International Journal of GEOMATE, March., 2021, Vol.20, Issue 79, pp. 28-33
ISSN: 2186-2982 (P), 2186-2990 (O), Japan, DOI: https://doi.org/10.21660/2021.79.6221
Geotechnique, Construction Materials and Environment

STUDY ON ADSORPTION OF HEAVY METALS BY RICE HUSK AND EXTRACTION OF HEAVY METALS ADSORBED IN RICE HUSK

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*Corresponding Author, Received: 16 Mar. 2020, Revised: 13 Jan. 2021, Accepted: 28 Jan. 2021

ABSTRACT: Heavy metals with strong toxicity are often contained in mine drainage from the suspended or abandoned mines where mining activities were once conducted. The mine drainage continues to flow semi-permanently. Thus the treatment of mine drainage must be continued. As the current treatment method for the mine drainage treatment, the neutralization treatment process utilizing alkali chemicals is mainly conducted. However, few alkali chemicals satisfy both low cost and high neutralizing ability. In addition, regarding the neutralized deposits generated during the treatment of mine drainage, it is difficult to secure the disposal sites. Moreover, in recent years, the metal demand has increased in IC chips and parts for electric vehicles. Thus, focusing on the rice husk which is an industrial waste, the purposes of this study are to verify the adsorption performance of rice husks for heavy metals and to verify whether the extraction of heavy metals from rice husks to which heavy metals are adsorbed is possible or not. In this study, the following two tests are carried out: The adsorption test of rice husk for heavy metals and the extraction test with acid from the rice husk which absorbs the heavy metals. From the test results, the adsorption isotherms of Zn, Cu and Cd on the rice husks are described from the adsorption tests, and the adsorption states of Zn, Cu and Cd on the rice husks are discussed. Furthermore, it is proved to be possible to extract them from the rice husks which adsorbs such heavy metals.
Keywords: Mine drainage, Rice husk, Adsorbent, Heavy metals, Extraction

1. INTRODUCTION

In recent years, the soil and groundwater pollution by heavy metals have been frequently confirmed in former factory sites. The purification methods for those pollutions are complicated, and many of them are costly as shown in [1]. The treatment of mine drainage in the suspended or abandoned mines has a similar problem. The mining activities are suspended or closed the suspended or abandoned mines which are scattered all over Japan. Heavy metals with strong toxicity are often contained in mine drainage from the suspended or abandoned mines. When the mine is once opened, the mine drainage continues to flow semi-permanently even if the mine is closed. If the mine drainage containing harmful substances such as heavy metals is discharged without any treatment, it causes pollution to river water and groundwater in the vicinity. Thus the treatment of mine drainage must be continued. Fig.1 shows the suspended or abandoned mines in Japan which conduct the mine drainage treatment as described in [2, 3]. Fig. 1 shows that, in Japan, there are nearly 100 suspended or abandoned mines where mine drainage treatment is being carried out as a mine pollution control project. Current main mine drainage treatment methods are neutralization treatment methods using alkali chemicals such as calcium hydroxide. The cost and performance of each alkaline chemical used in the mine drainage treatment as described in [4] are evaluated and the results are shown in Table 1. From Table 1, it can be seen that few alkali chemicals satisfy both low cost and high neutralization ability. In addition, the treatment process to purify the mine drainage to the level where it can be released into rivers is complicated. Additionally, the current treatment method requires costs such as chemical cost and facilities maintenance cost since it is necessary to continue the mine drainage treatment. In Japan, it costs about

Table 1 The cost and the ability for each alkaline chemical

Alkali chemicals	Low cost	Neutralizing ability
$Ca(OH)_2$	2	3
CaO	3	3
$CaCO_3$	4	2
NaOH	1	4
$Mg(OH)_2$	2 - 3	3
MgO	2 - 3	3

4: excellent, 3: good, 2: average, 1: poor

3 billion yen annually for the mine drainage treatment as shown in [5]. Moreover, there are agendas such as the disposal of neutralized deposits generated during the neutralization treatment and the security of the disposal site for the deposits. Furthermore, heavy metals contained in the neutralized sludge may be eluted from the sludge to clarified water when the neutralization treatment by calcium hydroxide are conducted as described in [6]. On the other hand, metals with high resource value such as zinc (Zn) and copper (Cu) are included in the mine drainage. In recent years, the development of "urban mine" in which metals are taken out from the waste is promoted as a resource recycling because the metal demand has increased in IC chips and parts for electric vehicles. In addition, there is an effort to reduce the neutralized sludge by the extraction and recovery of heavy metals from the sludge as shown in [7]. However, the cost of chemicals is high because heavy metals are extracted and recovered by multistage treatment using various chemicals. Therefore, the adsorption treatment is suitable as a simple treatment method instead of the current neutralization treatment in order to solve these problems. An adsorbent utilized as the mine drainage treatment method is desirable to consider the following three issues; one is that adsorbents are inexpensive, another is that heavy metals adsorbed after adsorption can be recovered, and the other is that the adsorbents after recovering heavy metals should be recycled.

Then, in this study, in order to achieve both low cost and high performance, focusing on the rice husk which is an industrial waste, the purposes are to verify the adsorption of heavy metals by rice husks and to verify whether the extraction of heavy metals from rice husks to which heavy metals are adsorbed is possible or not.

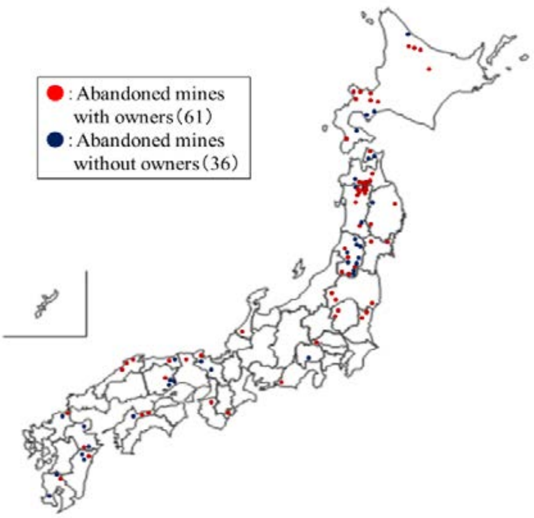

Fig.1 The suspended or abandoned mines in Japan

2. METHODOLOGY

Since zinc (Zn), copper (Cu), and cadmium (Cd) have been detected in mine drainage water leaked from many suspended or abandoned mines, three kinds of heavy metals are examined in this study.

2.1 Rice Husk Preparation

Photo. 1 shows the rice husk utilized as an adsorbent in this study. In Japan, about 2 million tons of rice husks are discharged annually. Rice husks containing much silica have high hardness, and it is difficult to process rice husks. Therefore, rice husks have no use other than simple agricultural materials, and most of them are discarded. At present, there are few effective utilization methods for rice husks, and various research institutes are actively conducting the research on utilization methods for rice husks. As an example, it is described that rice husk charcoal has adsorption performance for cesium (Cs) and strontium (Sr) in aqueous solution (Kobayashi et al.[8]). In addition, it is reported that the rice husk ash has an adsorption ability for divalent heavy metal ions such as lead (Pb), mercury (Hg), zinc (Zn), copper (Cu), nickel (Ni) and cadmium (Cd) as shown in [9-12]. However, labor and cost are expended in order to process to coal and ash. Additionally, it is difficult to collect rice husk charcoal or ash after used as an adsorbent. Moreover, there are few studies in which the adsorption performance and adsorption mechanism of raw rice husks for heavy metals and the reuse method considering the tight disposal site are investigated. In this study, various tests are conducted using the raw rice husks dried at 100 ° C for 24 hours.

Photo. 1 Raw Rice Husks (Not-crushed and unprocessed rice husks)

2.2 Heavy Metals Adsorption Test (Shaking Test)

Based on the adsorption isotherms obtained from shaking tests for zinc, copper and cadmium, the adsorption performance of raw rice husks

(RRH) for them is evaluated. In the test, three solutions are prepared. One contains zinc nitrate solution, another contains copper nitrate solution and the other contains cadmium nitrate solution.

First, seven initial concentrations (3 ppm, 4 ppm, 5 ppm, 6 ppm, 7 ppm, 30 ppm, 60 ppm) of each solution are prepared and the initial pH of these solutions is adjusted to 6. Next, 10 mL of the prepared solution is poured into a centrifuge tube to which 20 mg of raw rice husk is added. Then, 10 mL of solution with 20 mg of raw rice husk is shaken for 24 hours at 200 rpm at a temperature of 20 ° C. After that, the solutions are centrifuged at 2000 rpm for 3 minutes, and the residual concentration of heavy metals: Zn, Cu and Cd, in the solutions are analyzed by an ICP-AES. The test conditions are summarized in Table 2.

In the study, the adsorption amount per unit mass of the raw rice husks is employed as the evaluation of the test result. The adsorption amount per unit mass of the raw rice husks is defined by the following equation (1).

$$\mathrm{W_i(mg/g)} = \frac{\mathrm{V(C_o\text{-}C_i)}}{\mathrm{M_i}} \qquad (1)$$

In the equation (1), “*V*” is the amount of the solution, “C_o” is the initial concentration of the solution, “C_i” is the residual concentration (equilibrium concentration) and “M_i” is the mass of the raw rice husks. In order to ensure reproducibility, the mean value of 3 tests is adopted as a test result.

In addition, the test results are applied to Langmuir and Freundlich models so as to clarify the adsorption mechanism of the adsorbent for the heavy metals. Langmuir and Freundlich models are typical adsorption equilibrium equations in liquid-phase adsorption. Langmuir and Freundlich models are defined by the following equation (2) and (3), respectively.

Table 2 Test conditions (Shaking test)

Solution volume		10 mL
Zn, Cu, Cd (nitrate solution)		3 - 7, 30, 60 ppm
Initial pH		6.0
Adsorbent	Raw Rice Husks (RRH)	20 mg
Temperature		20 ℃
Shaking rate		200 rpm
Shaking time		24 hours
Centrifuge rate		2000 rpm
Centrifuge time		3 minutes

$$\text{Langmuir:} \frac{\mathrm{C_i}}{\mathrm{W_i}} = \frac{1}{\mathrm{aW_s}} + \frac{1}{\mathrm{W_s}}\mathrm{C_i} \qquad (2)$$

$$\text{Freundlich:} \log \mathrm{W_i} = \log \mathrm{K_F} + \frac{1}{\mathrm{n}} \log \mathrm{C_i} \qquad (3)$$

In the equation (2), “*a*” is the adsorption equilibrium constant, “W_s” is the amount of saturation adsorption. In the equation (3), “1/*n*” is the affinity between adsorbent and adsorbate, “K_F” is the adsorption capacity.

2.3 Heavy Metals Extraction Test

In order to confirm whether it is possible to recover heavy metals which are valuable resources from the used raw rice husks (uRRH) adsorbing heavy metals, the extraction of heavy metals adsorbed from the uRRH is attempted using nitric acid solution.

2.3.1 Preparation of the raw rice husks adsorbing heavy metals

First, the solutions similar to that used in the shaking test is prepared, and the initial concentration and the pH of these solutions are adjusted to 5 ppm and 6, respectively. Next, 50mL of the solution is poured into a centrifuge tube, and 1.0g of the raw rice husks is added. Then, the prepared solutions are shaken and centrifuged under the same conditions as has already mentioned in the shaking test. After that, the raw rice husks which adsorb heavy metals are separated from the solutions by a filtration apparatus, and the residual concentration of heavy metals in the solutions is analyzed by an ICP-AES. The difference between the initial concentration and the analyzed one is defined as the concentration of heavy metals contained in the raw rice husks which adsorb heavy metals. The test conditions are summarized in Table 3.

Table 3 Test conditions (Preparation of uRRH)

Solution volume		50 mL
Zn, Cu, Cd (nitrate solution)		5 ppm
Initial pH		6.0
Adsorbent	Raw Rice Husks (RRH)	1.0 g
Temperature		20 ℃
Shaking rate		200 rpm
Shaking time		24 hours
Centrifuge rate		2000 rpm
Centrifuge time		3 minutes

2.3.2 Extraction of heavy metals by nitric acid solution

First, 50 mL of a solution of nitric acid (Concentration: 0.1 mol/L) is poured into a centrifuge tube, and then the raw rice husks to which heavy metals have been adsorbed are added. Then, the solutions are shaken at 200 rpm for 6 hours by a shaking apparatus. After that, the solutions are centrifuged at 2000 rpm for 3 minutes, and the residual concentration of heavy metals in the solutions is analyzed in an ICP-AES. In order to ensure reproducibility, the mean value of 3 tests is adopted as a test result as has mentioned in the shaking test. The test conditions are summarized in Table 4.

3. RESULTS AND DISCUSSIONS

3.1 Heavy Metals Adsorption Test Results

The adsorption isotherms obtained in the tests with the Langmuir model are shown in Fig.2, and those with the Freundlich model are shown in Fig.3. The horizontal and vertical axes in Fig.2 are the equilibrium concentration of heavy metals (Zn, Cu and Cd), and the value obtained by dividing the equilibrium concentration by the adsorption amount of heavy metals (C/W), respectively. The horizontal and vertical axes in Fig.3 are the logarithm of the equilibrium concentration of heavy metals (logC) and the logarithm of the adsorption amount of heavy metals (logW), respectively.

The Langmuir model suggests whether the adsorption mode is monolayer adsorption or not. The applicability of the Langmuir model depends on whether the linear relationship between the equilibrium concentration of heavy metals and the value of equilibrium concentration divided by the adsorption amount of heavy metals holds or not. When the Langmuir model is not applied, it is possible that the adsorption mode is multi-molecular layer adsorption. In addition, the Freundlich model shows that a large amount of heavy metals is adsorbed in the case of logarithm shape, and the amount of heavy metals are adsorbed is not so large in the case of exponential shape.

Since the value of the coefficient of determination (R^2) is close to 1 in Fig.2, it is indicated that the adsorption mode of the raw rice husks to Cd is likely to be monolayer adsorption. Fig.3 shows that the amount of Cd adsorbed in the low concentration range is not so large. It is also confirmed that a large amount of Cd can be adsorb as the concentration increases. It is confirmed that the amount of Zn or Cu adsorbed in the low and high concentration ranges is not so large, and that a large amount of Zn or Cu can be adsorbed in the medium concentration range. Water molecules are more abundant than heavy metal ions in the low concentration range. As described in [13], liquid phase adsorption is a competitive adsorption of

Table 4 Test conditions (Extraction test)

Solution volume		50 mL
Solution	Nitric acid (HNO3) used	0.1 mol/L
Sample	Raw Rice Husks (uRRH)	nealy 1.0 g
Temperature		20 ℃
Shaking rate		200rpm
Shaking time		6 hours
Centrifuge rate		2000 rpm
Centrifuge time		3 minutes

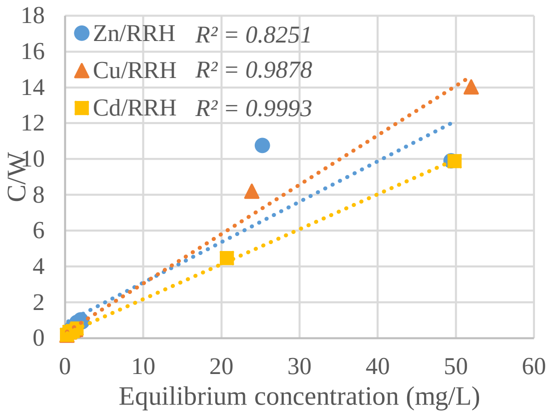

Fig.2 The adsorption isotherm (Langmuir model)

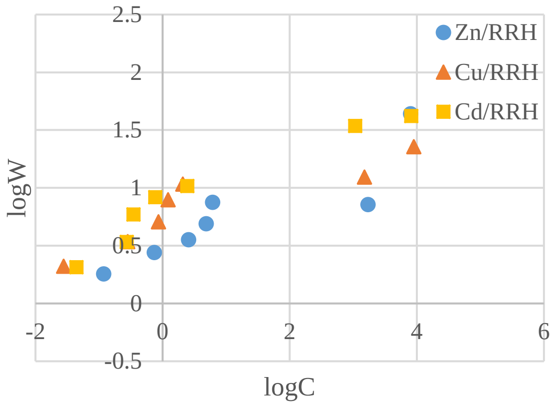

Fig.3 The adsorption isotherm (Freundlich model)

solvent and adsorbate on the adsorbent surface. In the low concentration range, it is considered that it does not become the adsorption of the logarithmic function type for either heavy metal, that is, a large amount of heavy metals is not adsorbed to an adsorbent. The adsorption mode of the raw rice husks for Cd is monolayer adsorption, and it seems to be able to adsorb more Cd because of the strong attractive force between adsorbent surface and adsorbate. On the other hand, with respect to Zn and Cu, it is considered that Zn and Cu are further attached on the first layer on which Zn and Cu have already been adsorbed, that is, the adsorption mode is likely to be multi-molecular layer adsorption. It is considered that the adsorption amount of Zn and Cu in the second and subsequent layers is less than that of Cd in the first layer, since the attractive force does not work between adsorbent in the adsorption of Zn and Cu.

3.2 Heavy Metals Extraction Test Results

Fig.4 shows the concentrations of heavy metals contained in the raw rice husks before and after the extraction tests using nitric acid solution. “before” and “after” indicate that the concentration of heavy metals contained in the raw rice husks before and after the extraction tests. The difference concentration between “before” and “after” means the extracted concentration of heavy metals. From Fig.4, more than 90% of Zn, about 60% of Cu, and about 90% of Cd are extracted, which indicates that heavy metals adsorbed in the raw rice husks can be extracted by nitric acid. This is considered to be because heavy metals adhering to the surface of raw rice husks were washed away by bleaching action of acid. The reason why there is the difference in the extraction concentration by the heavy metal is mainly dependent on whether the adsorption mode is monolayer adsorption or not. However, there is the difference in the extraction concentration between Zn and Cu both of which have similar adsorption mode. This is considered to be due to the elution of trace element Zn as well as Zn adsorbed on the raw rice husks before adsorbing Zn in the solution.

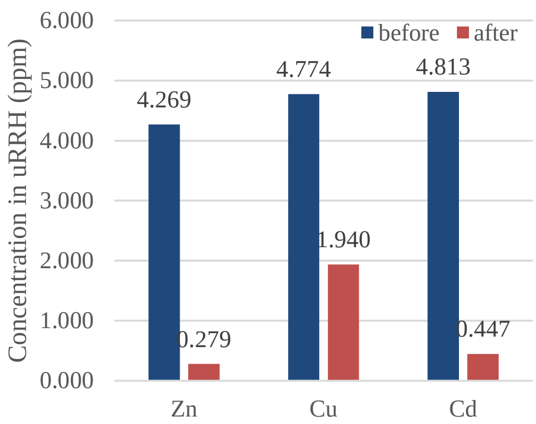

Fig.4 The result of extraction test (by HNO_3 aq)

4. CONCLUSIONS

As a current treatment method of mine drainage, the neutralization treatment process is frequently conducted utilizing alkali chemicals. However, few alkali chemicals satisfy both low cost and neutralizing ability. In addition, there are agendas such as the complication of the neutralization treatment process, the disposal of neutralized deposits generated during the neutralization treatment and the security of the disposal site for the deposits. Moreover, in recent years, the metal demand has increased by the development of IC chips and parts for electric vehicles. As the simple treatment method to solve these problems, the adsorption treatment is conducted utilizing the raw rice husks as an adsorbent with focusing on the rice husk which is industrial waste.

In this study, it is turned out the raw rice husks has the adsorption performance of heavy metals (Zn, Cu and Cd) contained in mine drainage. According to Langmuir model, it seems that the strong attractive force acts between the raw rice husks and Cd regarding the adsorption of the raw rice husk for Cd. According to Freundlich model, it is clarified that the degree of adsorption ability of raw rice husks for heavy metals (Zn, Cu, and Cd) targeted in this study varies according to the concentration range of solutions. Additionally, it is found that it is possible to recover heavy metals from the raw rice husks adsorbing heavy metals by a nitric acid. It is possible to reduce the material cost among the costs related to the removal of heavy metals contained in mine drainage by using the rice husk, which is industrial waste. In addition, the use of rice husk enables environmentally friendly treatment compared to the use of chemicals. Moreover, in recent years when the metal demand increases, it is possible to save limited natural resources. Furthermore, it is expected that the burden on the final disposal site utilized for the waste disposal such as the neutralized deposits will be reduced.

As the reuse method of raw rice husks after the adsorption of heavy metals, in the future, the following should be examined: the reuse of raw rice husk from which heavy metals are extracted as an adsorbent or the reuse as a concrete admixture by processing it into the rice husk ash [14].

5. ACKNOWLEDGMENTS

This work was supported by Seeds Development Research Fund (Emergence type) of Kagawa University Research Promotion Program 2019 and 2020 (KURPP) and Japan Society for Promotion of Science (JSPS), the Grants-in-Aid for

Scientific Research (KAKENHI) (Grant number: 20K04684, 18J12343).

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