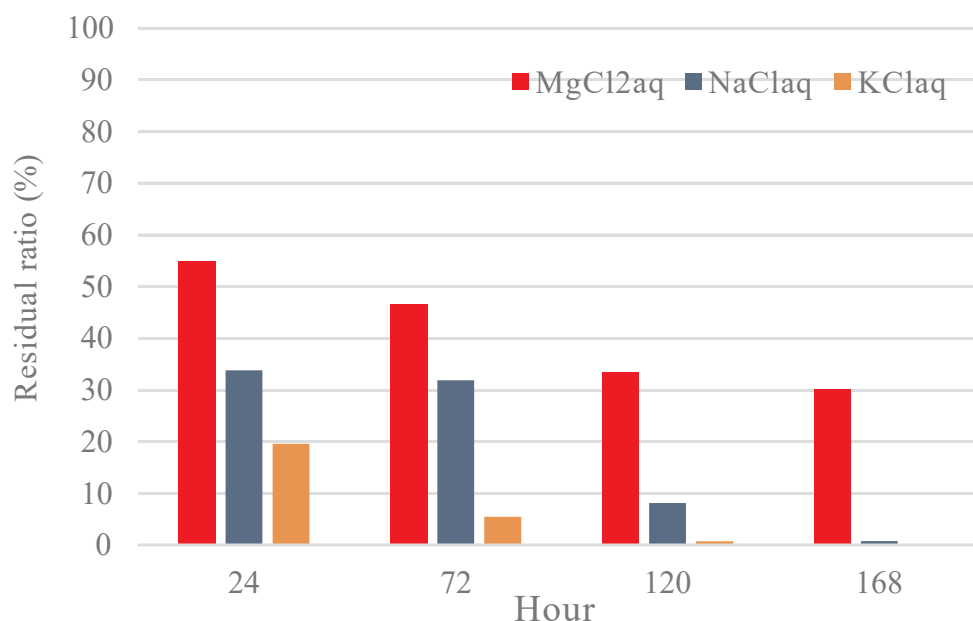


Fig. 3.10 Residual ratio of strontium in magnesium chloride, sodium chloride or potassium chloride solution for FbA

### Solutions without chloride for FbA

The experiment results of three solutions with non-involvement chloride are shown in Fig. 3.11. It is confirmed that the residual ratio of strontium in three solutions decreases with passage of

time. Alternatively, when three solutions are compared in the light of existence or non-existence of sodium, the residual ratio of strontium in the solution containing of sodium is relatively higher than that in the specimen using pure water. It is considered that the adsorption ability of the FbA for strontium is slightly influenced by sodium. Nevertheless, more than ninety percent of strontium is adsorbed to the FbA in case of utilizing each solution.

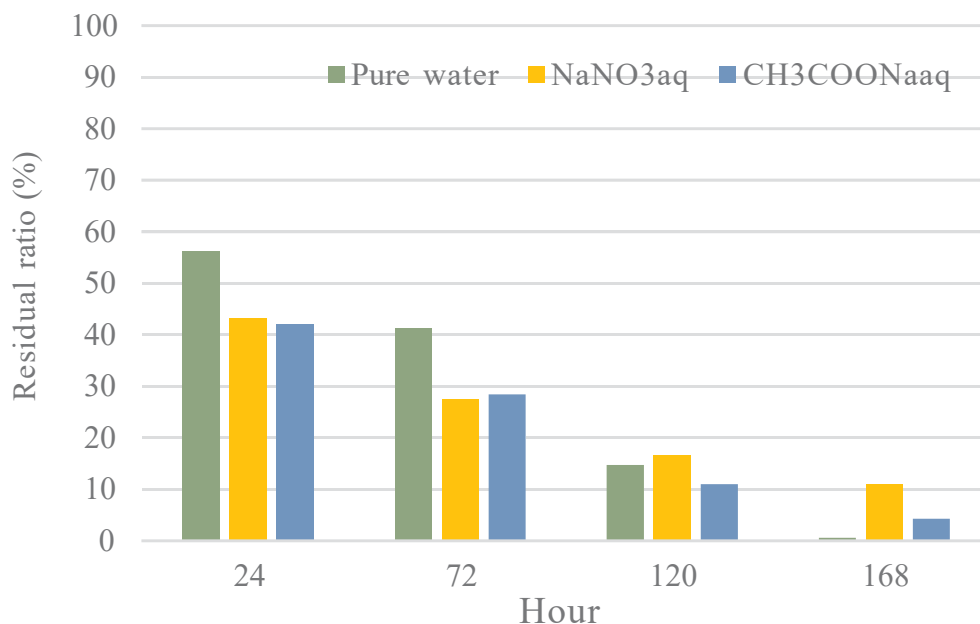


Fig. 3.11 Residual ratio of strontium in pure water, sodium nitrate or sodium acetate solution for FbA

### Solutions containing chloride for zeolite

The experimental results of three solutions with involvement chloride are shown in Fig. 3.12. The residual ratio of strontium remains virtually unchanged with passage of time when the sodium chloride solution or potassium chloride solution is utilized. It is confirmed that the strontium is inefficiently adsorbed because the residual ratio after 168 hours is about 80 percent.

### Solutions without chloride for zeolite

The experiment results of three solutions with non-involvement chloride are shown in Fig. 3.13. The residual ratio of strontium remains virtually unchanged with passage of time when the sodium nitrate solution or sodium acetate solution is utilized. The residual ratio after 168 h is about 90 percent. Alternatively, the residual ratio after 72 hours decreases by 50 percent when

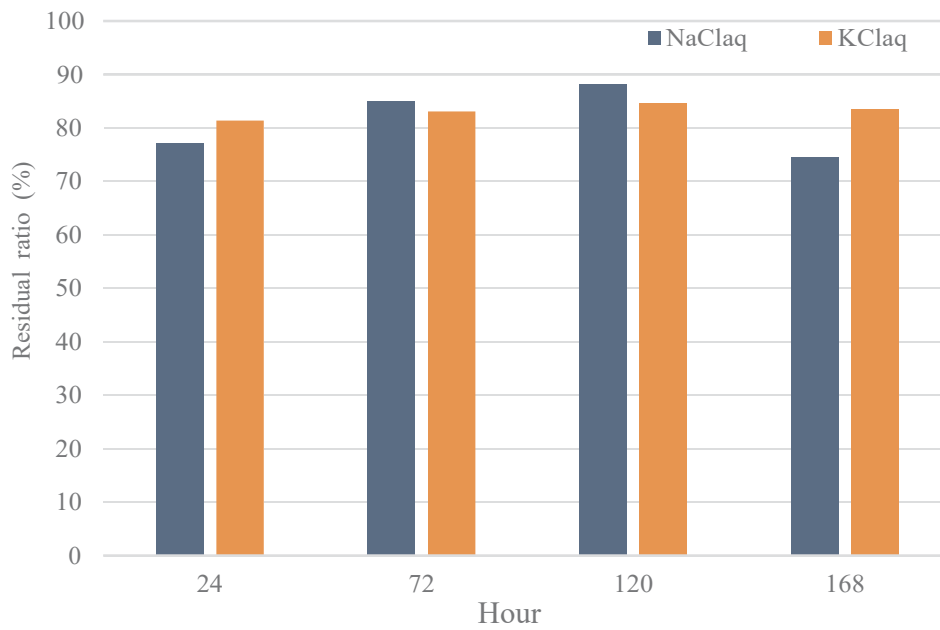


Fig. 3.12 Residual ratio of strontium in sodium or potassium chloride solution for zeolite

pure water is utilized. However, it remains unchanged after 72 hours. It is confirmed that the zeolite is not suitable as the adsorbent for adsorption of strontium because the adsorption ratio of the zeolite is lower than that of the FbA.

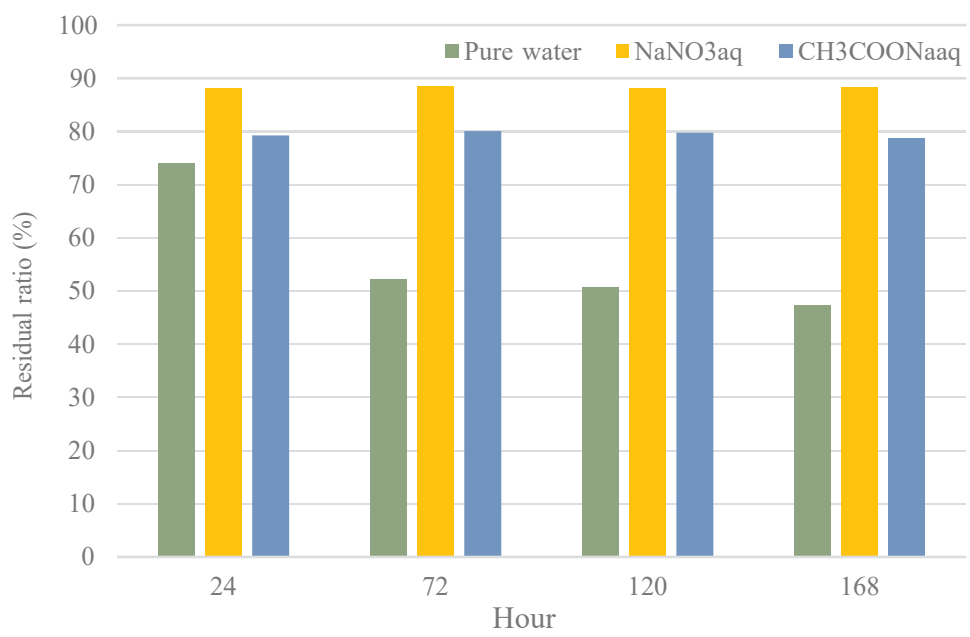


Fig. 3.13 Residual ratio of strontium in pure water, sodium nitrate or sodium acetate solution for zeolite

### 3.2.4 Test results for heavy metals

First, the results of the adsorption test using the FbA as an adsorbent for each heavy metal are shown in Fig. 3.14 and Fig. 3.15 which correspond to the adsorption test adding 1 mL (initial concentration is about 3.3 ppm) and 5 mL (initial concentration is about 16.4 ppm) of the heavy metal standard solutions, respectively. The 1 piece of the FbA (about 0.6 g) is used in the test. As shown in Fig. 3.14, the adsorption ratio for  $\text{Hg}^{2+}$  is the highest of all samples and 90 percent or more of  $\text{Hg}^{2+}$  is adsorbed to the FbA when 1 mL of the standard solution is added. Subsequently, the adsorption ratio of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  is high, and the results are similar to those of the test using the rice husk described in Chapter 2. On the other hand, the adsorption ratio to  $\text{Cr}^{6+}$  and  $\text{As}^{3+}$  is low, and the result is also similar to the case using the rice husk described in Chapter 2, while the adsorption ratio for  $\text{Mn}^{2+}$  is higher than that of the case using the rice husk. The adsorption ratio of  $\text{Mn}^{2+}$  is about 50 percent when the rice husk is used. However, it exceeded 70 percent in the case using the FbA. It is considered that  $\text{Mn}^{2+}$  has a property to promote the calcification of bone in increasing the adsorption ratio of the FbA to  $\text{Mn}^{2+}$ .  $\text{Mn}^{2+}$  is a necessary mineral for the calcification of bone and is more easily absorbed into bone than other ions. It is presumed that  $\text{Mn}^{2+}$  is adsorbed to the FbA rather than the rice husk because the FbA is derived from fish bone. Additionally, the adsorption ratio of  $\text{Cr}^{3+}$  is slightly higher than that of the case using the rice husk. A slight precipitate is confirmed when the specimen of  $\text{Cr}^{3+}$  using the FbA is observed. It is widely known that heavy metal ions might precipitate hydroxides by increasing the pH value<sup>43) 44)</sup>. The value is different by the heavy metal ion and the element coexisting in the solution, and the specimen of  $\text{Cr}^{3+}$  generates a precipitate due to this property. As a result, the adsorption ratio increases by decreasing the ion concentration in the solution. Even in the specimens except for the test specimen to which  $\text{Cr}^{3+}$  is added, the pH value is changed from a weak acid to neutral in the case of using the rice husk. On the other hand, it increased to weak alkalinity in some specimen when the FbA is used. The adsorption performances of rice husk and FbA are very similar, but their effects on pH value in solution are different. For this reason, the FbA is fired while the rice husk is not burned. The rice husk ash is often used as an adjuster for the soil to neutralize acidic soils<sup>45)</sup>. It is clarified that the rice husk and the FbA can be used not only as an adsorbent for heavy metals but also as a pH adjuster by controlling the added amount in the case of using the rice husk and the FbA as contaminated water on site.

As shown in Fig. 3.15, the adsorption ratios for  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  are relatively high when 5 mL of the sample is added, and the values exceed 60 percent. For  $\text{Hg}^{2+}$ , it is presumed that the adsorption limit amount is between 1 and 5 mL in the case adding the rice husk. The amount of adsorption for  $\text{Cd}^{2+}$  increases as the added amount increases. The solution is acidic because the

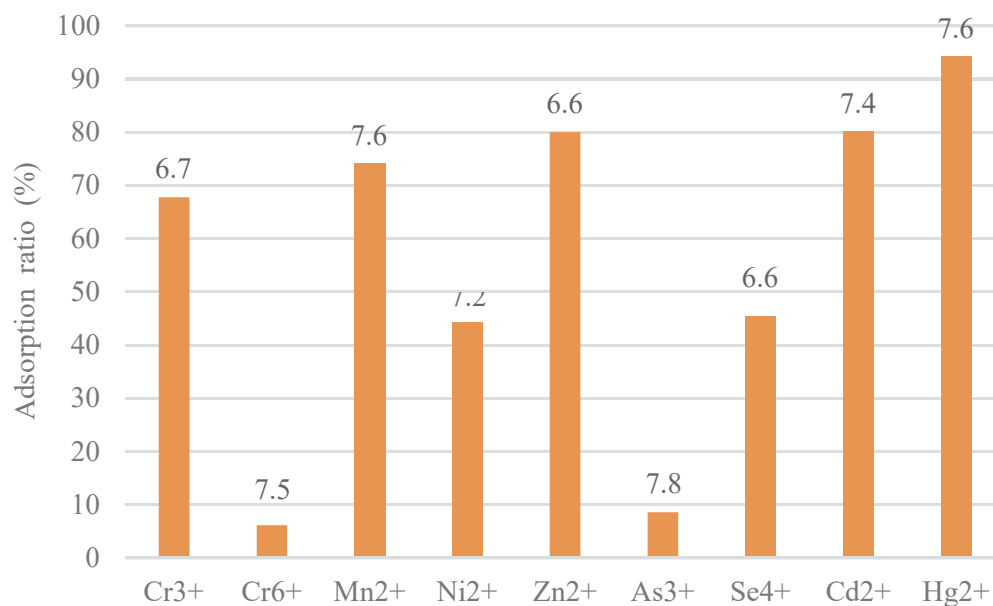


Fig. 3.14 Adsorption performance of FbA (adding amount of 1 mL)

pH value is low when 5 mL is added. It is considered that the pH value is low and the solution is acidic in the case of adding 5 mL. It is necessary to adjust the pH and conduct additional tests in order to clarify the mechanism. The adsorption ratio for other samples of adding 5 mL is lower than that of adding 1 mL, and the results show a similar tendency to those of 1 mL addition of heavy metals. It is needed to investigate each sample such as Hg<sup>2+</sup> and Mn<sup>2+</sup> of adsorption limit amount in detail. It is revealed that adsorption ability is higher for divalent cations, in particular, Group 12 elements, in both cases of the addition amount of 1 mL and 5 mL. As shown in Table 2.3, the ionic radius of the three kinds of ions which belong to group 12, is close to the ionic radius of Ca<sup>2+</sup>. This result suggests that the FbA may remove heavy metal ions from solution by physical adsorption. The heavy metal ions are adsorbed to the FbA and Ca<sup>2+</sup> is released instead, so that the adsorption performance may be higher for heavy metal ions with a close ionic radius of Ca<sup>2+</sup>. If the adsorption mechanism of FbA is physical adsorption, heavy metals adsorbed to the FbA can be taken out. In addition, not only the FbA but also heavy metals can be reused as new resources. Therefore, the adsorption mechanism should be examined in near future. The adsorption performance of the FbA is higher than that of the rice husk in the case of adding 5 mL of the most sample through all the test results. The rice husk has a high adsorption performance when an additive amount is about 1 mL. On the other hand, the FbA is more useful than the rice husk when the content of heavy metal ion in the solution exceeds a certain amount. Additionally, the adsorption performance of the FbA is higher than that of the rice husk in the case of adding

5 mL of sample. It is assumed that the FbA has more marginal adsorption than the rice husk.

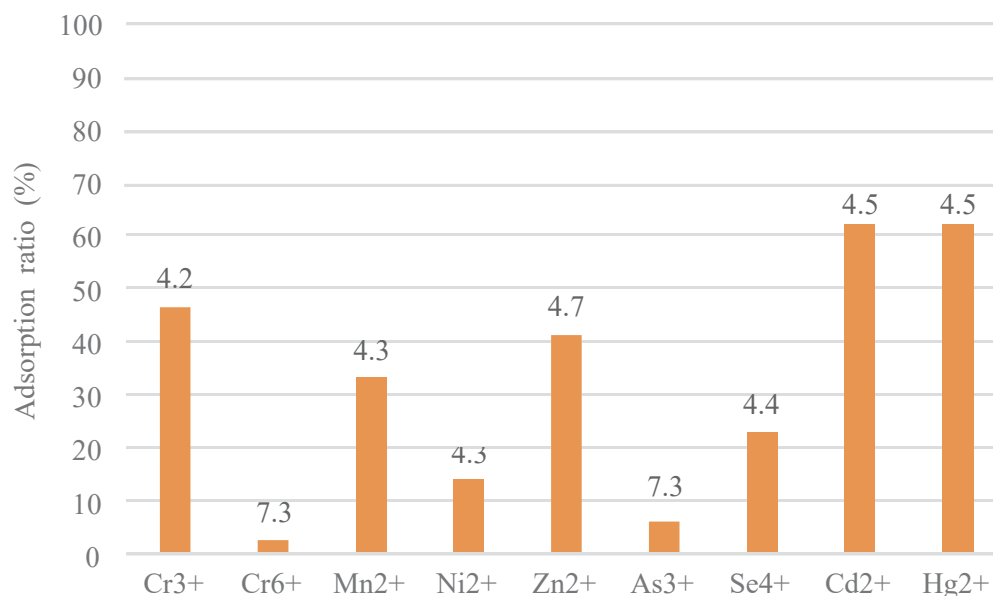


Fig. 3.15 Adsorption performance of FbA (adding amount of 5 mL)

### 3.2.5 Consideration of immersion test using FbA

#### Sr

In this study, adsorption experiments are conducted in various solutions to determine the adsorption ability of the FbA for Sr. It is confirmed that the FbA for Sr in the five solutions and pure water has the beneficial adsorption ability. The residual ratio of Sr is more or less zero percent in case of pure water, sodium chloride solution and potassium chloride solution. In particular, the residual ratio of Sr already declines up to twenty percent after 24 hours in the case of potassium chloride solution. It is considered that the ionization tendency of potassium is higher than that of Sr, which has an effect on the adsorption performance of the FbA. The influence on the FbA should be examined by increasing the concentration of potassium in near future. On the other hand, when the magnesium chloride solution is utilized, about thirty percent of Sr remains in the solution. It is considered that divalent cationic magnesium blocks Sr adsorption to the FbA. In fact, the seawater and the groundwater include various metal elements. Furthermore, it is necessary to examine the detailed influence of solutions on the adsorption performance of the FbA by conducting the experiment in which the concentrations of potassium, sodium and magnesium are similar. In addition, it is also confirmed that the adsorptive rate of the FbA is higher than the ratio of zeolite, which is selected as the comparative target. The adsorption

ability of the zeolite for Sr has a beneficial effect in four solutions and pure water. It is confirmed that the zeolite is not suitable as the adsorbent for Sr because the residual ratio exceeds 80 percent in the case of the immersion test with the four solutions. It is confirmed that the FbA is more effective adsorbent for Sr than the zeolite and the RH, but it is necessary to conduct the laboratory experiment in conditions including various environments so as to remove Sr from the seawater and marine mud in which the Sr is considered to be included. Alternatively, the FbA may have the potential to adsorb a large number of contaminants in addition to Sr. The FbA can become the effective material for the cleanup of air and water pollution.

## Heavy metals

In this study, the adsorbent manufactured from fishbones (FbA) and rice husk which are known as industrial waste are focused. The possibility as a new adsorbent is investigated by elucidating the fundamental adsorption performance for harmful substances and the principle of these materials. In the tests, the adsorption effect of rice husk and FbA on nine kinds of heavy metals which have harmful effects to the ecosystem are examined. The tests are conducted with preparing the additive amount to 1 mL, 5 mL of the heavy metals in order to ascertain the adsorption amount per unit piece of the adsorbent. As a result, it is confirmed that more than 40 percent of the additive amount of all metals except  $\text{As}^{3+}$  and  $\text{Cr}^{3+}$  can be absorbed by both adsorbents. In particular, both adsorbents have high adsorption ratio for Group 12 elements such as  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ . The rice husk and the FbA have the similar property of adsorption for 9 metals, and both adsorbents have powerful adsorption effect on divalent cations. Alternatively, it is presumed that other factors such as ionization tendency, ionic radius and specific gravity are related to ion adsorption as well as ionic valence. As shown in Table 1, in the case of the FbA, the ionic radius of the heavy metals well adsorbed to the FbA is close to that of the main component of the FbA. It is necessary to examine the influence of these factors such as the ionization tendency and the ionic radius on adsorption and the reason why the rice husks and the FbA have similar adsorption performance to heavy metals should be discussed in more detail. As the pH, the FbA tends to change the pH of the solution to alkaline more than the rice husk. It is considered to be caused by whether or not the calcination process is carried out. Depending on the firing temperature, organic acids is thermally decomposed or released as carbon dioxide in the process of burning substances including organic substances. Therefore, alkali metals and alkaline earth metals such as sodium, potassium and calcium remain on the surface of the material as oxides, carbonates and hydroxides. The pH value rises in the solution because this pyrolysis residue elutes. As a result, it is necessary to consider the influence of the pH value when the FbA is adopted as an adsorbent. For  $\text{As}^{3+}$  and  $\text{Cr}^{6+}$ , the adsorption ratio may also change by adjusting the pH value. Therefore, it is necessary to adjust the pH value and conduct the same test. Each limit amount of adsorption for FbA and rice husk are different for



heavy metal ion to compare the adsorption ratio according to the additive amount of the sample. The adsorption ratio of rice husk is high in the case of using 1mL, and that of the FbA is high in the case of using 5 mL. It is suggested that the FbA has a higher adsorption limit than the rice husk. Additionally, the adsorption performance of rice husk may be improved by adjusting the low concentration of heavy metal ion, and that of FbA by adjusting the high concentration. In near future, it is necessary to examine the adsorption performance by drastically decreasing or increasing the additive amount of heavy metal ion and widening the range of concentration.

### 3.3 Shaking test of FbP

As a result of verifying the adsorption performance of the FbA by the immersion test, it is found that the FbA has high adsorption performance for divalent cations (Cd, Zn, Hg). On the other hand, the adsorption performance for As and Cr is low, and there is room for improvement. Especially, the As is a harmful substance that is often regarded as a problem in developing countries <sup>46)</sup>. Therefore, it is important whether the adsorbent can adsorb As. Alternatively, in the immersion test, the adsorption performance can be grasped, though the adsorption mechanism cannot be mentioned; for example, chemical adsorption or physical adsorption. The adsorption mechanism of the FbA to heavy metals is verified in order to adsorb more harmful substances. As a verification method, a shaking test is performed to create an adsorption isotherm. The shaking test is conducted using the FbP in order to minimize the error of the test due to the difference in mass and specific surface area. In addition to Cd, Zn, Hg, and As, Cu is used for the test. Tests adjusting pH and tests using not only distilled water but also salt water are conducted. The characteristics of Cu are described in detail below.

#### Copper Cu

Conductivity of Cu has higher than that of other heavy metals, and it is used in electronic equipment and cooking utensils. In addition, Cu is an essential trace element, and the human body needs about 2 mg of copper per day. Cu is designated as a nutritional functional food by the Ministry of Health, Labor and Welfare, and there is concern about the risk of depletion due to increased consumption <sup>47)</sup>. Therefore, it is important to recover Cu from contaminated water. In this study, the adsorption performance of Cu is examined.

#### 3.3.1 Shaking test and analysis method (FbP)

1. Pure water, sodium chloride solution or magnesium chloride solution is poured into the centrifuge tube
2. Each heavy metal standard solution is added to the tube
3. pH value is adjusted and adsorbent is added to the tube
4. Tube is shaken in constant room temperature
5. Supernatant solution is analyzed by ICP-AES after centrifugation

Pure water (the pH value is non-adjusted) containing heavy metals is prepared as a base specimen. Furthermore, several test specimens with adjusted pH are prepared in order to verify whether the pH value affects the adsorption performance. The pH values of the specimens are adjusted to 2, 4, and 6. The pH values of the specimens in which the pH is not adjusted are shown in Table 3.2. The solvent of the heavy metal standard solution is nitric acid. Therefore,

the pH value of the undiluted solution is very low, and the diluted solution is also a strong acid. The initial pH of the specimen is approximately 3 excluding the specimen of As when the pH is not adjusted. The pH of the high concentration (30 and 60 ppm) specimen is very low, approximately 2. The standard solution of As is diarsenic trioxide - sodium chloride - hydrochloric acid solution. Alternatively, the initial pH of the As specimens (3-7 ppm) is approximately 6. Therefore, the specimen of As adjusted to pH value of 6 is not prepared (except for specimens at 30 and 60 ppm), and the test results of the non-adjusted specimen are cited. In addition, the specimens using sodium chloride solution or magnesium chloride solution are prepared to verify the adsorption performance for heavy metals in seawater. The pH value is not adjusted when using these solutions. The mass concentration of sodium chloride and magnesium chloride is 3.0 percent and 0.3 percent, referring to the ratio of components contained in seawater (see Fig. 3.16). Among the salinity contained in seawater, the sodium chloride is the most and magnesium chloride is the second. The shaking test is conducted to verify the adsorption performance and to create an adsorption isotherm. Therefore, the specimens with multiple concentrations are prepared and tested for each. The concentrations are 3, 4, 5, 6, 7, 30 and 60 ppm. The test procedure is described in detail.

First, 10 mL of pure water, sodium chloride solution or magnesium chloride solution is put in a centrifuge tube, and a standard solution of each heavy metal which is adjusted to 3, 4, 5, 6, 7, 30 or 60 ppm is added. Secondly, the pH value of specimen is adjusted to 2, 4 or 6. One mol/L sodium hydroxide solution and one mol/L nitric acid solution are added dropwise in small portions to adjust the pH. Twenty mg of adsorbents are immersed in the solution. The specimen is shaken at 200 rpm in a constant room temperature set at 20 degree for 24 hours. After the shaking test, the centrifuge for the specimen is conducted for 3 minutes at 2000 rpm. Using the supernatant obtained by centrifugation as the test solution, the concentration of each heavy metal ion in the test solution is analyzed by ICP-AES.

Table 3.2 Initial pH value

Initial concentration (ppm)	Cu	Cd	Zn	Hg	As
3	3.67	3.36	3.11	3.25	5.86
4	3.42	3.23	3.17	3.27	5.86
5	3.43	3.09	3.16	3.28	5.97
6	3.33	3.09	3.15	3.21	5.78
7	2.98	2.90	3.00	2.90	5.90
30	2.32	2.42	2.38	2.48	4.57
60	2.18	2.14	2.03	2.10	4.19

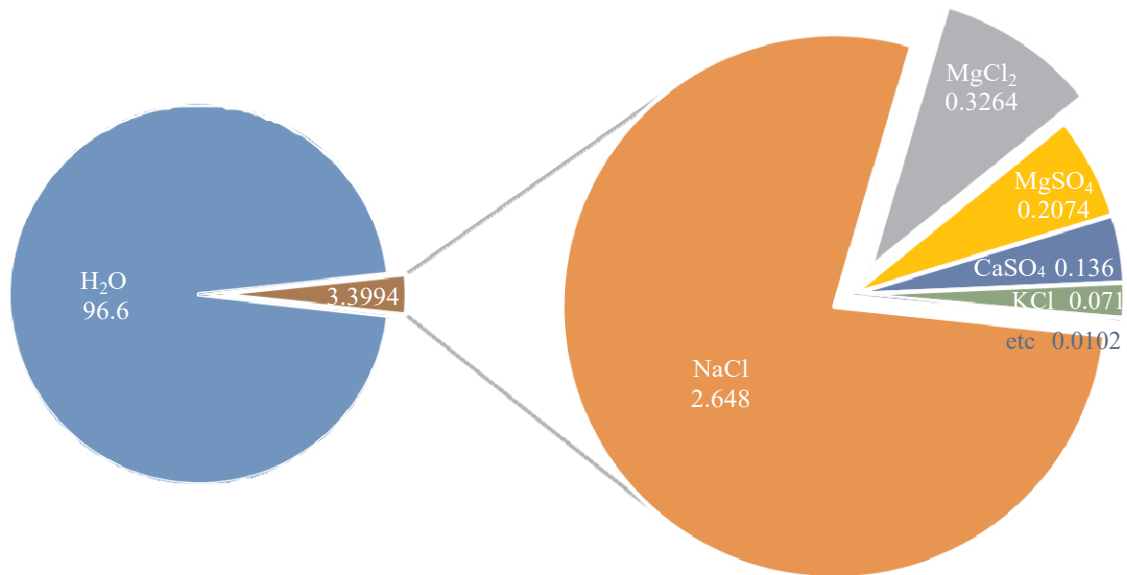


Fig. 3.16 Seawater composition

### 3.3.2 Adsorption

#### isotherm Adsorption

#### phenomenon

Adsorption is the phenomenon that attracts gas and liquid on the surface of an object. The adsorption phenomenon varies depending on the shape of the solid surface and the physical or chemical state of the surface. The surface shape can be grasped with an optical microscope such as SEM. On the other hand, the chemical surface cannot be understood only by observing an object, and it is necessary to consider the characteristics based on the actual measurement values obtained by the adsorption test. There is an adsorption isotherm as a method to understand the surface characteristics. The adsorption isotherm is utilized in the gas or the liquid adsorption, and in this study, the liquid phase adsorption is applied. There are three components in the liquid phase adsorption, and three interactions between them must be considered (see Fig. 3.17). In addition to the adsorbent-solute, the interaction between the solute-solvent and the adsorbent-solvent is involved in the adsorption. Affinity A includes van der Waals force, electrostatic attraction, hydrogen bond, etc. Affinity B depends on the solubility of solute in solvent, and

Affinity C is related to the adsorption to adsorbent. Usually, the solvent is adsorbed to the adsorbent in advance because the number of solvent molecules is predominantly higher than that of solute molecules. Therefore, it is necessary to desorb the solvent so as to adsorb the solute depending on the type of solvent. From the property of each Affinity, the adsorption for the solute appears strongly when Affinity A is large and Affinity B and C are small <sup>48)</sup>.

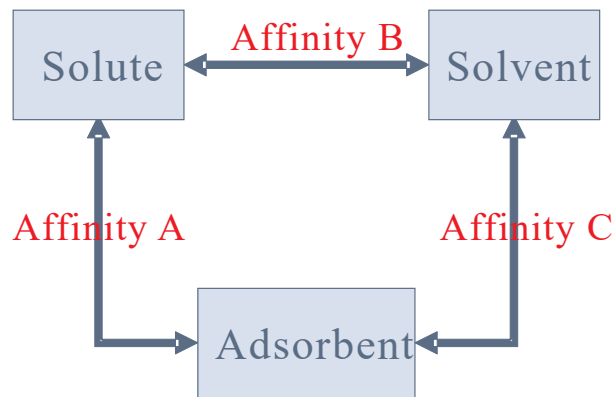


Fig. 3.17 Interactions acting on liquid phase adsorption

### Calculation method of adsorption isotherm

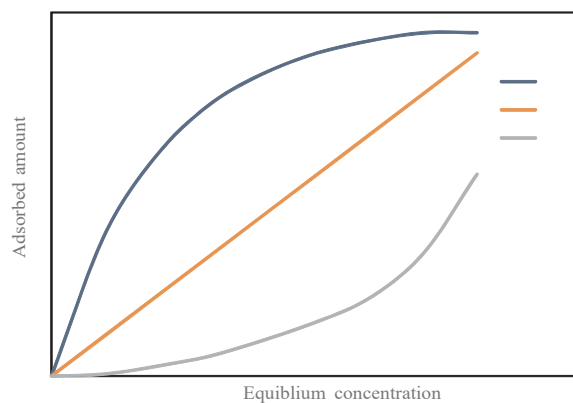


Fig. 3.18 Adsorption isotherm types

The adsorbent is placed in a sealed container to measure the adsorption isotherm, and a solution with a solute concentration  $C_0$  is added to the container at a constant volume  $V$ . Additionally, the mass of the adsorbent is  $M_i$ . Multiple tests are conducted with different

values of  $M_i$  or  $C_0$ . The sealed container is shock until the concentration of the solute reaches an equilibrium concentration at constant temperature. After that, the specimen is treated appropriately and the concentration of the solute remaining in the test solution is measured by an appropriate method. The residual concentration is  $C_i$  (equilibrium concentration). The equilibrium adsorption amount  $W_i$  per unit mass of adsorbent is calculated using these values. The calculation formula is as follow.

$$W_i = \frac{V(C_0 - C_i)}{M_i} \dots \dots \dots (3.1)$$

An adsorption isotherm such as Fig. 3.18 is obtained by plotting " $C_i$ " on the horizontal axis and  $W - i$  on the vertical axis. Type I in Fig. 3.18 indicates the presence of attractive forces that promote adsorption between the adsorbent and the solute. Also, type II shows an occurrence of phenomena such as absorption or a small amount of adsorption and distribution. Besides, type III indicates that the attractive force is very weak. The type I is desirable for industrial use as an adsorbent. If the concept of gas phase adsorption is used, type I can be further divided to two types. One is Type I-A which has a large energy for monolayer adsorption. Also, the other is Type I-B which the surface adsorption sites have high reaction activity. Furthermore, the adsorption of type I-A is often irreversible since type I-A exhibits an electron transfer type adsorption action. In other words, the irreversible adsorption is chemical adsorption. In this case, a test result is often analyzed by the Langmuir equation described later. Type I-B can be obtained when a solute is adsorbed to a solid such as activated carbon in which the external surface area with micropores is much smaller than the internal surface area of the pores. The type I-B is also a monolayer adsorption, and it is very difficult to distinguish between the type I-A and the type I-B in liquid layer adsorption.

### Equilibrium adsorption formula

The adsorption isotherm can be expressed approximately by an appropriate function under the assumption that the quantitative relationship (model of adsorption mechanism of adsorption isotherm) between the equilibrium concentration " $C$ " of solute and the adsorption amount " $W$ " obtained experimentally. The information on the adsorption mechanism is obtained by function provides. In this study, two typical adsorption formulas are used for the adsorption from a dilute solution and an ignorable adsorption for adsorption of solvent in order to create the model. This means that A FFInities B and C mentioned above are extremely small.

### Adsorption equation of Langmuir

The Langmuir equation is the theoretical equation that applies to most chemical adsorption. It is modeled by the concept that one molecule is adsorbed to one adsorption site. There are two assumptions, one is that only monolayer adsorption occurs, and the other is that an interaction

does not occur between adsorbed molecules. In other words, it is assumed that the solid surface is evenness. The actual solid surface is unevenness, and it is not good to discuss the adsorption mechanism by Langmuir equation only the adsorption. Therefore, the number of adsorption sites is discussed by comparing with another equation described later. The Langmuir equation in a liquid phase adsorption is expressed as follows.

$$W = aW_s C / (1 + aC) \dots\dots\dots (3.2)$$

The saturated adsorption amount is defined as  $W_s$  and the adsorption equilibrium constant is defined as  $a$ . One of the following Langmuir linear plot equations (3.3-3.5) are used to determine whether the measured data fits the Langmuir equation. Also, one of the formulas is used to check whether a linear relationship is established.  $C$  and  $W$  are values obtained from tests. Eq. (3.3) plots " $1/C$ " and " $1/W$ ", Eq. (3.4) plots " $C$ " and " $C/W$ ", and Eq. (3.5) plots " $W$ " and " $W/C$ ". Besides, both slope and intercept of the line are calculated by the least-square method. From these elements, the adsorption constants  $W_s$  and  $a$  are obtained, and the two values are substituted into the Eq. (3.2) to create the Langmuir adsorption isotherm. The linear plot produced by Eq. (3.4) is the best when the test data analyzed by three linear equations. Therefore, in this study, the Langmuir equation using the Eq. (3.4) is adopted.

$$1/W = 1/W_s + (1/aW_s)(1/C) \dots\dots\dots (3.3)$$

$$C/W = (1/aW_s) + (1/W_s)/C \dots\dots\dots (3.4)$$

$$W/C = aW_s - aW \dots\dots\dots (3.5)$$

### Adsorption equation of Freundlich

The Freundlich equation is one of the empirical equations representing the adsorption equilibrium. In the Freundlich equation, only monolayer adsorption occurs as in the Langmuir equation. Alternatively, it is modeled on the assumption that one adsorption molecule adsorbs to  $n$  pieces of adsorption sites. Usually, the more the molecules are adsorbed, the closer the distance between the adsorbed molecules becomes. Therefore, the physical collisions may occur. The phenomenon can be considered more than the Langmuir equation since the Freundlich equation is an empirical equation. Therefore, it is important to consider the Langmuir equation and the Freundlich equation together <sup>49)</sup>. The Freundlich equation is shown below.

$$W = K_F C^{1/n} \dots\dots\dots (3.6)$$

" $K_F$ " and " $1/n$ " are adsorption constants. From the logarithm of both sides, a linear expression like Eq. 3.6 is obtained. " $K_F$ " is calculated from the slope of this line and the amount of adsorption when " $C = 1$ ".

$$\log W = \log K_F + (1/n) \log C \dots\dots\dots (3.7)$$

"n" is a dimensionless number, and the shape of the adsorption isotherm depends on the "n" value. The advantage of chemisorption and physical adsorption is determined with the shape of the adsorption isotherm.

### 3.3.3 Shaking test results using FbP

The results of shaking tests using FbP are summarized for each heavy metal from the viewpoint of adsorption concentration. The sample in which the pure water as the test solution without adjusting the initial pH is the base specimen. The test results of the specimens with adjusted pH are shown in Fig. 3.19, Fig. 3.21, Fig. 3.23, Fig. 3.25 and Fig. 3.27. The adjusted initial pH value is 2, 4 and 6, and the initial concentration of heavy metal ions is 3, 4, 5, 6 and 7 ppm. Alternatively, the test results of the specimens using pure water and two types of solutions (sodium chloride solution and magnesium chloride solution) are shown in Fig. 3.20, Fig. 3.22, Fig. 3.24, Fig. 3.26 and Fig. 3.28. The initial pH is unadjusted and the initial concentrations are 3, 4, 5, 6, 7, 30 and 60 ppm. The vertical axis of the graph represents the residual concentration of each heavy metal ion in the test solution, and the horizontal axis represents initial concentration of heavy metal ions.

#### Test results of specimen adjusted pH for Cu

The NA in the graph is a specimen in which the pH is not adjusted, and the number at the top of the bar graph is the pH value of the test solution after the test. Cu is hardly detected from the specimens other than the initial pH 2. It is clarified that the FbP has high adsorption performance for Cu. Alternatively, there is almost no difference in the residual concentration when the initial concentration increases. According to the wastewater standards set by the Ministry of the Environment, the permissible concentration of Cu is 3 ppm or less. The residual concentration of Cu in the test solution is well below 3 ppm, and it is considered that the FbP is effective for the actual wastewater containing Cu. Furthermore, focusing on the initial pH, Cu is more easily adsorbed by the FbP when the initial pH is near neutral. Especially, the residual concentration decreases significantly when the initial pH value is adjusted to 2. The reason why the acidity is too high. The FbP surface may be dissolved by the strong acid solution. The pH value is increased by the eluted hydroxide ions when the FbP is added to the solution. The pH after the test of the initial pH 4, 6 and NA of specimens increase. However, the pH value after the test of the initial pH 2 of specimen is approximately 4.5, and the pH value is rarely below 2 in the natural environment. Therefore, the FbP can be used as an adsorbent.



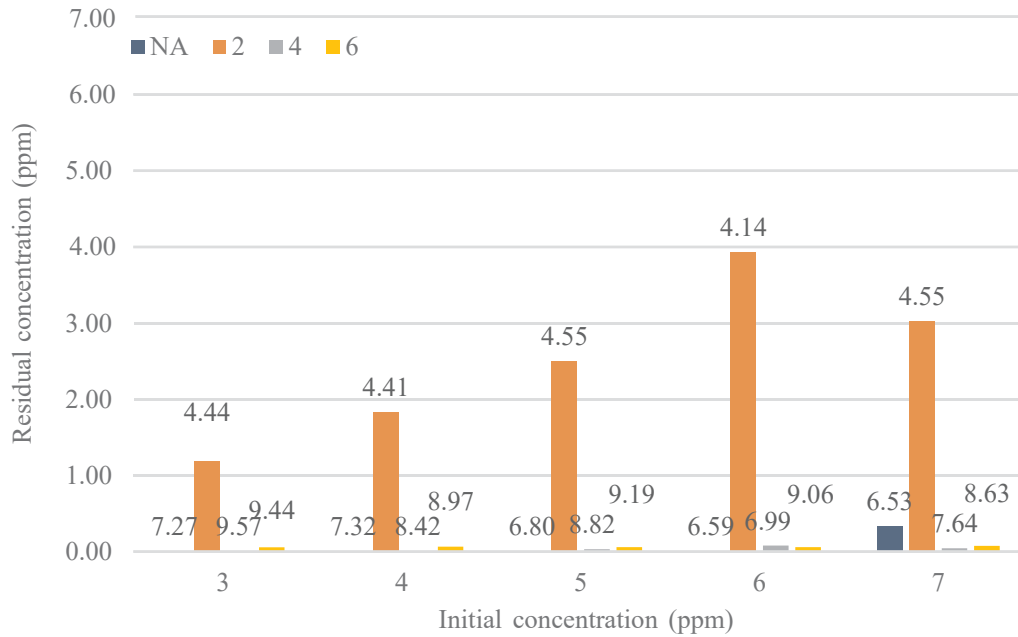


Fig. 3.19 Test results of specimen adjusted pH for Cu

### Test results of specimen eaery solutions for Cu

The results of the shaking test for the Cu for each solution is shown in Fig. 3.20. In all specimens, similar results are shown regardless of the initial concentration and solution type. The FbP selectively adsorbs Cu even when chlorine, sodium and magnesium are mixed in the solution. In particular, the magnesium is the same divalent cation as Cu, but the adsorption is not inhibited. It is found that Cu not only in fresh water but also in saltwater can be adsorbed by the FbP. The pH is neutral in the initial concentration range of 3-7 ppm, and weakly acidic at 30, 60 ppm. It is important that the pH is close to neutral considering drainage.

### Test results of specimen adjusted pH for Cd

The results of a shaking test on the specimen using Cd with adjusted pH are shown in Fig. 3.21. As with the test results for Cu, the residual concentration of Cu is not detected in most of the specimens. The adsorption performance improves as the pH approaches neutrality. The Cd effluent standard is 0.03 ppm, and the residual concentration of Cd in the specimen at pH 6 is lower than the effluent standard. On the other hand, the adsorption performance of the specimen at pH 2 is significantly reduced. The pH after the test is about 4.5, and slightly acidic regardless of the initial concentration. As has mentioned above, it is considered that the adsorption performance decreases due to the dissolution of the FbP. It becomes clear that the

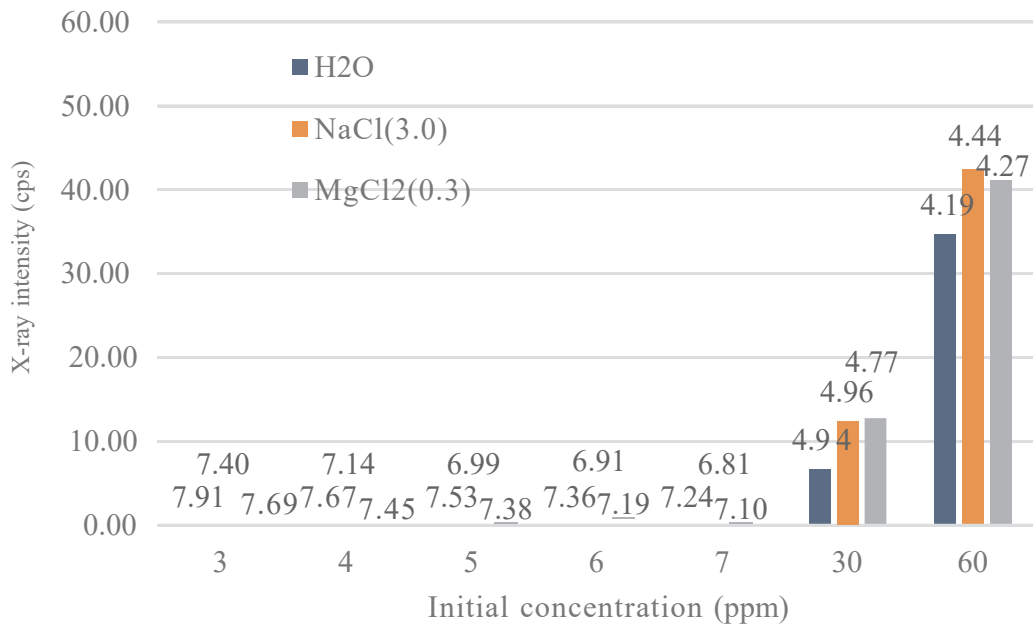


Fig. 3.20 Test results of specimen every solutions for Cu

pH value must be at least 3 in order to adsorb Cd.

### Test results of specimen every solutions for Cd

The results of the shaking test for Cd for each solution is shown in Fig. 3.22. Cd residual concentration of specimens using sodium chloride and magnesium chloride solution is slightly lower than that of specimens using pure water. There is hardly difference in the residual concentration in the initial concentration range of 3-7 ppm, but the residual concentration at the initial concentration of 60 ppm shows a difference of about 10 ppm. It is considered that chlorine, sodium or magnesium inhibits adsorption. However, there is hardly difference in the adsorption performance at the initial concentration of 3-7 ppm, and the pH value is around neutral. Therefore, it is clarified that Cd can be removed from Cd-containing wastewater not only in freshwater but also in saltwater environment.

### Test results of specimen adjusted pH for Zn

The results of a shaking test on the specimen using Zn with adjusted pH is shown in Fig. 3.23. The test results for Zn are almost the same as the test results for Cu and Cd. The residual concentration of the specimen whose initial pH is close to neutral is low. The effluent standard

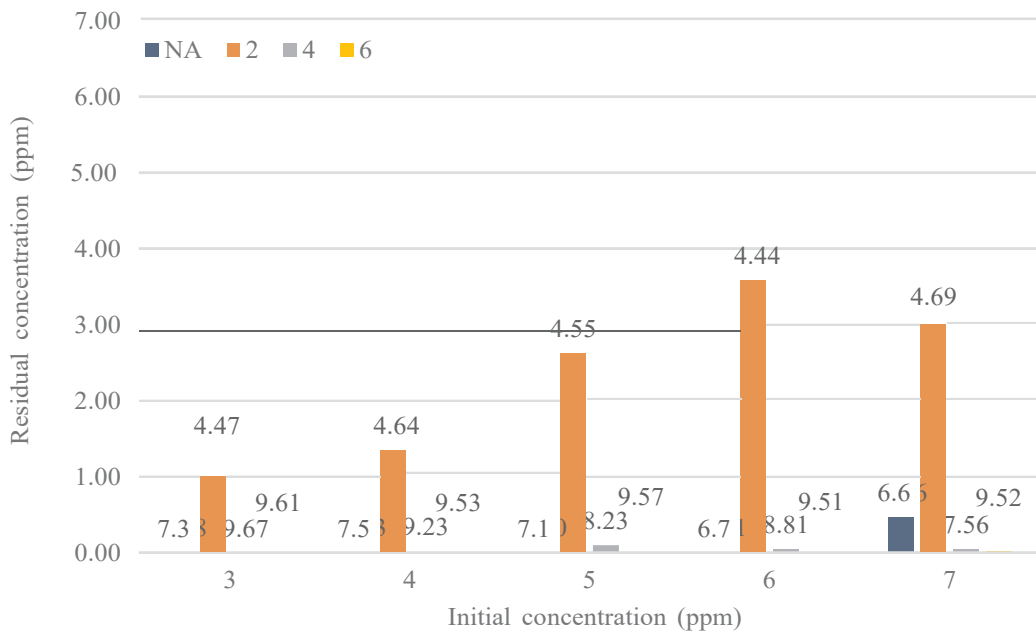


Fig. 3.21 Test results of specimen adjusted pH for Cd

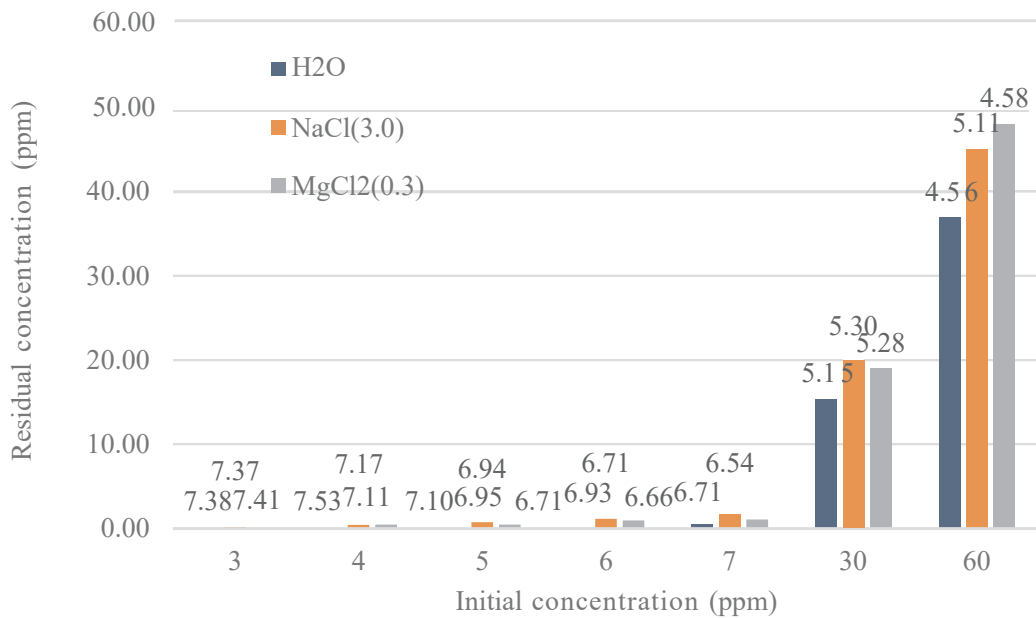


Fig. 3.22 Test results of specimen every solutions for Cd

for Zn is 2 ppm, and the residual concentration of most specimens is below that value. On the other hand, the adsorption performance decreases in a strong acid environment. It is found that the solution of the neutrality is desirable to adsorb Zn efficiently.

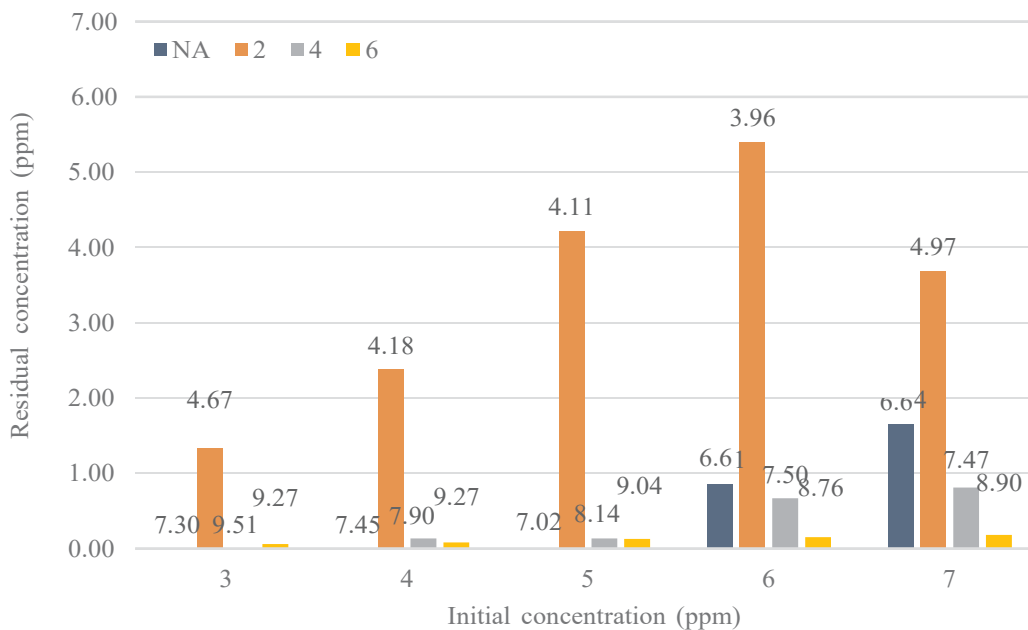


Fig. 3.23 Test results of specimen adjusted pH for Zn

### Test results of specimen eaery solutions for Zn

The results of the shaking test for Zn for each solution is shown in Fig. 3.24. The residual concentration also increases as the initial concentration increases. The test results of the specimen using between the pure water and the sodium chloride solution are almost the same, and a high adsorption performance of the FbP for Zn is shown. On the other hand, the adsorption performance decreases when the magnesium chloride solution is used. It is considered that the magnesium, which is the same divalent cation as Zn, inhibits the adsorption. The adsorption performance decreases due to low pH value when the initial concentration is high. It is necessary to adjust the pH to neutral in order to use the FbP as an adsorbent for high-concentration Zn in a saline environment. However, in a natural environment, the concentration of Zn rarely exceeds 30 ppm. Therefore, it can be said that the FbP has sufficient performance as an adsorbent for Zn.

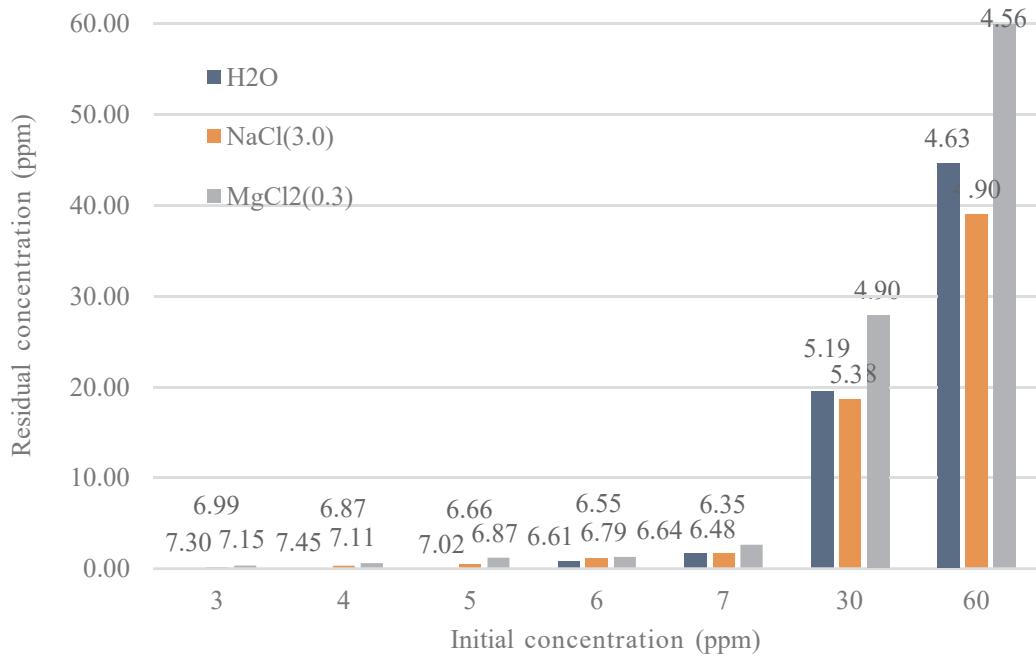


Fig. 3.24 Test results of specimen every solutions for Zn

### Test results of specimen adjusted pH for Hg

The results of a shaking test on the specimen using Hg with adjusted pH is shown in Fig. 3.25. Hg is a divalent cation like Cu, Cd, and Zn, though the test result for Hg is different from those of the three ions. It is confirmed that the residual concentration is low when the initial pH value is low. Also, Hg is hardly adsorbed when the initial pH is close to neutral. Hg effluent standard is 0.005 ppm, and the adsorption performance of the FbP to Hg is not sufficient. It may be necessary to improve the adsorbent in order to adsorb Hg instead of changing the test conditions.

### Test results of specimen every solutions for Hg

The results of the shaking test for Hg for each solution is shown in Fig. 3.24. As a test result, it is clarified that Hg in the sodium chloride or the magnesium chloride solution is hardly adsorbed on the FbP. The residual concentration is lower in the order of the pure water, the sodium chloride solution and the magnesium chloride solution. Hg is hardly adsorbed to the FbP by the existence of sodium and magnesium, and the residual concentration is the same as the initial concentration in the specimen using the magnesium chloride solution.

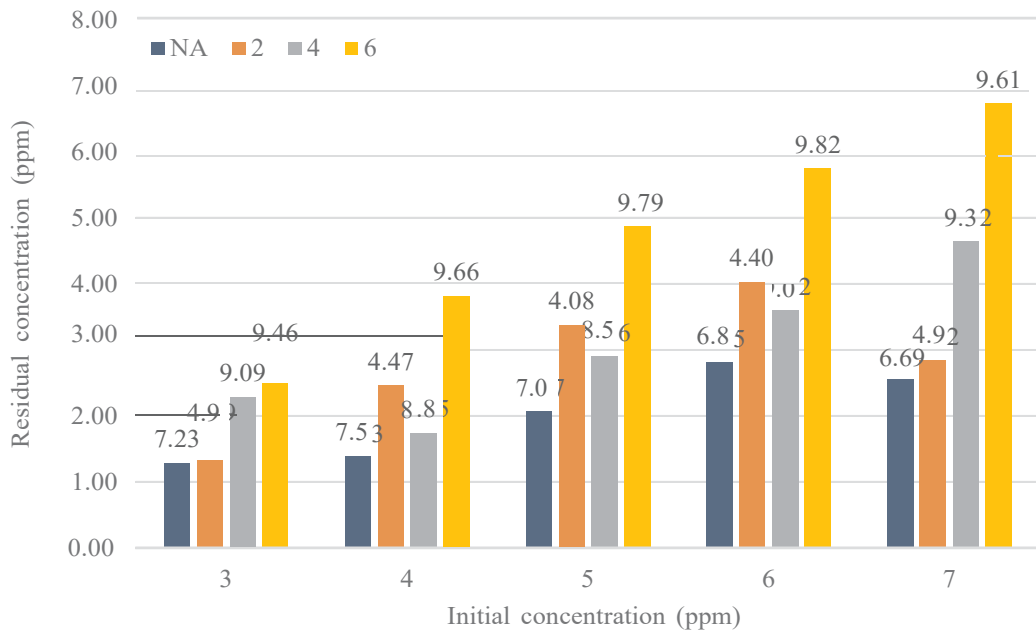


Fig. 3.25 Test results of specimen adjusted pH for Hg

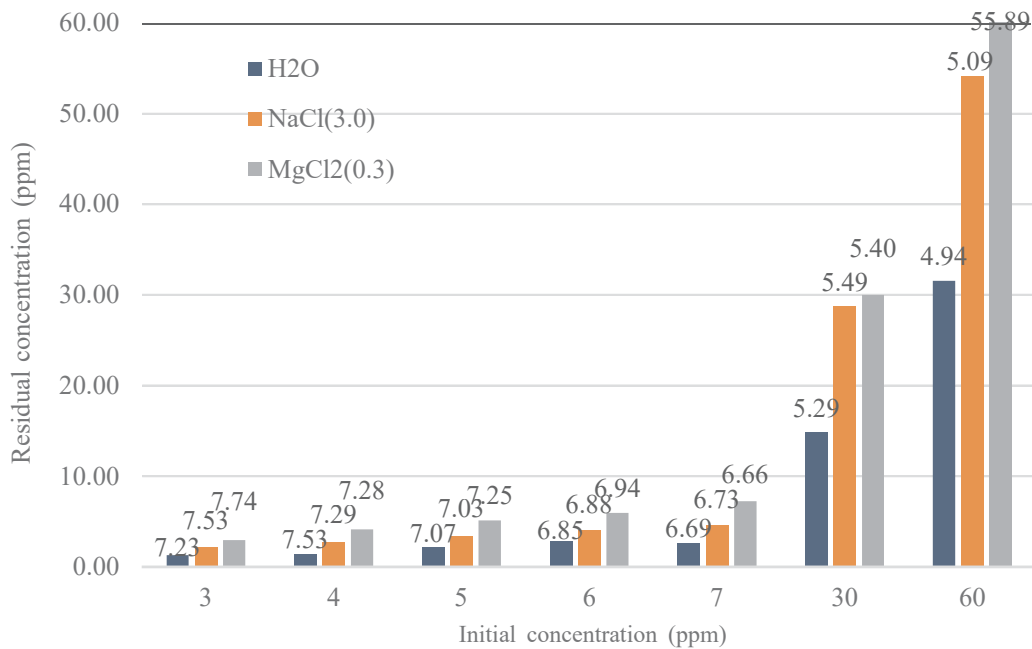


Fig. 3.26 Test results of specimen every solutions for Hg

### Test results of specimen adjusted pH for As

The results of a shaking test on the specimen using As with adjusted pH is shown in Fig. 3.27. It is confirmed that As is hardly adsorbed to the FbP. In particular, the residual concentration of the specimen with an initial pH value of 2 is high. As exists in solution as an anion. The FbP may have high adsorption performance for cations, though it may have low adsorption performance for anions. The FbP is calcium hydroxide phosphate derived from fish bone. The cations contained in the calcium hydroxide phosphate are calcium ions, and the anions are phosphate ions and hydroxide ions. The hydroxide ions are abundant in the solution, which may make the adsorption of anions difficult. It is necessary to improve the adsorbent in order to adsorb As as well as the Hg.

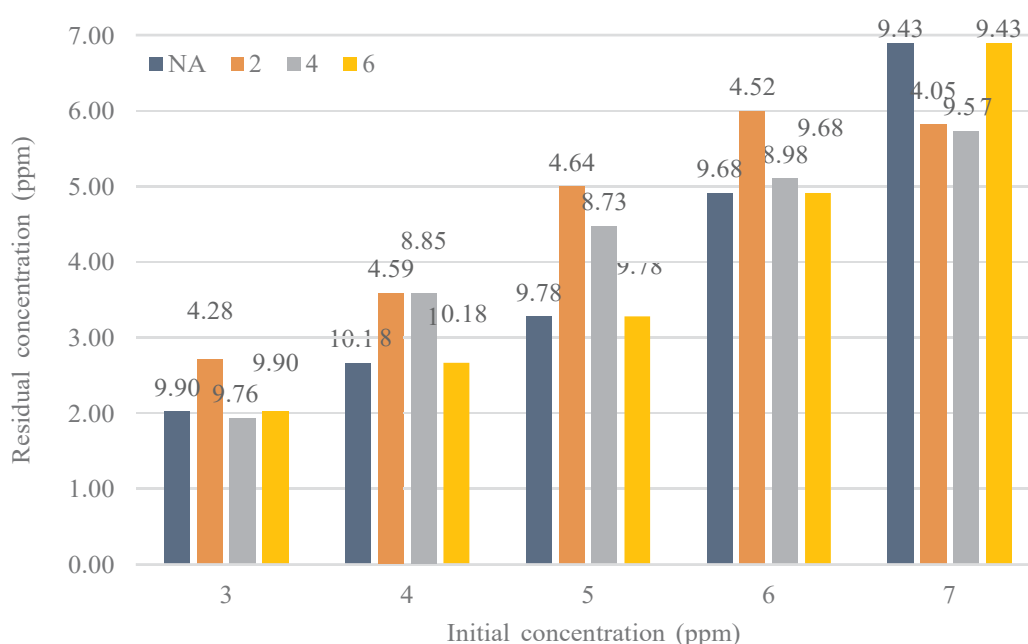


Fig. 3.27 Test results of specimen adjusted pH for As

### Test results of specimen every solutions for As

The results of the shaking test for As for each solution are shown in Fig. 3.28. It is revealed that As is not absorbed to the FbP regardless of the type of solution. At high concentrations, As in sodium chloride or magnesium chloride solutions is not adsorbed at all. The chlorine which is an anion may inhibit adsorption.

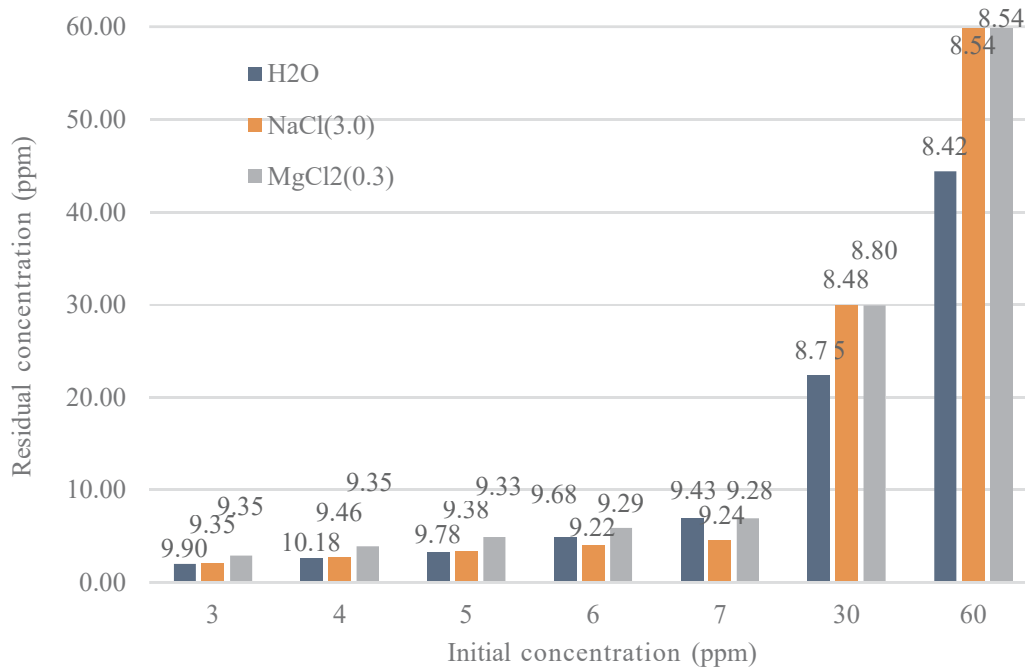


Fig. 3.28 Test results of specimen every solutions for As

### 3.3.4 Deriaation of adsorption isotherm (FbP)

The results of shaking tests using the FbP are summarized for each heavy metal from the view-point of adsorption isotherm. The adsorption isotherm is calculated from the test results of the specimen without adjusting the pH value. Also, the adsorption isotherms of each specimen using pure water, sodium chloride and magnesium chloride solutions are calculated. First, the adsorbed amount per gram of adsorbent is determined from the equilibrium concentration obtained by the shaking test. Secondly, the equilibrium concentration and the adsorbed amount are substituted into Langmuir's linear equation and plotted. At that time, a monolayer adsorption occurs if there is a linear relationship. Finally, the function is found by plotting the values according to the Freundlich equation. The magnitude of the adsorption energy and the type of adsorption are discussed based on the shape of the plotted points.

#### Adsorption isotherm of FbP for Cu

The graphs of the FbP adsorption isotherms for Cu in pure water, the sodium chloride solution and the magnesium chloride solution are shown in Fig. 3.29, Fig. 3.30 and Fig. 3.31, respectively. Alternatively, Langmuir plot, Freundlich plot and adsorption isotherm are shown in the upper left, the upper right and the lower in each graph, respectively. The vertical axis of the graph represents the adsorbed amount per gram of adsorbent, and the horizontal axis represents the equilibrium concentration.



Focusing on the Langmuir plot in Fig. 3.29, the plot values at low initial concentrations do not deviate significantly from the approximate line. On the other hand, the plot values when the initial concentration is high are slightly out of the line. In other words, at low concentrations, the monolayer adsorption is conducted on Cu without inhibiting by other molecules. Alternatively, focusing on the Freundlich plot, the shapes of the plots differ between the pure water and the two solutions. In the Freundlich plot of the specimen using the pure water, a linear function with a large slope appears first, then levels off, and then a linear function with a large slope appears again at the end of the graph. The adsorption energy is large when the initial concentration is low. However, the adsorption energy is small when the initial concentration is high. In other words, there is a possibility that the adsorption phenomenon occurs twice (multilayer adsorption). A chemical adsorption may be performed on Cu when the initial concentration is low. Also, a physical adsorption may become apparent or chemical adsorption may not be performed satisfactorily when the initial concentration is high. Finally, focusing on the adsorption isotherm, it is confirmed that there is a discrepancy between the experimental formula and the Freundlich formula. The lower the initial concentration of Cu, the more strongly the Cu is adsorbed. However, the ideal Freundlich and the experimental formulas are gradually diverging. From these facts, it is assumed that the sufficient chemical adsorption is not conducted from a certain concentration. The physical adsorption may be apparent at higher concentrations. Each Langmuir plots and Freundlich plots in Fig. 3.30 and Fig. 3.31 is very similar, and all plots are almost straight lines. It is considered that only monolayer adsorption occurs by the uniform adsorption energy regardless of the initial concentration. Additionally, considering the adsorption concentration described in the previous section, the adsorption concentration of the specimen using pure water is the highest. From the facts, it is suggested that secondary adsorption does not occur after monolayer adsorption in the sodium chloride or the magnesium chloride solution. This may be due to the predominance of sodium and magnesium in the solution. Also, it may be difficult to extract the Cu for reuse because the adsorption between the FbP and the Cu is too strong.

### Adsorption isotherm of FbP for Cd

The graphs of the FbP adsorption isotherms for Cd in pure water, the sodium chloride solution and the magnesium chloride solution are shown in Fig. 3.32, Fig. 3.33 and Fig. 3.34, respectively. The results shown in Fig. 3.29, Fig. 3.30, and Fig. 3.31 are very similar to the results shown in Fig. 3.32, Fig. 3.33, and Fig. 3.34. It can be said that the adsorption mechanism of the FbP for the Cd is almost the same as that of the Cu. It is a Langmuir plot of the specimen using the magnesium chloride solution if there is any difference. The adsorption amount is the lowest, though almost perfect linear function. It is considered that the effect of

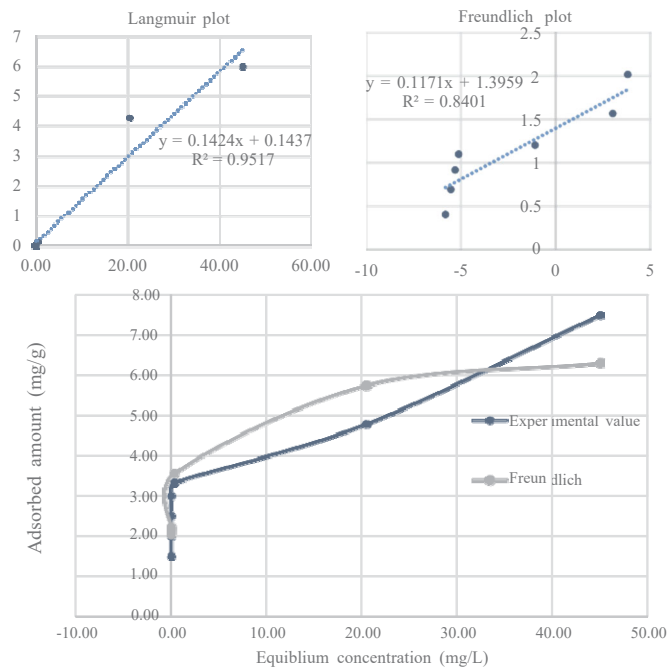


Fig. 3.29 Adsorption isotherm of FbP for Cu in pure water

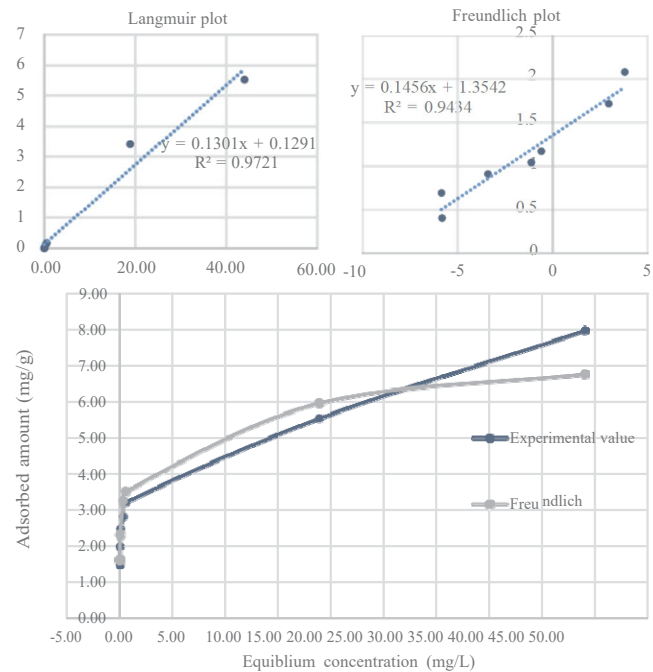


Fig. 3.30 Adsorption isotherm of FbP for Cu in sodium chloride solution

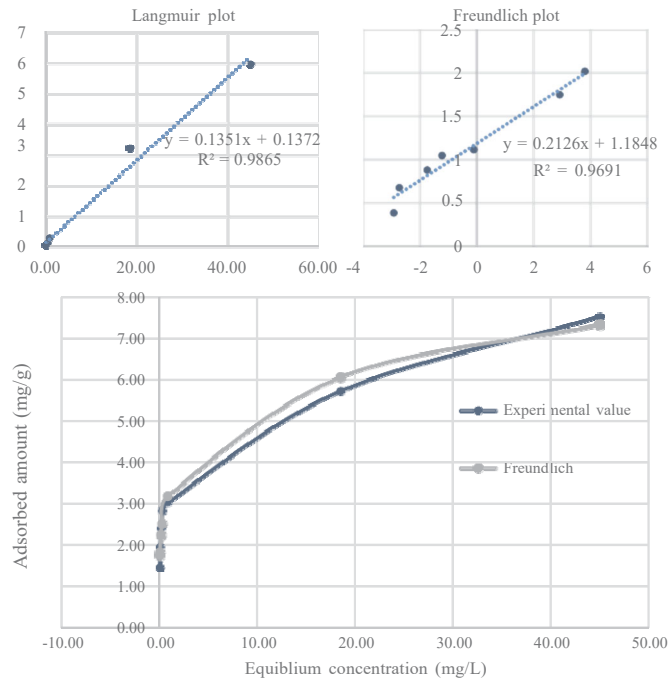


Fig. 3.31 Adsorption isotherm of FbP for Cu in magnesium chloride solution

magnesium is the strongest. The secondary adsorption phenomena may not be occurred.

### Adsorption isotherm of FbP for Zn

The graphs of the FbP adsorption isotherms for Zn in pure water, the sodium chloride solution and the magnesium chloride solution are shown in Fig. 3.35, Fig. 3.36 and Fig. 3.37, respectively. The Langmuir plot, the Freundlich plot and the adsorption isotherm of the specimens using the pure water and the sodium chloride solution are similar to those of the Cu and the Cd. In other words, it is considered that not only monolayer adsorption but also multilayer adsorption occurs for the Zn in pure water. Also, only monolayer adsorption may occur for the Zn in the sodium chloride solution. On the other hand, a quadratic function convex downward is shown in the Langmuir plot of the specimen using the magnesium chloride solution. It is clarified that the multilayer adsorption occurred by the strong influence of the solvent. It is difficult to use the FbP as an adsorbent for the Zn-containing water of high-concentration. However, it may be possible to recover the Zn and reuse the FbP if the concentration of the Zn is low.

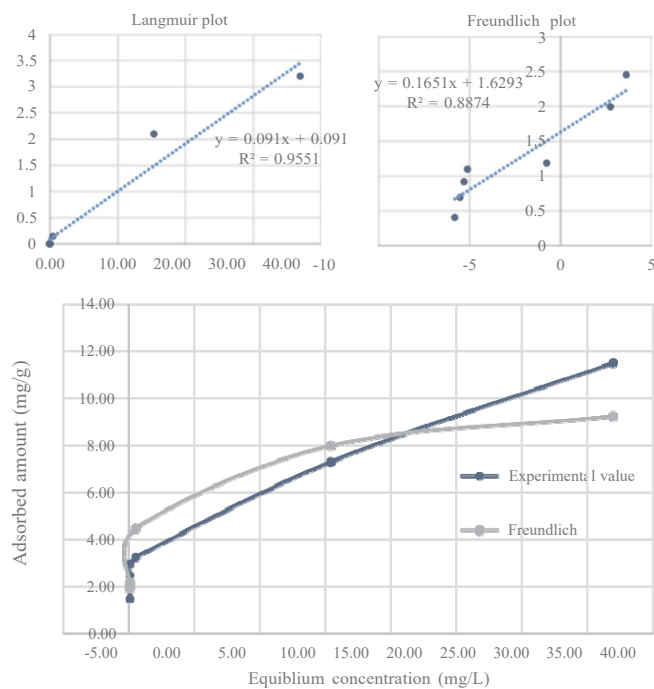


Fig. 3.32 Adsorption isotherm of FbP for Cd in pure water

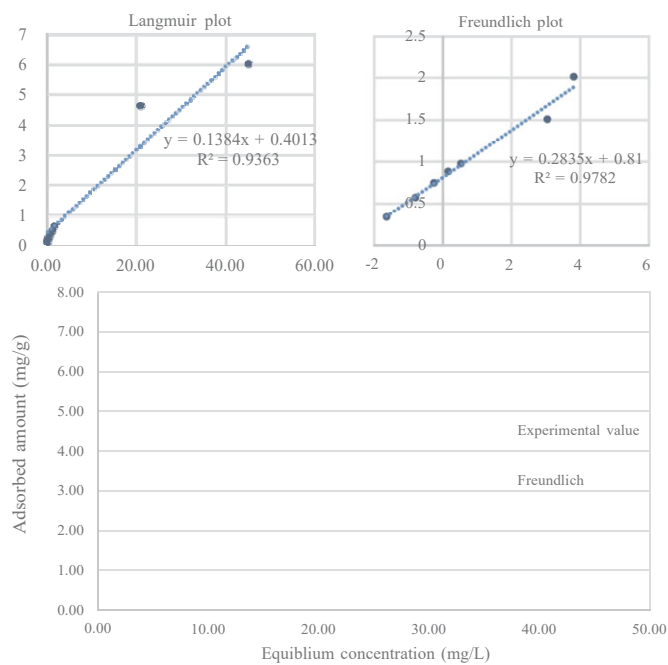


Fig. 3.33 Adsorption isotherm of FbP for Cd in sodium chloride solution

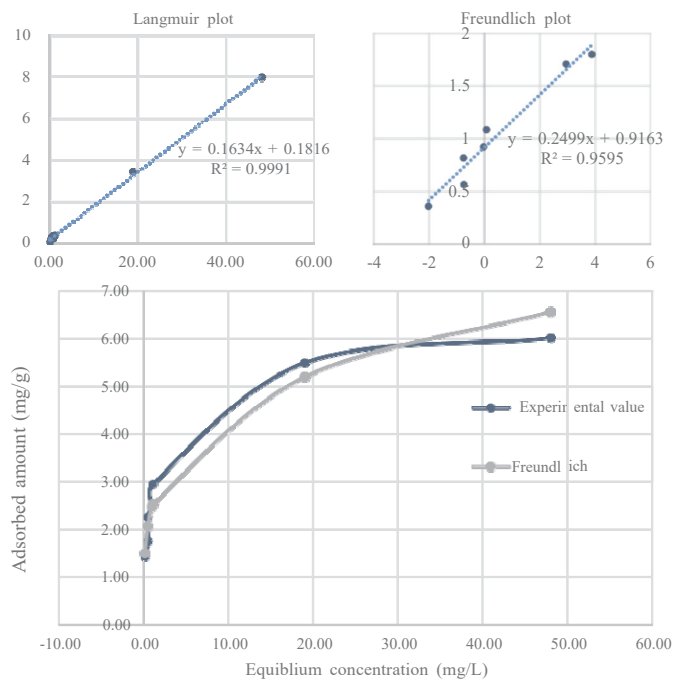


Fig. 3.34 Adsorption isotherm of FbP for Cd in magnesium chloride solution

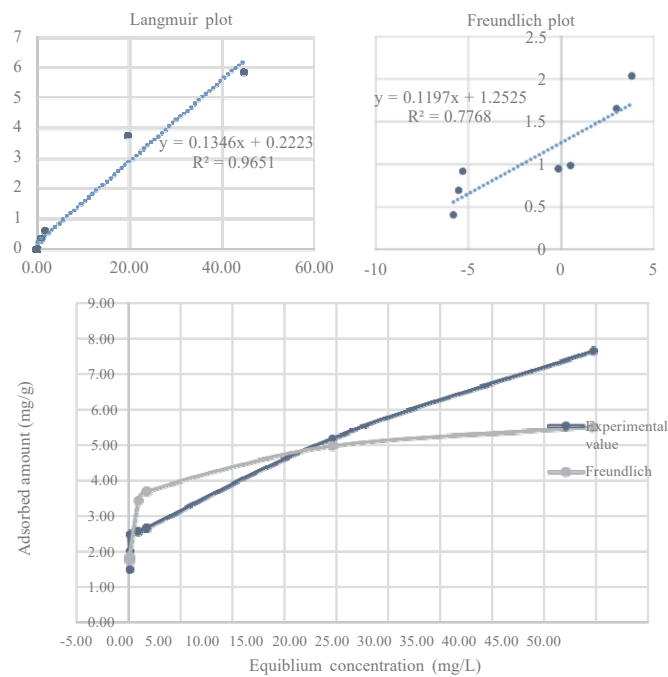


Fig. 3.35 Adsorption isotherm of FbP for Zn in pure water

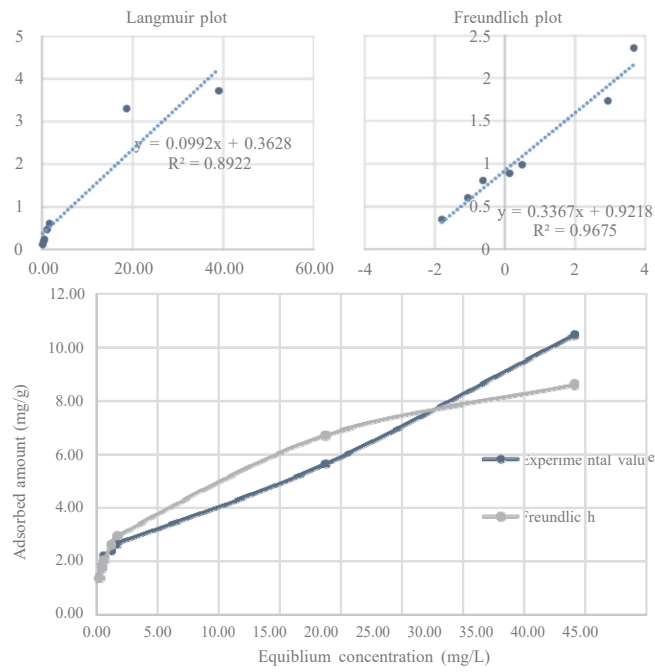


Fig. 3.36 Adsorption isotherm of FbP for Zn in sodium chloride solution

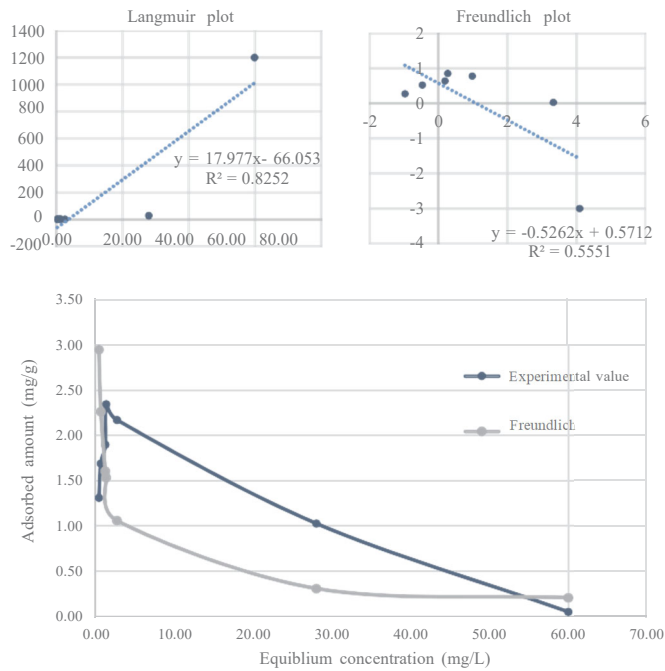


Fig. 3.37 Adsorption isotherm of FbP for Zn in magnesium chloride solution

## Adsorption isotherm of FbP for Hg

The graphs of the FbP adsorption isotherms for Hg in pure water, the sodium chloride solution and the magnesium chloride solution are shown in Fig. 3.38, Fig. 3.39 and Fig. 3.40, respectively. The Langmuir plots of specimens using the pure water and the sodium chloride solution vary widely. Especially, the Freundlich plot of the specimen using the sodium chloride solution also has irregular shape. Besides, the Hg in the sodium chloride solution and the magnesium chloride solution are hardly adsorbed. From these facts, it is difficult to determine the adsorption mechanism of the Hg. Alternatively, the Freundlich plot of the specimen using the pure water is a linear function, and the adsorbed concentration is low. Therefore, it is found that the monolayer adsorption occurs between the Hg and the FbP, and that the adsorption energy is small.

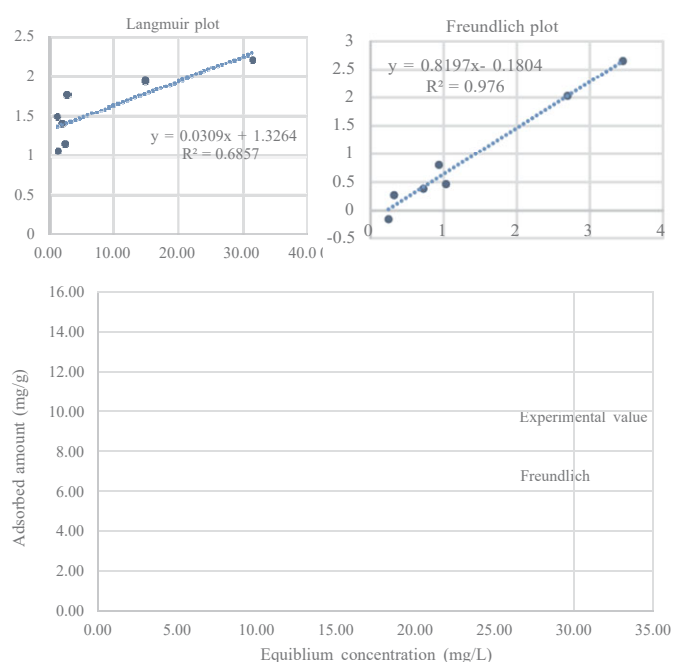


Fig. 3.38 Adsorption isotherm of FbP for Hg in pure water

## Adsorption isotherm of FbP for As

The graphs of the FbP adsorption isotherms for As in pure water, the sodium chloride solution and the magnesium chloride solution are shown in Fig. 3.41, Fig. 3.42 and Fig. 3.43, respectively. The FbP hardly has an adsorption property for the As. However, a linear relationship is shown in the Langmuir plots of the specimens using the sodium chloride solution or the magnesium chloride solution. This is because the adsorption energy acting between the solvent

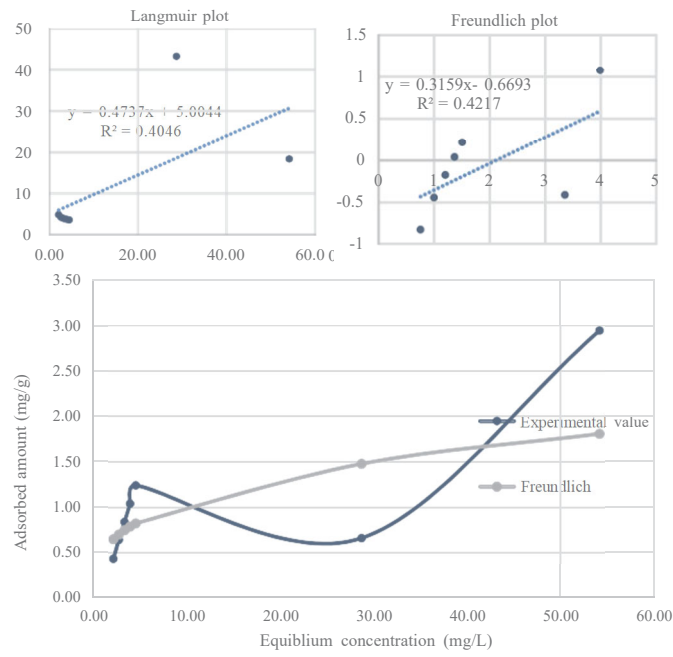


Fig. 3.39 Adsorption isotherm of FbP for Hg in sodium chloride solution

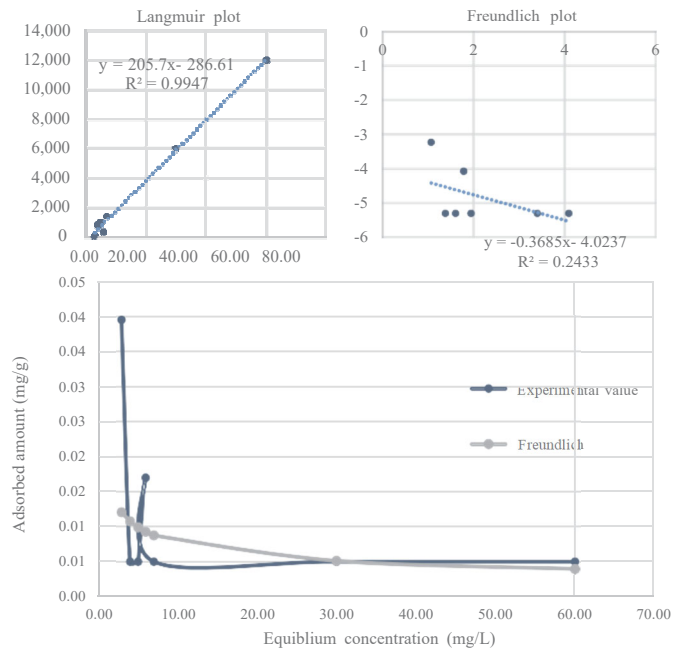


Fig. 3.40 Adsorption isotherm of FbP for Hg in magnesium chloride solution



and the adsorbate is the same as that of between the solute and the adsorbate. The Langmuir plot is a correlation between the equilibrium concentration and the equilibrium concentration for the adsorbed amount. Therefore, a linear function appears even when the adsorption amount is extremely small. It is necessary to determine whether the monolayer adsorption is conducted by considering the adsorbed amount.

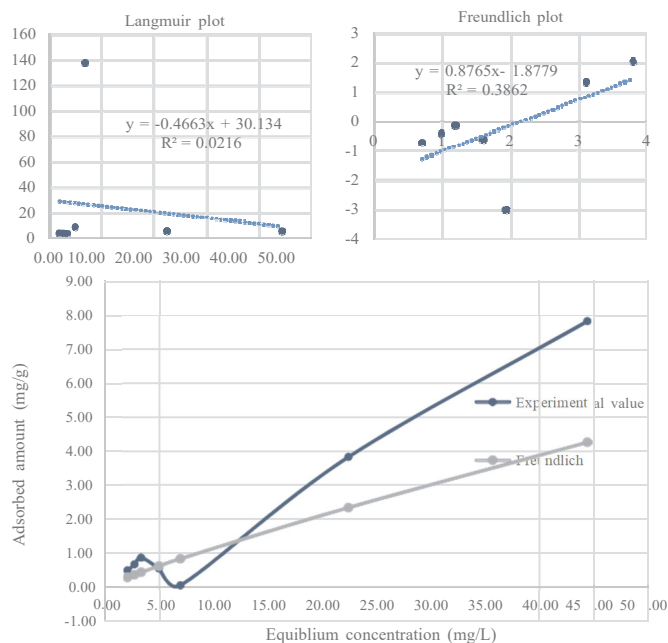


Fig. 3.41 Adsorption isotherm of FbP for As in pure water

### 3.3.5 Consideration of shaking test using FbP

It is revealed that the FbP has high adsorption performance for Cu, Cd and Zn. However, the adsorption performance decreases when the pH is low. It is considered that the FbP is dissolved by the strong acid solution as the reason. The pH value should be at least 3 or more when the FbP is used as an adsorbent. In addition, it is found that the FbP has high adsorption performance for Cu and Cd not only in fresh water but also in saltwater. From the adsorption isotherm, it is confirmed that the chemical adsorption occurred regardless of the type of solution. Therefore, the Cu and the Cd are preferentially adsorbed. Additionally, the physical adsorption becomes apparent for Zn in magnesium chloride. This result indicates two possibilities, one is that the adsorption interaction between the FbP and the Zn is small, and the other is that the recovery of the Zn is easy. The Zn is used as a plating material, ultraviolet absorber and antibacterial agent.

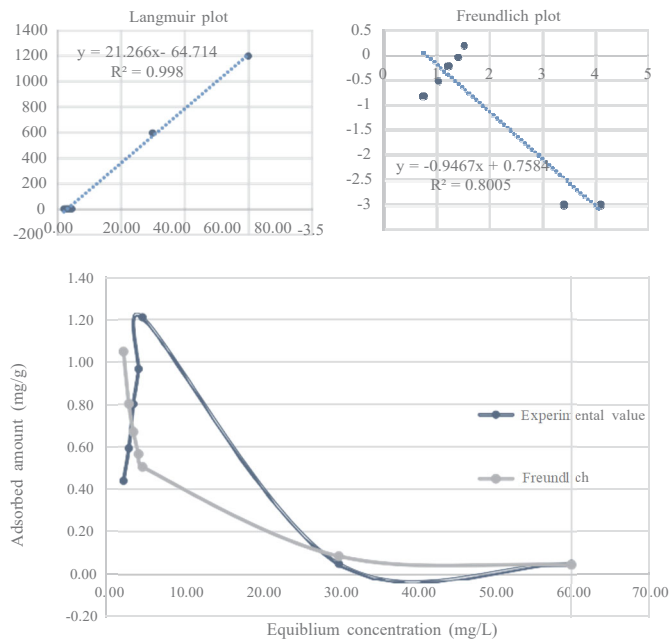


Fig. 3.42 Adsorption isotherm of FbP for As in sodium chrolide solution

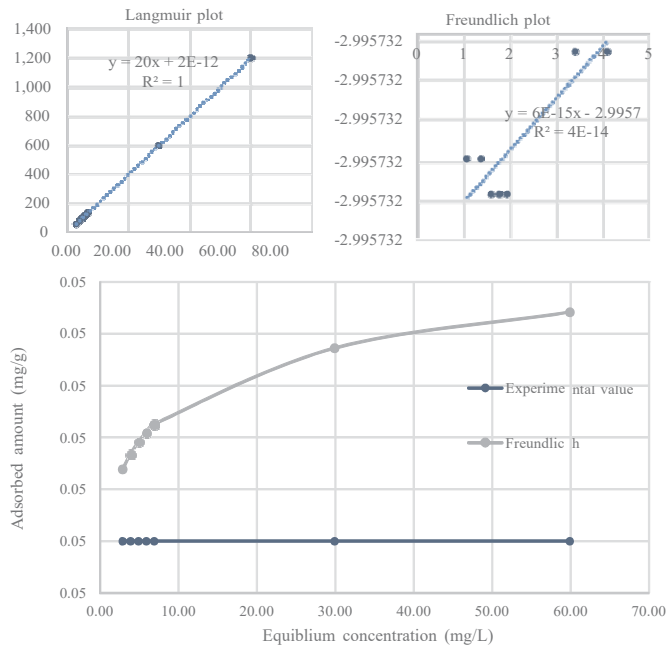


Fig. 3.43 Adsorption isotherm of FbP for As in magnesium chrolide solution

If the Zn and the FbP can be separated and recovered, they can be reused.

The adsorption performance of FbP for Hg and As is low. Especially, the As is hardly adsorbed regardless of pH or solution type. The adsorption amount was too small and the adsorption isotherms have irregular shapes. Therefore, the adsorption mechanism cannot be mentioned. It is necessary to improve the adsorbent in order to adsorb both heavy metals.

## 4 . Functional Fishbone Powder (FFP)

Preparing the patent application, please wait for its publication.

## 5 . Waste syrup

Preparing the patent application, please wait for its publication.

## 6. Conclusions

In this study, the recycling methods of three types of food waste (rice husk, fish bone, and sugar syrup) were examined. The utilization of each property was tried to recycle as an industrial material.

First, the rice husk was reused as an adsorbent for cesium or heavy metals. Cesium contained in contaminated soil enclosed in a flexible container bag was removed using a combination of rice husk and electrophoresis. As a result, approximately 25 percent of the cesium adsorbed on the soil was desorbed, and 60 percent was adsorbed on the rice husk. A similar test was conducted using powdered zeolite, which is a typical adsorbent for the cesium, and the adsorption performances of the zeolite and the rice husk were almost similar. The amount of powdered zeolite used in the test was 10 g, while the amount of rice husk was 3 g. These results suggest that rice husk is an effective means of removing contaminated soil containing cesium. Also, the volume of used adsorbent may be reduced. The amount of radioactive contaminated soil generated by the Fukushima nuclear accident has been increasing, and its removal requires a lot of cost and materials. The volume of radioactive contaminated soil can be reduced at low cost by using the rice husk as an adsorbent. At the same time, not only volume reduction of radioactive contaminated soil but also volume reduction of rice husk of food waste are achieved. The rice husk recycling can be a solution to several different environmental problems. Besides, it was verified whether the rice husk can adsorb heavy metal ions in the solution. As a result, the rice husk had high adsorption performance for divalent cations, while any other heavy metals hardly were adsorbed into the rice husk. Environmental pollution by heavy metals is still occurring frequently after the period of high economic growth. Old factory sites such as Toyosu Market and mine wastewater contain heavy metals and are purified. Rice husks can be a solution to contamination with some of these heavy metals.

Secondly, the FbA and the FbP, adsorbents derived from fish bone, were reused as adsorbents for strontium and heavy metals. Adsorption tests for strontium in different solutions were conducted assuming adsorption to radioactive strontium diffused in the ocean, river and groundwater. As a result, the strontium was adsorbed not only in freshwater but also in the environment where chlorine, magnesium and sodium contained in seawater coexist with strontium. Additionally, the adsorption test for heavy metals had high adsorption performance for divalent cations as well as

rice husk. Especially, it was clarified that the FbP has high adsorption performance for Cu, Cd and Zn. Also, it was found that the heavy metals are chemically adsorbed by the adsorption isotherm. A fishbone recycling can be a solution for the waste volume reduction and environmental pollution. On the other hand, the adsorption performance for As and Hg was low, and a new adsorbent was developed to improve the performance. The FFP, a new adsorbent, was developed using the FbP as the substrate material. Colloidal iron hydroxide was formed with the ability to adsorb anions and was coated with the FbP.

The recycling method of each of the three food wastes was proposed to be reused as an adsorbent or a material for reducing elution, and all of them could be recycled. It is considered that the volume reduction of food wastes and the improvement of environmental pollution are sufficiently conducted.

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Three years have passed since I started my research in the doctoral course at Kagawa University Graduate School of Engineering. I have spent more than 6 years as a student at Yoshida's Lab. It was a day when I was bothered by my disappointment and low ability, but it was also a fun day. I think that I was able to have a hard time happily because I learned the fun of learning specialized knowledge and meeting new knowledge in my research activities. Encounter with my supervisor, Professor Hidenori Yoshida, was an important turning point in my life. If I do not belong to the Yoshida's lab, I do not know whether I went on to a master's course as well as a doctoral course. Prof. Yoshida taught me the setting of the research theme, the policy, the writing of the dissertation, and the attitude toward research. I'm so grateful that I couldn't express in words because you guided me without giving up on me. Especially in the master's course, sometimes there were strict guidance. However, in the doctoral course, when I had more opportunities to teach my juniors, I realized how grateful and difficult it was. Thank you very much for your long-term involvement in unrelated conversations unrelated to our research. Prof. Yoshida is my eternal goal. Alternatively, Prof. Yoshihiro Suenaga and Associate Prof. Shinichiro Okazaki, who were the assistant advisors of this paper, provided various advices on the dissertation. In addition, both of them provided me with waste materials, which are indispensable for my research. I appreciate you sincerely. Furthermore, many teachers, technical staff, lab juniors, and clerks helped me not only both teachers. Thanks to your kindness, I was able to pursue my research without bothering and losing motivation. In particular, technical staff Mr. Naomichi Matsumoto and Mr. Toshinori Matsui had lectures on experimental equipment, arranged materials, and had a drink party. I look forward to go out eating with you when I visit to Shikoku. Finally, I am deeply grateful to my family for allowing my selfishness and supporting my long student life. I was very stubborn and decided on myself without even asking my mother about the course. However, each time my mother affirmed and helped me. Thank you very much. In the future, I would like to try to give back even a little. Also, although I haven't listed my name here, I would like to thank everyone who has met and supported me with my sincere thanks.

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