STUDY ON ADSORPTION PERFORMANCE OF FOOD WASTES FOR VARIOUS HEAVY METALS

Keiichiro Shibata¹, Hidenori Yoshida², Tsumugi Inoue³, Matsumoto Naomichi² and Yoshihiro Suenaga²

¹Graduate School of Engineering, Kagawa University, Japan; ²Kagawa University, Japan; ³Okayama City, Japan

*Corresponding Author, Received: 11 June. 2018, Revised: 31 Dec. 2018, Accepted: 11 Jan. 2019

ABSTRACT: The harmful materials are come to a head through the redevelopment in empty lots in recent years. The soil and groundwater contaminations are often caused by heavy metals and the volatile organic compounds. 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. However, the activated carbon has a low adsorption performance for inorganic substances such as the heavy metals. Thus, in this study, the rice husk and fish bones which are an industrial waste are focused on. The material cost is saved by using industrial waste. The product process of the fish bone is only burning, and the rice husk is not manufactured. It is examined whether both materials can be used as the adsorbent for the heavy metals. As the results of examinations, it is clarified that some heavy metals such as Zn²⁺ and Cd²⁺ are well adsorbed into both materials and both materials are useful as the recycling materials.

Keywords: Soil and groundwater contamination, Fish bone absorber, Rice husk, Heavy metals

1. INTRODUCTION

In recent years, the soil contamination and groundwater contamination because harmful materials come to a head through the redevelopment in empty lots. According to the reports of each prefecture's soil pollution case and groundwater pollution case released by the Ministry of the Environment as in [1], [2], 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 among 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 deeply because most of the heavy metals are easily adsorbed by minerals in the soil. However, the certain 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, it 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 rice husk and fish bones which are an industrial waste are focused on. The material cost is saved by using industrial waste. The unprocessed rice husk and only burned fish bone are used as an adsorbent in order to reduce the manufacturing cost. Also, the adsorption performance of the rice husk and fish bone for heavy metals are examined whether both materials can be used as a new adsorbent.
2. MATERIALS AND METHODS

In this study, the rice husk and fish bone, food waste, are adopted as an adsorbent for the heavy metals as has noted above. Their material properties are explained below.

2.1 Rice husk

The rice husk is the shell of berry taken from the spike of rice. The rice husk is covered with a wax component which protects the surface of the organism called the cuticle. The rice husk is hard to decompose since the wax component shed the water. The rice husk is shown in Fig. 1, and has the feature that about 20 percent of silica is contained. Bamboo is also said to have a lot of silica, but even it is less than 0.1% in the case of raw bamboo. The silica is the silicon dioxide or the generic name of substances which constituted by silicon dioxide. The rice husk 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 rice husk emissions is about 2 million tons annually nationwide, and most of them are discarded as industrial waste since the usage of unprocessed rice husk is limited. The unprocessed rice husk has been used for packing or seedling cover materials, but the usage as plastics material has been increasing in recent years. Although it is considered that the optimum processing and utilization method of unprocessed rice husk are few, the rice husk ash made by burning rice husk has been studied for many uses. In Thailand, the rice husk ash given off from this generation is used for the material of cement. As a similar technology, the researches for making building materials for houses from rice husk, 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 rice husk as a heat source, the rice husk ash, 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 rice husk ash is mixed in concrete is also conducted as in [3]. In addition, it is confirmed by the studies of Nakanoku University of Chukyo University that rice husk ash has high adsorption rate for radioactive materials such as the cesium and strontium.

As noted above, various usage methods are studied for the rice husk ash, but it is necessary to control the temperature at 400 ~ 600 °C and burn in order to produce the high quality rice husk ash as in [4]. Crystallized silicic acid and dioxin may be generated when the burning temperature falls below 400 °C. The practical realization has not progressed much due to the difficulty of such processing. In order to propose a new method of utilizing raw rice husk and to reduce the cost of processing, in this study, an adsorption performance of dried rice husk for heavy metals without processing is examined (see Fig. 1).

Fig. 1 Dried rice husk

2.2 FbA (Fishbone Absorber)

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 teeth and bones. In addition, hydroxyapatite has many functions such as high adsorptive property (especially amino acids, proteins, lipids, sugars, etc.), ion exchange properties, catalytic properties, and ionic conduction properties as in [5], [6], [7]. 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 as in [8]. Some hydroxyapatite is derived from cattle bones and pig bones, but in this study, the adsorbent based on hydroxyapatite derived from fish bones (Fishbone Absorber, hereinafter referred to as FbA and, see Fig. 2) is used for various tests. The size of the piece is approximately 1 cm square and its weight is approximately 0.6 g. The FbA

Fig. 2 FbA

is produced by burning fish bone discarded at a fishing port.

3. RESULTS AND DISCUSSION

Among various materials which are harmful to the
environment and the human body, and in this study, 9 types of Cr\(^{6+}\), Cr\(^{3+}\), Mn\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), As\(^{3+}\), Se\(^{4+}\), Cd\(^{2+}\), 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. Se\(^{4+}\) is the cation in the solution though Se\(^{4+}\) is a nonmetallic element. Furthermore, Se\(^{4+}\) is targeted in the test because 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 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. 3. 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 °C for 168 hours, and the concentration of each heavy metal ion in the solution is analyzed by an ICPS emission spectrometer. 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. All tests are conducted three times in order to ensure reproducibility, and the test results are shown by their average values.

3.1 Test results

The test results using the rice husk and the FbA as the adsorbent are shown graphically. The adsorption ratio of heavy metal and heavy metal are shown in the vertical and horizontal axes, respectively. 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 1 shows the pH values of each test specimen before adding the adsorbent. The pH of all test specimens indicates from a weak acid to strong acid before adding adsorbent because the standard solution is an acidic solution.

3.2 Adsorption test of rice husk

First, the results of the adsorption test using the rice husk as an adsorbent for each heavy metal are shown in Figs. 4 and 5, 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. The mass of rice husk is 0.6 g, and this mass is almost equal to the mass of FbA single piece. As shown in Fig. 4, 80 percent or more of Zn\(^{2+}\), Cd\(^{2+}\), and Hg\(^{2+}\) are adsorbed to rice husk when 1 mL of the sample was 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 (see Table 2). The high adsorption rate for ions whose ionic radii are close suggests that rice husk may adsorb the ions by physical adsorption rather than chemically adsorbed. 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\(^{2+}\) with high adsorption ratio to the absorbent. However, the adsorption ratio remains around 50 percent. 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 Cr\(^{3+}\).

Table 1 pH value before adding adsorbent

<table>
<thead>
<tr>
<th></th>
<th>Cr(^{6+})</th>
<th>Cr(^{3+})</th>
<th>Mn(^{2+})</th>
<th>Ni(^{2+})</th>
<th>Zn(^{2+})</th>
<th>As(^{3+})</th>
<th>Se(^{4+})</th>
<th>Cd(^{2+})</th>
<th>Hg(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mL</td>
<td>3.4</td>
<td>4.6</td>
<td>3.5</td>
<td>3.5</td>
<td>3.4</td>
<td>5.8</td>
<td>3.6</td>
<td>3.4</td>
<td>3.5</td>
</tr>
<tr>
<td>5 mL</td>
<td>2.8</td>
<td>3.5</td>
<td>2.8</td>
<td>2.7</td>
<td>2.8</td>
<td>4.8</td>
<td>2.6</td>
<td>2.8</td>
<td>2.8</td>
</tr>
</tbody>
</table>
and other factors also need to be examined in the near future. Focusing on pH, the pH value of Cr^{6+} and As^{3+} is higher than that of the other specimens and show 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.

As shown in Fig. 5, the adsorption ratio decreases in most of the specimens to compare with using 1 ml 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 rice husk may be clarified by increasing the amount of sample added. Although the adsorption ratio decreases as the most of samples, the divalent cations, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} tend to be relatively adsorbed. Especially, the rice husk for Hg^{2+} has a relatively high adsorption ratio even if the addition amount is increased five times. The fact that 50% of the added amount is adsorbed suggests the adsorption amount increases. Almost all of Hg^{2+} is adsorbed in the 1 ml of addition amount and about half adsorption in 5 ml, and there is a possibility that the adsorption limit amount for Hg^{2+} is between 1 and 5 ml. These results show that the adsorption limit amount for Hg^{2+} may be between 1 and 5 ml. The reason why the adsorption ratio decreases in most samples are considered to depend on the difference in the initial pH value (see Table 1). The heavy metal ion is easily adsorbed in the lower initial pH value. On the other hand, among all specimens, the adsorption ratio in the only specimen of As^{3+} is 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 rice husk.

### 3.3 Adsorption test of FbA

First, the results of the adsorption test using the FbA as an adsorbent for each heavy metal are shown in Figs. 6 and 7 which correspond to the adsorption test 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. The 1 piece of FbA (about 0.6 g) is used in the test.

As shown in Fig. 6, the adsorption ratio for Hg^{2+} is the highest all of samples and 90% or more of Hg^{2+} is adsorbed to the FbA when 1 ml of the sample is added. Subsequently, the adsorption ratio of Zn^{2+} and Cd^{2+} is high, and the results are similar to those of the test using rice husk. On the other hand, the adsorption ratio to Cr^{6+} and As^{3+} is low, and the result is also similar to the case using the rice husk, while the adsorption ratio for Mn^{2+} is higher than that of the case using rice husk. The adsorption ratio of Mn^{2+} is about 50% when the rice husk is used. However, it exceeded 70% in the case using the FbA. It is considered that Mn^{2+} has a property to promote the calcification of bone in increasing the adsorption ratio of the FbA to Mn^{2+}. 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 Mn^{2+} is adsorbed to the FbA rather than rice husk because the FbA is derived from fish bone. Additionally, the adsorption ratio of Cr^{3+} is slightly higher than that of the case using the rice husk. A slight precipitate is confirmed when the specimen of Cr^{3+} using the FbA is observed. It is widely known that heavy metal ions

![Fig. 4 Adsorption performance of rice husk (adding amount of 1 mL)](image)

![Fig. 5 Adsorption performance of rice husk (adding amount of 5 mL)](image)

<table>
<thead>
<tr>
<th>Ionic radius (Å) (Shannon)</th>
<th>Cr^{5+}</th>
<th>Cr^{6+}</th>
<th>Mn^{2+}</th>
<th>Ni^{2+}</th>
<th>Zn^{2+}</th>
<th>As^{3+}</th>
<th>Se^{4+}</th>
<th>Cd^{2+}</th>
<th>Hg^{2+}</th>
<th>Si^{4+}</th>
<th>Ca^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.62</td>
<td>0.44</td>
<td>0.67</td>
<td>0.69</td>
<td>0.74</td>
<td>0.58</td>
<td>0.50</td>
<td>0.95</td>
<td>1.02</td>
<td>0.40</td>
<td>1.00</td>
</tr>
</tbody>
</table>
might precipitate hydroxides by increasing the pH value as in [9], [10]. The value varies depending on the heavy metal ion and the element coexisting in the solution, and the specimen of 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 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 performance 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 a conditioner for the soil to neutralize acidic soils as in [11]. It is clarified that the rice husk and FbA can be used not only as an adsorbent for heavy metals but also as a pH value adjustment material by controlling the used amount in the case of using both materials as contaminated water on site.

As shown in Fig. 7, the adsorption ratio for Cd\(^{2+}\) and Hg\(^{2+}\) is relatively high when 5 mL of the sample is added, and the values exceed 60%. For Hg\(^{2+}\), it is presumed that the adsorption limit amount is between 1 and 5 mL as in the case of adding the rice husk. The amount of adsorption for Cd\(^{2+}\) increases as the added amount increases. The solution is acidic because the 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 consideration. The adsorption ratio for other samples is lower than that of adding 1 mL, and the results show a similar tendency of those of 1 mL addition of heavy metals. Some samples increase the amounts of adsorption such as Hg\(^{2+}\) and Mn\(^{2+}\), and it is needed to investigate each sample 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, the ionic radius of the three kinds of ions which belong to group 12, is close to the ionic radius of Ca\(^{2+}\). 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\(^{2+}\) is released instead, so that the adsorption performance may be higher for heavy metal ions with a close ionic radius. If the adsorption mechanism of FbA is physical adsorption, heavy metals adsorbed to the FbA can be taken out. In addition, both the FbA and heavy metals can be reused. Therefore, the adsorption mechanism may be examined in the near future.

The adsorption performance of FbA is higher than that of 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 as small as 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 FbA is higher than that of rice husk in the case of adding 5 mL of sample. It is assumed that the FbA has more marginal adsorption than rice husk.

**CONCLUSIONS**

In this study, the hydroxyapatite (FbA) derived from fish bones and rice husk which are known as industrial waste were focused. The possibility as a new adsorbent was 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 was examined. The test was conducted preparing the addition amount of the heavy metals to 1 mL, 5 mL in order to ascertain the adsorption amount per unit mass of the adsorbent. As
a result, it is confirmed that more than 40% of the additive amount of all metals except As$^{3+}$ and Cr$^{6+}$ can be absorbed by both adsorbents. In particular, both adsorbents had high adsorption ratio for Group 12 elements such as Hg$^{2+}$, Cd$^{2+}$, Zn$^{2+}$. The rice husk and FbA have the similar property of adsorption for 9 metals, and both adsorbents had 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 well adsorbed heavy metal ions is close to the ionic radius of the main component Ca$^{2+}$ of the FbA. It is necessary to examine the influence of these factors on adsorption and the reason why the rice hulls and FbA have similar adsorption performance to heavy metals should be discussed in more detail. For 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 the adsorbent. For As$^{3+}$ and 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 were 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 FbA is high in the case of using 5mL. 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.

5. ACKNOWLEDGEMENTS

This work was supported by Japan Society for the Promotion of Science, the Grants-in-Aid for Scientific Research (C) (Grant number: 18J12343). Also, in carrying out this study, Nihon Kogyo Co., Ltd. provided FbA. We express our gratitude here.

6. REFERENCES

[10]Naoki K, The relationship between pH and the concentration of heavy metal ions, The

Copyright © Int. J. of GEOMATE. All rights reserved, including the making of copies unless permission is obtained from the copyright proprietors.