International Journal of GEOMATE, Feb., 2022, Vol.22, Issue 90, pp.79-84
ISSN: 2186-2982 (P), 2186-2990 (O), Japan, DOI: https://doi.org/10.21660/2022.90.gxi383
Geotechnique, Construction Materials and Environment

ADSORPTION PROPERTIES OF MATERIALS ADSORBING SELECTIVELY ARSENIC FROM AQUEOUS SOLUTIONS CONTAINING MULTIPLE CHEMICAL SPECIES

* Ayane Yanaka[1], Yuri Takeshita[2], Keiichiro Shibata[3], Yoshihiro Suenaga[4,] and Hidenori Yoshida[4]

[1] Graduate School of Engineering, Kagawa University, Japan; [2] T-NET JAPAN CO., Ltd., Japan; [3] Kajima Corporation, Japan; [4] Faculty of Engineering and Design, Kagawa University, Japan

*Corresponding Author, Received: 30 Nov. 2021, Revised: 28 Dec. 2021, Accepted: 13 Jan. 2022

ABSTRACT: Arsenic contamination has been confirmed in groundwater around the world. In particular, health hazard by arsenic occurs frequently in developing countries such as Bangladesh. In these countries, it is urgent to remove arsenic from water sources such as groundwater from the viewpoint of the security of safe and sufficient drinking water because population growth is predicted in the future. Especially, inexpensive and simple technology for removing arsenic is required at arsenic-contaminated sites. As a simple method for removing arsenic, the adsorption method is mentioned. However, the adsorption method has two problems. One is that the cost required for the adsorption method is higher than that for other methods, and the other is that it is difficult to adsorb only arsenic selectively when arsenic is mixed with other chemical species. Thus, in this study, the inexpensive adsorbent (improving hydroxyapatite derived from fishbone [Patent No. 6351008 given by Japanese Patent Office], which has a low material cost) to remove arsenic is developed, and the effect of other chemical species on the adsorption performance for the arsenic of the adsorbent is examined. In the case of no chemical species mixing (arsenic only), the case of mixing one or more kinds of chemical species, the adsorption test by the shaking test is carried out, and the adsorption performance is evaluated by the adsorption isotherm. From the test results, it is proven that arsenic is selectively adsorbed, even if the chemical species are mixed.

Keywords: Arsenic, Selectively adsorption performance, Chemical species, Adsorbent

1. INTRODUCTION

In recent years, arsenic contamination in groundwater has been frequently confirmed all over the world. For example, according to the research survey by Ohno et al. [1], it has been found that the arsenic concentration in all wells of the 10 sites in the central area of Nawabganji City in Bangladesh exceeded 0.01 mg/L which is the WHO guideline value (the guideline value) for drinking water quality. In addition, Bretzler et al. [2] reported that 14.6 % of drinking water wells in rural areas of Burkina Faso, West Africa, have arsenic concentrations exceeding the guideline value of 0.01 mg/L. According to this fact, about 560,000 people, one-fifth of 2.8 million people who live in areas with a high risk of arsenic contamination in the rural areas, may be exposed to arsenic-contaminated groundwater. Similarly, arsenic concentrations exceeding the guideline value have been detected in arsenic-contaminated groundwater of other developing countries in Asia and Africa. Additionally, in these countries, there are many patients with chronic arsenic poisoning such as keratosis and skin cancer due to continued intake of arsenic-contaminated groundwater as drinking water as described in [3], [4]. Furthermore, in these countries where the health hazard caused by arsenic contamination is serious, population growth is predicted in the future, so it is essential to secure safe and sufficient drinking water. Therefore, it is urgent to remove arsenic from water sources such as groundwater.

There are mainly two methods in the current arsenic removal technologies, the aggregation method (coprecipitation method) and the adsorption method. According to Tonokai [5], the coprecipitation method has been used since the 1970s and is the arsenic removal technology generally adopted, since some flocculants used in the coprecipitation method are inexpensive and easily available. However, as shown in [6], a large amount of waste such as excess sludge is generated because a large amount of flocculant is required to reduce the arsenic concentration to the standard value depending on the flocculant used. That is why the disposal of the generated waste is costly. In addition, the coprecipitation method has many problems as follows: it is necessary to secure a large installation area to construct treatment facilities and it takes a lot of effort to manage them due to the complexity of the processing equipment, and so on. On the other hand, the adsorption method is a very convenient one compared with other methods for removing arsenic and large-scale treatment facilities are not required. However, depending on the adsorbent used, pretreatment such as pH adjustment may be required according to the past study [7]. Additionally, in the adsorption method, the manufacturing cost of the adsorbent is expensive, and the adsorption performance of the adsorbent is strongly affected by the substance (chemical species) which coexists with arsenic in the solution as an adsorption object. It is desirable to adopt a simple method for removing arsenic in addition to low material costs in developing countries in Asia and Africa where arsenic contamination is serious. When the adsorption method is selected with an emphasis on simplicity, the following three are required for the adsorbent. The first is that the adsorbent is cheap, the second is that the pretreatment is unnecessary in the adsorption treatment, and the third is that it has the adsorption performance which is not affected by other chemical species which coexists with arsenic. According to [1], [2], [8], [9], it is clarified that sodium (Na), magnesium (Mg), potassium (K), calcium (Ca), manganese (Mn), iron (Fe), bicarbonate ion (HCO_3), sulfate ion (SO_4) and nitrate ion (NO_3) are contained in a relatively high concentration as chemical species coexisting with arsenic in the groundwater of developing countries in Asia and Africa where arsenic contamination has been confirmed.

Therefore, in this study, an inexpensive adsorbent for the removal of arsenic is developed by improving low-cost fishbone hydroxyapatite [Patent No. 6351008 given by the Japanese Patent Office]. At the same time, the effect of other chemical species (Na, Mg, K, Ca, Mn, Fe, HCO_3, SO_4, and NO_3) coexisting with arsenic on the adsorption performance for arsenic is investigated.

2. ADSORPTION TEST (SHAKING TEST)

The selective adsorption properties of the developed arsenic adsorbent (Functional Fishbone Powder, FFP) for arsenic in the solution containing not only arsenic but also other chemical species are verified. Therefore, the adsorption test by the shaking test is carried out in the case of no chemical species mixing (arsenic (As) only), the case of mixing one kind of chemical species, and the case of mixing multiple kinds of chemical species assuming the water quality in the actual arsenic contamination site. After that, the adsorption performance of the FFP for arsenic is evaluated based on the adsorption isotherm.

In the test, an arsenic standard solution (As_2O_3 · NaCl (0.05%) · HCl acidic solution) is used. First, the arsenic standard solution is prepared to seven initial concentrations (3 ppm, 4 ppm, 5 ppm, 6 ppm, 7 ppm, 30 ppm, 60 ppm), and the prepared solutions are mixed with a chemical species (one type or multiple types) set to a predetermined concentration. This prepares simulated solutions. Next, 10 mL of the simulated solution is poured into a centrifuge tube to which 20 mg of FFP is added. These are the specimens in the test. Then, these specimens are 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 arsenic in the solutions is analyzed by an ICP-AES.

Here, Table 1 shows the chemical species detected in the arsenic-contaminated areas of developing countries as mentioned above in Asia and Africa and their concentrations. Each concentration shown in Table 1 is the average value of the concentration in each chemical species listed in [1], [2], [8], [9]. In this study, 9 types of chemical species are listed in Table 1 and their corresponding concentrations are adopted as test conditions. Regarding 9 types of chemical species, chloride-based solutions (sodium chloride solution, magnesium chloride solution, potassium chloride solution, calcium chloride solution, manganese chloride solution, and iron chloride solution) are used for cation (Na, Mg, K, Ca, Mn, Fe), and sodium-based solutions (sodium bicarbonate

Table 1 The concentration of each chemical species

Chemical species	Concentration (mg/L)
Na	491.7
Mg	30.9
K	5.5
Ca	56.1
Mn	241.7×10^{-3}
Fe	1.6
HCO_3	267.7
SO_4	1371.3
NO_3	19.3

Table 2 The combination of chemical species

Sample1	Sample2	Sample3
Mn, Fe, HCO_3	Na, Mg, K, Ca, HCO_3, SO_4, NO_3	Na, Mg, K, Ca, Mn, Fe, HCO_3, SO_4, NO_3

solution, sodium sulfate solution and sodium nitrate solution) are used for anion (HCO_3, SO_4, NO_3). In addition, in the test with mixed multiple chemical species, a typical three types of water quality that have been confirmed in arsenic-contaminated areas of the developing countries in Asia and Africa are assumed. Table 2 shows the combinations of chemical species in each water quality.

In the study, the adsorbed amount per unit mass of the FFP is employed as the evaluation of the test results. The adsorbed amount per unit mass of the FFP is defined by the following equation (1).

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

where "V" is the amount of the solution, "C_o" is the initial concentration of the solution, "C_i" is the residual concentration (equilibrium concentration) after the tests and "M_i" is the mass of the FFP. To ensure reproducibility, the mean value of three tests is adopted as a test result. In addition, the test results are applied to the Langmuir model to clarify the adsorption mechanism of the adsorbent for arsenic. The Langmuir model is a typical adsorption equilibrium equation in liquid-phase adsorption. The Langmuir model is defined by the following equation (2).

$$\boldsymbol{\frac{C_i}{W_i} = \frac{1}{aW_s} + \frac{1}{W_s}C_i} \qquad (2)$$

where "a" is the adsorption equilibrium constant and "W_s" is the amount of saturation adsorption.

3. ADSORPTION TEST RESULTS

In the case of mixing one chemical species, the adsorption isotherms plotted the test results obtained from the shaking tests are shown in Fig. 1 (cation, Na and K), Fig. 2 (cation, Mg and Ca), Fig. 3 (cation, Fe and Mn) and Fig. 4 (anion), respectively. In addition, Table 3 shows the coefficient of determination obtained by applying the results of shaking tests with one chemical species to the Langmuir model. The horizontal and vertical axes in Fig. 1 to Fig. 4 are the equilibrium concentration of As, and the equilibrium concentration divided by the adsorbed amount (C/W), respectively. The adsorption isotherm, as described in [10], indicates the relationship between the solute concentration in equilibrium under certain temperature conditions and the adsorbed amount at that time. The adsorption isotherm shows various types of curves depending on the combination of the adsorbent (refers to FFP in this study) and the adsorbate (a substance to be adsorbed, refers to As in this study). Its shape shows how As is adsorbed to FFP, i.e., the physical or chemical interaction between FFP and As. The adsorption isotherms obtained by plotting the residual concentration (equilibrium concentration) of the solute analyzed after the adsorption test on the horizontal axis and the adsorbed amount per unit mass of FFP on the vertical axis is in three patterns. One is that the adsorbed amount increases logarithmically as the equilibrium concentration increases, i.e., an upward convex curve, another is that the adsorbed amount increases exponentially as the equilibrium concentration increases, i.e., a downward convex curve, and the other is that a linear relationship exists between the equilibrium concentration and the adsorbed amount, i.e., a straight line which tends to rise to the right. The upward convex curve indicates that an attractive force acting between the FFP surface and As promotes adsorption of As by FFP, while the downward convex curve indicates that the attractive force which acts between the FFP surface and As is weak. Additionally, when a linear relationship is established between the equilibrium concentration and the adsorbed amount, it means the adsorption of As by FFP from a very dilute solution, which indicates the competitive adsorption of the solvent and As on the FFP surface. On the other hand, the Langmuir model expresses whether the adsorption mode is monolayer adsorption or not. The applicability of the Langmuir model depends on whether there is a linear relationship between the equilibrium concentration of As and the value of equilibrium concentration divided by the adsorbed amount of As.

Fig. 1 to Fig. 4 indicates that the adsorption isotherm shows an upward convex curve in mixing any one kind of chemical species, although the adsorbed amount is inferior to the case without chemical species. From this, it can be said that an attractive force acting between the FFP surface and

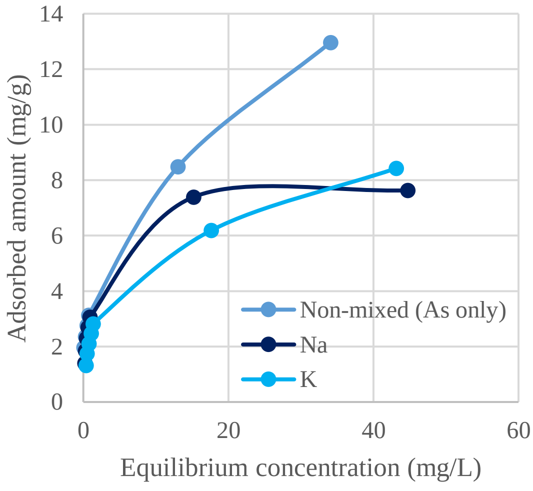

Fig. 1 Adsorption isotherm (Mixing one chemical species (Na, K))

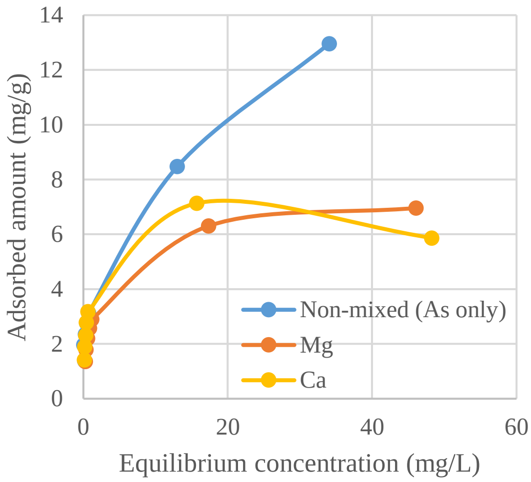

Fig. 2 Adsorption isotherm (Mixing one chemical species (Mg, Ca))

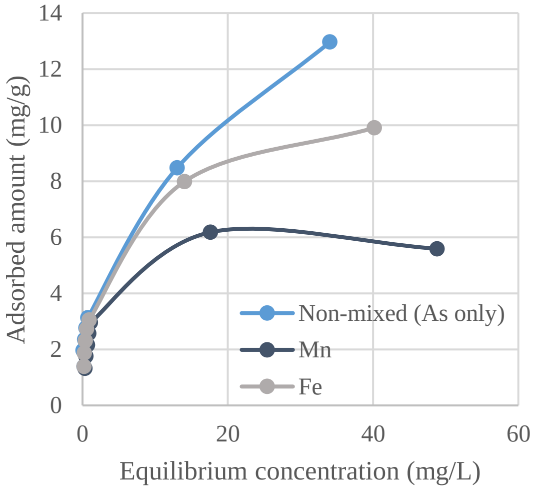

Fig. 3 Adsorption isotherm (Mixing one chemical species (Mn, Fe))

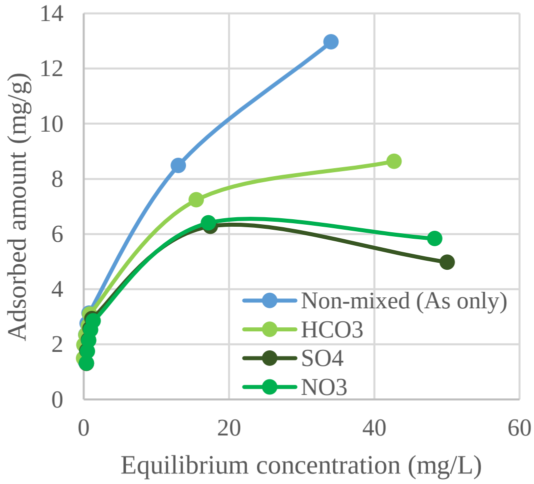

Fig. 4 Adsorption isotherm (Mixing one chemical species (Anion))

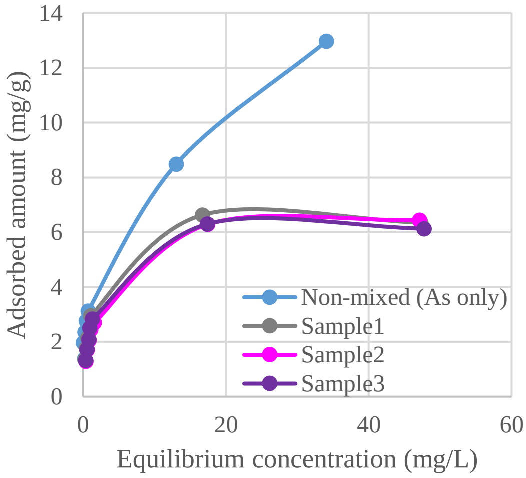

Fig. 5 Adsorption isotherm (Mixing multiple chemical species)

Table 3 Coefficient of determination obtained by applying test results to the Langmuir model (Mixing one chemical species)

Chemical species	R^2
Non-mixed (As only)	0.9977
Na	0.9699
Mg	0.9164
K	0.9176
Ca	0.9534
Mn	0.9019
Fe	0.9892
HCO_3	0.9641
SO_4	0.9064
NO_3	0.9193

Table 4 Coefficient of determination obtained by applying test results to the Langmuir model (Mixing multiple chemical species)

Chemical species	R^2
Non-mixed (As only)	0.9977
Sample1	0.9341
Sample2	0.9154
Sample3	0.9135

As promotes adsorption of As by FFP. In addition, the coefficient of determination R^2 listed in Table 3 shows high values of 0.9 or more in each case. From these results, it is considered that the adsorption mode of FFP for As is monolayer adsorption and that As is chemically adsorbed on the FFP surface (such as chemical bonding), even when no chemical species (As only) or one kind of chemical species is mixed. On the other hand, it can be seen that the coefficient of determination R^2 in the case of mixing K, Mg, Mn, SO_4, or NO_3 respectively is lower than that in the case of no chemical species mixing (As only) (< 0.95). These results suggest that the chemical species of Mg, K, Mn, SO_4, and NO_3 may affect the adsorption performance of FFP for As. Further examinations are needed to gain clearer insights into the effect of these chemical species on the adsorption performance of FFP for As.

In the case of mixing multiple chemical species, the adsorption isotherms plotted the test results obtained from the shaking tests are shown in Fig. 5, and the coefficient of determination obtained by applying the test results to the Langmuir model is shown in Table 4. The horizontal and vertical axes of Fig. 5 are the same as those of Fig. 1 to Fig. 4. Similar to Fig. 1 to Fig. 4, Fig. 5 indicates that the adsorption isotherm shows an upward convex curve in any combination patterns of chemical species, although the adsorbed amount is inferior to the case without chemical species. In addition, the coefficients of determination R^2 listed in Table 4, as well as those listed in Table 3, show high values of 0.9 or more in each case. However, it is found that the coefficient of determination R^2 in the case of mixing multiple chemical species is lower when more than one chemical species is mixed in any combination pattern of chemical species than when no chemical species is mixed (As only). Since the coefficient of determination R^2 decreases as the number of chemical species increases, the adsorption performance of FFP for As may be affected by the number of chemical species.

4. CONCLUSIONS

In this study, the selective adsorption property of FFP for arsenic was verified in the solution containing not only arsenic but also other chemical species (Na, Mg, K, Ca, Mn, Fe, HCO_3, SO_4, and NO_3). Concretely, the adsorption test by the shaking test was carried out in the case in which arsenic alone was mixed, the case in which one kind of chemical species was mixed except for arsenic, and the case in which multiple kinds of chemical species were mixed on the assumption of the water quality in an actual arsenic contamination field. The adsorption performance of FFP for arsenic was evaluated based on the adsorption isotherms obtained from the test results. The results obtained are as follows.

- In the case of mixing one or more kinds of chemical species, the adsorption isotherm showed an upward convex curve in mixing either kind of chemical species, though the adsorbed amount of arsenic was a little inferior to the case in which only arsenic was mixed.
- FFP has an adsorption performance for arsenic even without the addition of acid or alkali. Therefore, it can be an adsorbent which utilizable safely. In addition, it is an environmentally friendly adsorbent because FFP is developed using fishbone, which is food waste.
- From the value of the coefficient of determination R^2 obtained by applying the results of shaking tests to the Langmuir model, it is considered that the chemical species of K, Mg, Mn, SO_4, and NO_3 may affect the adsorption performance of FFP for arsenic. Further examinations are needed to gain clearer insights into the effect of these chemical species on the adsorption performance of FFP for arsenic.

From these results, to clarify the effect of the chemical species of K, Mg, Mn, SO_4, and NO_3 on the adsorption performance of FFP for arsenic, it is necessary to analyze the changes in the concentration of K, Mg, Mn, SO_4 or NO_3 respectively when the arsenic adsorption test is conducted in the case of mixing each chemical species and verify how much chemical species are adsorbed on FFP. Additionally, it is needed to carry out an adsorption test in which the concentration of mixed chemical species (K, Mg, Mn, SO_4, and NO_3) is changed.

5. ACKNOWLEDGMENTS

This work was supported by A General Incorporated Association Shikoku Create and JSPS KAKENHI Grant Number JP20K04684. Also, in carrying out this study, Nihon Kogyo Co., Ltd. provided FbP. We express our gratitude here.

6. REFERENCES

[1] Ohno K., Furukawa A., Hayashi K., Kamei T., and Magara Y., Relation between arsenic and other metals and ions in groundwater in Bangladesh, Environmental Engineering Research, Vol. 41, 2004, pp. 591-600.

[2] Bretzler A., Lalanne F., Nikiema J., Podgorski J., Pfenninger N., Berg M., and Schirmer M., Groundwater arsenic contamination in Burkina Faso, West Africa: Predicting and verifying

regions at risk, Science of the Total Environment, Vol. 584-585, 2017, pp. 958-970.

[3] Ando M., Arsenic contamination of groundwater in India and Bangladesh and its health effect, Journal of the National Institute of Public Hearth, Vol. 49, No. 3, 2000, pp. 266-274.

[4] Mazumder. D. N., Ghosh A., Majumgar K. K., Ghosh N., Saha C., and Mazumder N. R., Arsenic Contamination of Grand Water and its Health Impact on Population of Distinct of Nadia, West Bengal, India, Indian Journal of Community Medicine, Vol. 35, Issue 2, 2010, pp. 331-338.

[5] Tonokai K., Method of purification of arsenic-contaminated groundwater, Global Environment, Vol. 22, No. 1, 2017, pp. 91-98.

[6] Uyama H., Shan J., and Yano T., Development of Secure and Convenient Remediation Technology for Arsenic-contaminated Water, Manufacturing & Technology, Vol. 60, No. 3, 2008, pp. 81-84.

[7] Yanagida T., Jiang Y., and Nakamura M., Arsenic Adsorption Properties of New Iron Hydroxide, Journal of Japan Society on Water Environment, Vol. 36, No. 5, 2013, pp. 149-155.

[8] Berg M., Stengel C., Trang K. T. P., Hung V. P., Sampson L. M., Leng M., Samreth S., and Fredricks D., Magnitude of arsenic pollution in the Mekong and Red River Deltas – Cambodia and Vietnam, Science of the Total Environment, Vol. 372, Issue 2-3, 2007, pp. 413-425.

[9] Malana A. M. and Khosa A. M., Groundwater pollution with special focus on arsenic, Dera Ghazi Khan-Pakistan, Journal of Saudi Chemical Society, Vol. 15, Issue 1, 2011, pp. 39-47.

[10] Abe I., Chemistry of Adsorption, Oreo Science, Vol. 2, No. 5, 2002, pp. 275-281.