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EFFECT OF DIFFERENT CALCINATION TEMPERATURES DURING THE MANUFACTURING OF FISHBONE-BASED ADSORBENT ON THE ADSORPTION CAPACITY OF THE ADSORBENT

*Ayane Yanaka[1], Naomichi Matsumoto[1], Yoshihiro Suenaga[1] and Hidenori Yoshida[1]

[1] Faculty of Engineering and Design, Kagawa University, Japan

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ABSTRACT: In Japan, soil and groundwater contamination by harmful substances such as heavy metals and radioactive substances remains a persistent issue. In the treatment methods for removing such harmful substances, there is a lack of solutions that balance high treatment capacity with low cost, and they are not always environmentally friendly. On the other hand, economic growth has led to increased waste emissions, but the disposal capacity of existing sites is decreasing year by year due to the difficulty of securing new final disposal sites. Since Goal 12 of the SDGs calls for a drastic reduction of waste generated in the production process by controlling and recycling it, the recycling of waste has been actively promoted in recent years. However, the recycling rate of food waste is low, especially fish residues, which are mostly used as feed or fertilizer, and have not been recycled beneficially. Therefore, this study aims not only to utilize fish bones as an adsorbent material but also to enhance the functionality and versatility of fishbone-derived adsorbents to adsorb a wide variety of harmful substances more efficiently and effectively. Three patterns of fishbone-based adsorbents with different manufacturing methods are tested for zinc (Zn), copper (Cu), cadmium (Cd), mercury (Hg), and strontium (Sr) with and without initial pH adjustment by immersion tests. The results show that some adsorbent types show high adsorption rates for all substances except Hg, with or without initial pH adjustment, but suggest for Hg a relationship between adsorption capacity of adsorbents and pH value in the solution.

Keywords: Food waste, Fish bones, Adsorbent, Functionality, Multifunctionality

1. INTRODUCTION

In recent years, while anthropogenic environmental pollution has decreased, soil contamination of naturally occurring harmful substances and the resulting groundwater contamination have become more apparent. According to the survey results on soil and groundwater contamination cases published by the Ministry of the Environment [1, 2], the number of occurrences of both cases has been increasing year by year. Notably, the enforcement of the Soil Contamination Countermeasures Act (SCCA) in 2003 and its amendment in 2010 have led to a sharp increase in the number of reported cases. In addition, from 1991 to 2021, the cumulative number of cases exceeding soil environmental standards was overwhelmingly due to heavy metals and other similar contaminants, accounting for approximately 80% of all cases. Heavy metals generally tend to adsorb onto soil particles, so even when soil contamination occurs, it rarely extends to groundwater contamination. Meanwhile, the contamination from natural sources occurs frequently. When the contamination from natural sources occurs, heavy metals contained in soils, rocks, and geological formations leach out at high concentrations, potentially spreading contamination not only within the soil but also to the groundwater [3]. As a case of contamination other than heavy metals in Japan, the giant tsunami caused by the March 2011 off the Pacific coast of Tohoku earthquake led to the severe accident at the Tokyo Electric Power Company's Fukushima Daiichi Nuclear Power Station, resulting in the widespread dispersal of a large amount of radioactive substances into the environment. Due to concerns about environmental risks, decommissioning work at the Fukushima Daiichi Nuclear Power Plant is ongoing. However, the medium to long-term decommissioning plan is currently behind schedule, and the process is being reviewed and revised [4]. As a result of delays in decommissioning planning, contaminated water containing radioactive substances accumulates inside the nuclear reactor buildings. Remediation technologies and treatment methods for soil and groundwater contamination by heavy metals and wastewater include excavation removal, solidification and insolubilization, containment, chemical treatment, such as hydroxide precipitation and sulfide methods, and adsorption treatment, such as ion-exchange and chelation resins [5, 6]. However, few of these technologies simultaneously achieve both low cost and high treatment capacity. In addition, there are various problems such as the complexity of the treatment process, difficulty in securing disposal site, costs associated with disposal and treatment, concerns about long-term stability, and the disposal of materials after treatment. The contaminated water from the Fukushima Daiichi Nuclear Power Plant is treated in a cesium removal equipment and the Advanced Liquid Processing System (ALPS). This treatment process employs various adsorbents, such as zeolite-based adsorbents and titanium silicate-based adsorbents. Since these adsorbents often contain expensive constituents such as titanium and silver, the treatment of contaminated water using these materials incurs high cost [7]. In addition, slurry waste is discharged during treatment in the ALPS and temporarily stored in a High Integrity Container (HIC). However, there are problems associated with the storage of HIC, such as water leakage from the slurry contained in the HIC and the deterioration of the HIC due to radiation. Therefore, stabilization treatment of this slurry is currently under consideration [8]. Thus, current treatment methods face several challenges, including a lack of solutions that balance high treatment capacity with low cost. Additionally, these methods are not always environmentally friendly, presenting issues in terms of cost, treatment efficiency, and environmental impact. It is considered that a simplified treatment is suitable for on-site applications. Therefore, when the adsorption treatment is selected as a simple treatment method, the materials are required to be inexpensive and environmentally friendly. In addition, since few materials can efficiently adsorb harmful substances such as heavy metals and radioactive materials using a single material in adsorption treatment, there is a demand for adsorbents that can effectively adsorb a wide range of harmful substances with a single material.

In Japan, economic growth has led to an increase in waste emissions. However, the disposal capacity of existing sites is decreasing year by year because of the difficulty in securing new final disposal sites. In the 12th goal of SDGs, which aims to "Substantially reduction of waste generation through prevention, reduction, recycling and reuse of waste by 2030", and Japan actively promotes the recycling of waste materials. However, the recycling rate of food waste is not so high in Japan. Among various types of food waste, Japan has a notably higher consumption of seafood compared to other countries. Consequently, the amount of discarded seafood residues, such as shells and bones, is also significantly larger, yet the recycling rate for these materials remains low. According to the supply and demand data for fish and seafood in the fiscal year 2020 [9], Japan's estimated fish residue output is a substantial 2.3 million. Currently, seafood residues are disposed of as industrial waste, and this disposal incurs costs. Therefore, effectively utilizing seafood residues, which incur disposal costs, and improving their recycling rate is important from the perspective of SDGs. Nevertheless, the current recycling rate of seafood residues remains at approximately 30% of the total, and their uses are still limited to low-value products such as feed and fertilizers [10]. In conclusion, recycling seafood residues as adsorbents could contribute to improving the recycling rate of food waste. Furthermore, if seafood residues, as a single material, can adsorb a wide variety of harmful substances, it would enable high-value recycling of these residues.

Thus, in this study, from the viewpoints of low cost and high environmental compatibility, fish bones, one of the fish residues, are focused on. To achieve high-value recycling of fish bones, it is essential to enhance their functionality and versatility. Specifically, enabling fish bones to adsorb a wide variety of harmful substances requires diversifying their inherent properties and improving both the capacity and range of their adsorption capabilities. Kobayashi [11], Michikawa *et al.* [12] and Fukumitsu *et al.* [13] state that changing the calcination temperature during manufacturing makes the production of various materials can render the surface of various materials porous, and the porosity may affect the material's adsorption capacity. In addition, previous studies have reported that there is a relationship between the pH of the solution and the adsorption capacity of the adsorbent [14-17]. Therefore, this study aims not only to recycle waste but also to add new value to it. Specifically, the goal of this study is to repurpose fish bones as an adsorbent and to enhance their functionality and versatility to adsorb a wide variety of harmful substances more efficiently by changing the calcination temperature during the manufacturing of the adsorbent and the pH of the solution.

2. RESEARCH SIGNIFICANCE

As has mentioned above, in Japan, soil and groundwater contamination by harmful substances such as heavy metals and radioactive substances remains a persistent issue. In addition, few treatment methods and materials for the removal of such harmful substances can efficiently and effectively remove a wide variety of harmful substances using a single material. The significance of this study lies in its ability to efficiently adsorb a wide variety of harmful substances using a single adsorbent material. This not only contributes to the achievement of the SDGs but also creates added value for fish bones.

3. TEST METHOD

In order to enhance the functionality and versatility of fishbone-based adsorbents, an immersion test is conducted by adding fishbone-based adsorbents with different calcination temperatures to various heavy metal solutions with and without initial pH adjustment. Through this test, it is verified whether or not the calcination temperature during the manufacturing of the fishbone-based adsorbent and the initial pH have an effect on the adsorption performance of the adsorbent. In this test, three types of fish bone-based adsorbents (Type A, Type B and Type C) with calcined at different temperatures are prepared. The target substances are zinc (Zn), copper (Cu), cadmium (Cd), mercury (Hg) and strontium (Sr) are selected. Zn and Cu are detected in mine wastewater, which is a source of natural groundwater contamination. Additionally, Cd and Hg are representative natural contaminants. Furthermore, radioactive Sr is present in large quantities in the contaminated water remaining inside the Fukushima Daiichi Nuclear Power Plant buildings.

The test procedure is as follows (see Fig. 1). First, standard solutions of each heavy metal are diluted to initial concentration of 3 mg/L and adjusted to the specified initial pH (see Table 1). Although heavy metals tend to precipitate beyond a certain pH level, in this study, the initial pH of each solution is set to prevent any precipitation of the heavy metals. At the same time, the solution without initial pH adjustment is also prepared. Next, 150 mL of the prepared solution is poured into a cylindrical container, into which a piece of each adsorbent is added. These specimens are then immersed at 20°C for 24, 72, 120 and 168 hours. After 24, 72, 120 and 168 hours in the immersion test, the supernatant solution of the immersion test specimens is collected as the test solutions. Finally, the pH of the test solution and the residual concentration of each heavy metal in the test solutions are measured and analyzed with a pH meter and an ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy), respectively. The ICP-AES is an analytical instrument that utilizes emission spectrometry with an inductively coupled plasma (ICP) as the light source. Emission spectrometry involves measuring the spectral lines emitted by atoms and ions excited by the energy from an Argon (Ar) plasma. The positions (wavelengths) of these spectral lines are used to identify the types of constituent elements, while the intensity of the lines is used to determine the concentration of each element. Therefore, this instrument is used to measure the concentration of various elements in a sample. In the test, the adsorption rate is employed to evaluate the adsorption performance of each adsorbent. The adsorption rate is defined by the following Eq. (1).

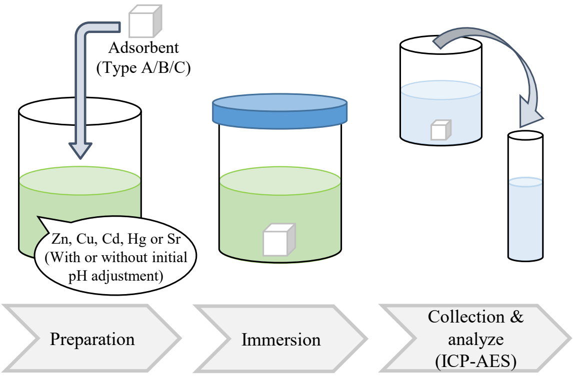

Fig. 1 Test overview diagram

Table 1 Initial pH value of each heavy metal

Adsorption target substances	Initial pH
Zn(II)	6
Cu(II)	4
Cd(II)	6
Hg(II)	5
Sr(II)	6

$$A_r\ (\%) = \frac{C_0 - C_i}{C_0} \times 100 \tag{1}$$

In the Eq. (1), "A_r" is the adsorption rate of each heavy metal, "C_0" is the initial concentration of each heavy metal in the solution at the time of standard solution addition, "C_i" is the residual concentration of each heavy metal in the solution analyzed at the end of the immersion test. In order to ensure reproducibility, each test is conducted three times, and the average values of the these are presented as the test results.

4. RESULTS AND DISCUSSION

Figs. 2 to 11 show the immersion test results for various heavy metals both with and without initial pH adjustment. The horizontal axis, primary vertical, and secondary vertical axis of the figures represent the immersion time, the adsorption rate of each heavy metal, and the pH values measured after the specified immersion period, respectively. It is noted that the pH value at the start of immersion (0 hours immersion) in these figures represents the initial pH.

Figs. 2 and 3 show that the adsorption rate of Zn generally increases for all adsorbents with increasing the immersion time, and that Type A exhibits the highest adsorption performance for Zn when the initial pH is not adjusted, whereas Type B shows the highest adsorption performance for Zn when the initial pH is adjusted. On the other hand, from 24 hours to 168 hours after the start of the immersion test, there is not much significant change in the pH values of the two figures, except for Type C when the initial pH is not adjusted. Although there is no significant difference in the variation of pH values between the cases with and without initial pH adjustment, there is a difference in adsorption performance depending on the type of adsorbent. This is the reason that the factors other than pH affect the adsorption performance of the adsorbents.

Figs. 4 and 5 show that the adsorption rate of Cu as well as Zn for all adsorbents increases as the

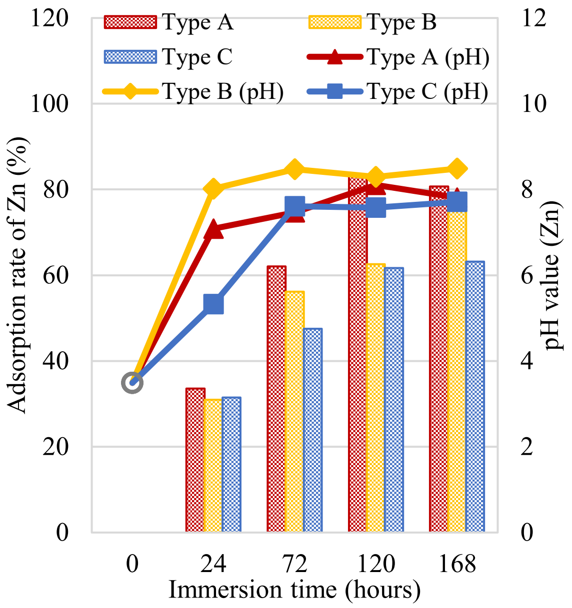

Fig. 2 Result of immersion test for Zn without initial pH adjustment

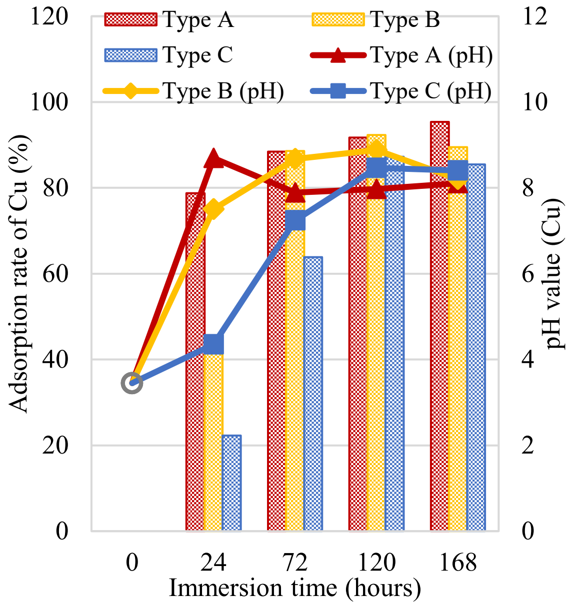

Fig. 4 Result of immersion test for Cu without initial pH adjustment

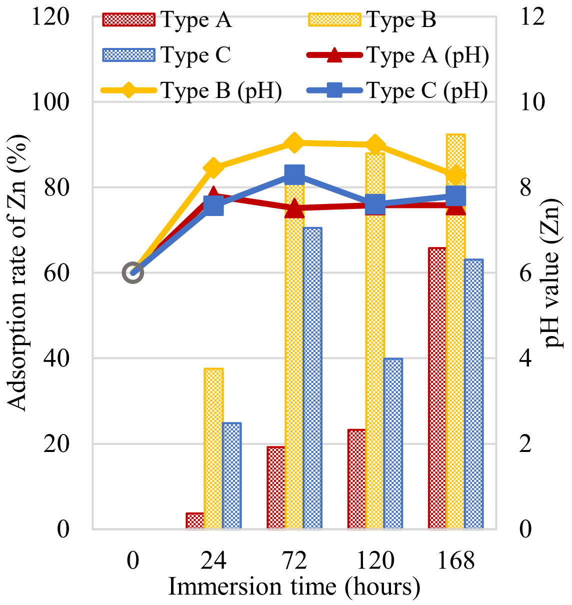

Fig. 3 Result of immersion test for Zn in case of initial pH adjusted to 6

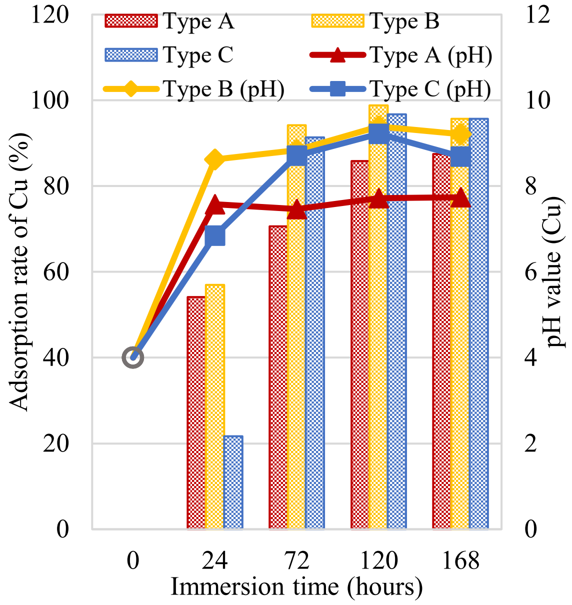

Fig. 5 Result of immersion test for Cu in case of initial pH adjusted to 4

immersion time progresses. When the initial pH is not adjusted, the adsorption performance of Type A and Type B is relatively high. Particularly, the adsorption rate of Cu is approximately 80% after 24 hours from the start of the immersion test for Type A. In contrast, when the initial pH is adjusted, the adsorption performance for Type B and Type C is relatively high. The adsorption rate of Cu for both Types is over 90% after 72 hours from the start of the immersion test. Since the pH values when the adsorption rate of Cu is 80% or more generally indicate a pH value of 8 or higher, it is suggested that the adsorption performance for Cu may be higher when the pH is 8 or higher under the conditions of this test.

Figs. 6 and 7 indicate that the adsorption rate of Cd as well as Zn and Cu for all adsorbents increase as the immersion time progresses. After 168 hours from the start of the immersion test, the adsorption rate of Cd for all adsorbents except Type C is over

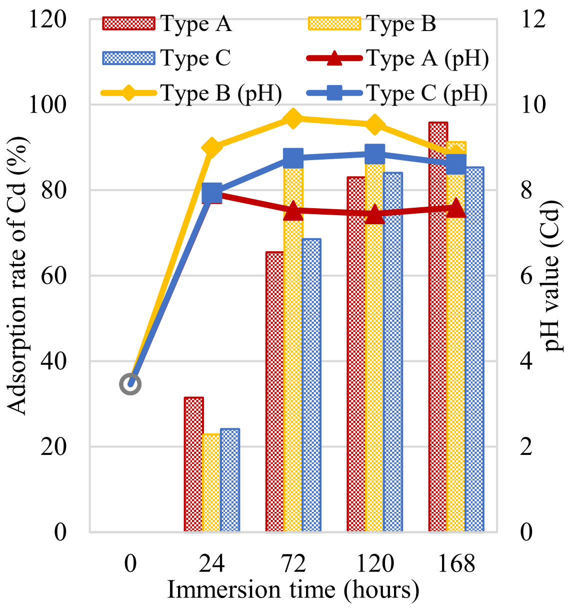

Fig. 6 Result of immersion test for Cd without initial pH adjustment

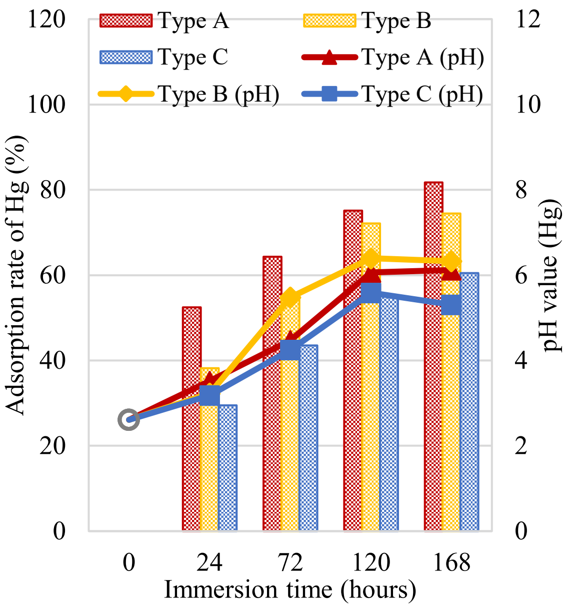

Fig. 8 Result of immersion test for Hg without initial pH adjustment

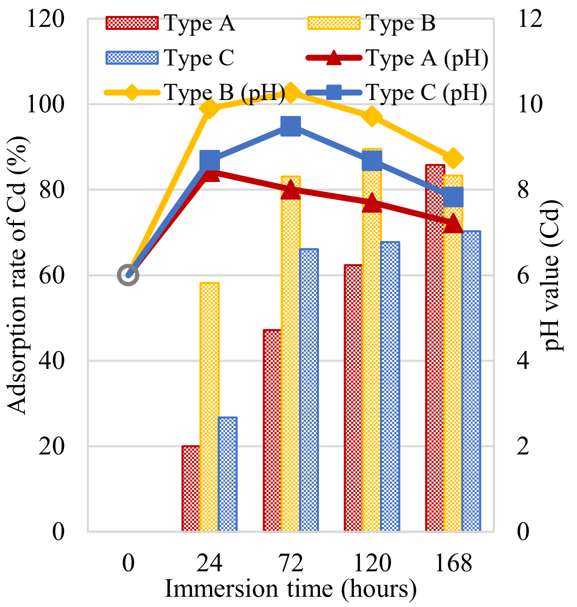

Fig. 7 Result of immersion test for Cd in case of initial pH adjusted to 6

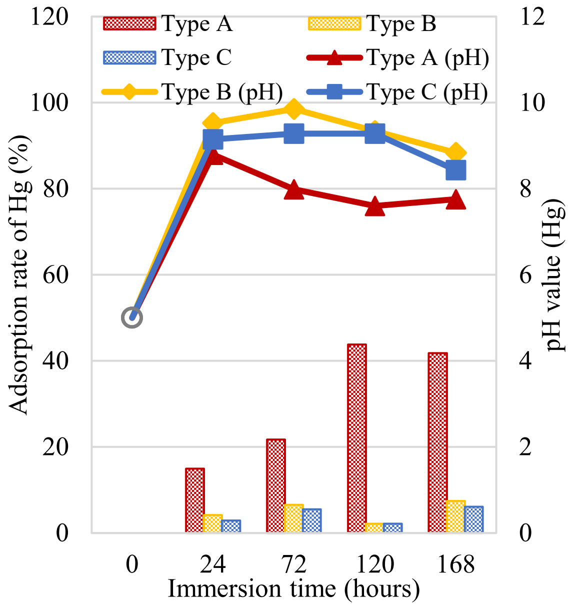

Fig. 9 Result of immersion test for Hg in case of initial pH adjusted to 5

80% regardless of whether the initial pH is adjusted. Additionally, Type B has the highest adsorption velocity for Cd, and the adsorption rate of Cd exceeds 80% after 72 hours from the start of the immersion test regardless of whether the initial pH is adjusted. On the other hand, for all adsorbents except Type B, the adsorption performance with initial pH adjustment is slightly lower than that without initial pH adjustment. There is no significant difference in the variation of pH values from 24 hours to 168 hours after the start of the immersion test between the cases with and without initial pH adjustment. Therefore, as well as Zn, it is presumed that factors other than pH affect the adsorption performance of the adsorbents for Cd. As shown in Fig. 8, when the initial pH is not adjusted, the adsorption rate of Hg for all adsorbents increases with the passage of immersion time. Additionally, Type A exhibits the highest adsorption rate, fol-

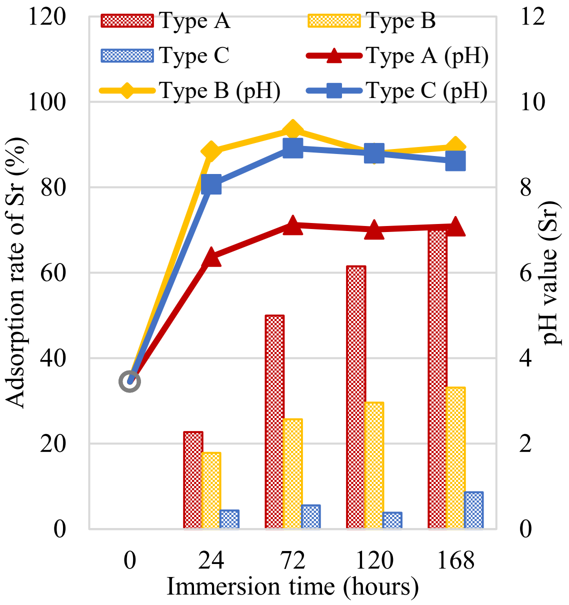

Fig. 10 Result of immersion test for Sr without initial pH adjustment

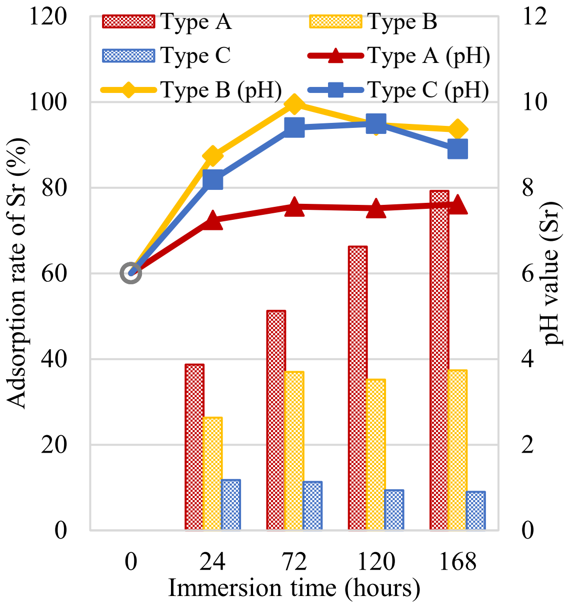

Fig. 11 Result of immersion test for Sr in case of initial pH adjusted to 6

lowed by Type B and Type C, at all immersion periods.

In contrast, Fig. 9 shows that the differences in adsorption rates among the types of adsorbents with initial pH adjustment are more pronounced than those without initial pH adjustment. For Type A, the maximum adsorption rate of Hg is around 40%, whereas for Type B and Type C, these rates are less than 10%. Examining these two figures, it is found that the change in pH values varies significantly over time. Additionally, when the initial pH is not adjusted, the pH values are below 7 at all immersion periods, whereas, when the initial pH is adjusted, the pH values are above 7 at all immersion periods. The Hg reagent used in this test is $HgCl_2$. The dissolved forms of divalent mercury are $HgCl_4^{2-}$, $HgCl^{3-}$, or $HgCl_2$ in acidic conditions, and are the hydrolyzed products; $HgCl(OH)$ and $Hg(OH)_2$, near neutral and alkaline conditions [18]. Yoshida *et al.* [19] reported that Hg is easily adsorbed onto activated carbon in the form of halogen complex anions (HgX_4^{2-}), and that, for heavy metal complex anions to be adsorbed onto activated carbon, it is necessary for the heavy metal ions to form stable complex anions and for the resulting complex anions to have significant affinity for the surface of the activated carbon. Since the pH value without initial pH adjustment indicates an acidic range, it is considered that the high adsorption rate of Hg without initial pH adjustment is due to mercury being adsorbed in the form of complex anions onto the adsorbent used in this test. On the other hand, only Type A exhibits adsorption behavior for Hg in the case of adjusting the initial pH, suggesting that the adsorption performance for Hg can be improved by changing the calcination temperature during the manufacturing of the adsorbent.

Figs. 10 and 11 indicate that Type A exhibits the highest adsorption rate of Sr, followed by Type B and Type C, at all immersion periods regardless of whether the initial pH is adjusted. On the other hand, unlike other heavy metals, there are significant differences in the adsorption rates of Sr among the various adsorbents as the immersion time progresses. The adsorption rate for Type A is the highest in the Sr adsorption tests, reaching up to approximately 80%. There is no significant difference in the variation of pH value from 24 hours to 168 hours after the start of the immersion test between the cases with and without initial pH adjustment. This is the reason that the difference in calcination temperature during the manufacturing of the adsorbents affects the adsorption performance for Sr.

5. CONCLUSION

This study aimed not only to utilize fish bones as an adsorbent material but also to enhance the functionality and versatility of fishbone-derived adsorbents to more efficiently and effectively adsorb a wide variety of harmful substances such as heavy metals. In the test, in order to discuss the optimal conditions for the adsorption of harmful substances such as heavy metal, it was verified whether or not the calcination temperature during the manufacturing of the fishbone-based adsorbent and the initial pH of the solution have an effect on the adsorption performance of the adsorbent for representative heavy metals such as Zn, Cu, Cd, Hg and Sr.

From the series of test results, although there were differences in the adsorption rates of various heavy metals depending on the calcination temperature during the manufacturing of fishbone-based adsorbents, these adsorbents generally exhibited high adsorption performance for heavy metals other than Hg with and without adjusting the initial pH. Regarding Hg, the adsorption rate with the initial pH adjustment was lower than that without the initial pH adjustment. This indicates that the pH of the solution affects the adsorption performance of the fishbone-based adsorbent. However, the adsorption performance of the fishbone-based adsorbents for Hg can be improved by changing the calcination temperature during the production of the adsorbent, even when the initial pH is adjusted. From these observations, it is possible to develop adsorbent materials that can adsorb a wide variety of harmful substances more efficiently by altering the manufacturing conditions. Since the results suggest that it is possible to adsorb a wide variety of harmful substances using only fish bones, not only the contribution to the achievement of the SDGs, but also the high-value recycling of discarded fish bones can be realized.

In the future, in order to manufacture adsorbents that exhibit high adsorption performance for Hg even when the initial pH is adjusted, it is necessary to vary the calcination temperature during the manufacturing of the adsorbents, and to conduct the adsorption test using these adsorbents. Additionally, when considering the use of fishbone-based adsorbents in actual contaminated sites, it is important to recognize that not only harmful substances but also other chemical species are contained at these sites. Therefore, it is necessary to investigate how the presence of these coexisting chemical species affects the selective adsorption performance of fishbone-based adsorbents for harmful substances.

6. ACKNOWLEDGMENTS

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