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PREPARATION OF FLUORIDE ADSORBENT FROM ZIRCON SAND USING MECHANOCHEMICAL TREATMENT, AND ITS APPLICATION FOR FLUORIDE REMOVAL

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ABSTRACT: Removal of low-concentration fluoride in natural water is an important issue all over the world. Japan is a volcanic country with many hot springs, and the removal of low-concentration fluoride from hot spring drainage is desired. In this study, we attempted to prepare a novel adsorbent with high selective removal ability of fluoride from zircon sand using mechanochemical treatment, and applied it for removing fluoride from hot spring water. Mechanochemical treatment of zircon sand was carried out using a planetary ball mill, and fluoride removal of the product was examined using fluoride aqueous solution and hot spring water. The hot spring water is collected from one of the hot spring in Japan, and a typical sulfuric acid hot spring water pH 2 including high contents of SO_4^{2-}(12000 mg⋅L^{-1}) and Cl^- (5000 mg⋅L^{-1}) with 11 - 15 mg⋅L^{-1} of fluoride ion. Regardless of ball sizes, with increasing the mechanochemical treatment time to 10 min, the removal ability of the product for fluoride increases, and then be almost constant. With decreasing pH of the solution to 2, the adsorption amount increases, and then be almost constant. With increasing the temperature of the solution, the adsorption amount decreases, while the rate of adsorption increases and the amount increases. The adsorption isotherm at pH 2 follows much better Langmuir model than Freundlich model, and the calculated maximum adsorption amount is 0.11 mmol⋅g^{-1}. Fluoride can be adsorbed selectively from hot spring water below Japanese effluent standard for fluoride (8.0 mg⋅L^{-1}).

Keywords: Zircon sand, Fluoride removal, Mechanochemical treatment, Hot spring water

1. INTRODUCTION

Fluorine is a dangerous anionic species, and excessive ingestion of fluorine causes fluorosis and neurological abnormalities in the human body. Therefore, removal of low concentrations of fluoride in natural water is an important issue all over the world. There are coagulation-sedimentation, reverse osmosis membrane, and adsorption as methods of removing fluoride in wastewater. However, coagulation-sedimentation method has a problem of sludge treatment, and reverse osmosis membrane method is a high equipment cost [1].

In Japan, there are many hot spring containing fluoride with some cations and anions. Therefore, selective removal for low concentrations of fluoride in hot spring wastewater is desired, and simple on-site adsorption method for fluoride is focused on.

Zirconia (ZrO_2) have high chemical stability, mechanochemical strongh and stable structure[2], and attracts as an adsorbent having Zr-O-H on its surface, which has a selective adsorption capacity for fluorine by ion exchange between OH^- and F^-[3, 4]. However, the zirconia adsorbents are expensive because its manufacturing requires a multi-steps with a lot of energy [4]. In previous studies, zircon sand can be converted into the adsorbent with Zr-O-H using simple mechanochemical treatment, and phosphorus in seawater can be removed selectively [5, 6].

In this study, we prepare a new adsorbent with high selective fluoride adsorption ability from zircon sand by mechanochemical treatment, and applied it to remove fluoride from hot spring water. Effects of mechanochemical treatment time and ball size on fluoride adsorption of the treated zircon sand product, fluoride adsorption abilities of the product, such as pH dependence, selectivity, adsorption amount and adsorption kinetics, and application of the product to fluoride removal from hot spring water were investigated.

2. EXPERIMENTAL

2.1 Sample

In this study, raw zircon sand ($ZrSiO_4$) (WAKO) was used, and hot spring water used was collected from one of hot spring water in Japan. The chemical composition of hot spring water is shown in Table 1, and the pH of hot spring water is about 2. This hot spring water is sulfuric acid water with 12 mg·L^{-1} of F^-, which is higher than Japanese effluent standard for fluoride (8.0 mg·L^{-1}). It is noted that coexisting anions of Cl^- and SO_4^{2-} are 5101 mg·L^{-1} and 12720 mg·L^{-1}, which are 425 times and 1060 times higher than F^- content.

Table 1 Chemical composition of hot spring water.

Ion	Concentration [mg/L]
F^-	12
Cl^-	5101
SO_4^{2-}	12720
Na^{2+}	210
K^+	140
Mg^{2+}	103
Ca^{2+}	25
Fe^{2+}	149
Al^{3+}	122

2.2 Mechanochemical treatment

A planetary ball mill (P-6, Fritsch) was used for mechanochemical treatment. Pots and balls were made of silicon nitride with high wear resistance. Treatment was carried out at rotation speed of 400 rpm for 1 to 60 min using three different diameter balls (ϕ 5, 10, 15 mm). The volume filling rate of the ball into the pot was about 30 %, and the number of balls with ϕ 5 mm, ϕ 10 mm and ϕ 15 mm were 180, 18 and 7, respectively.

The products obtained under each mechanochemical treatment condition for fluoride adsorption was estimated as follows. 0.1 g of the product after mechanochemical treatment was added into 10 mL of KF aqueous solution with 0.1 mmol·L^{-1} in 50 mL of the tube, and shaken with reciprocal shaker at room temperature for 12 h. After shaking, the tube was centrifuged, and a part of the supernatant was collected. The pH of the collected solution was measured with a pH meter (F-72, HORIBA), and the fluoride concentration in the collected solution was measured with a fluoride ion meter (TiN-5101, TOKO). The adsorption amount (mmol·g^{-1}) and removal percent (%) for fluoride were calculated from the measured fluoride concentration using the following equations:

$$q = (C_0 - C) \cdot L \cdot W^{-1} \quad (1)$$

$$R = \{(C_0 - C) * 100\} \cdot C_0^{-1} \quad (2)$$

where q is adsorption amount [mmol·g^{-1}], C_0 is initial fluoride concentration [mmol·L^{-1}], C is fluoride concentration after shaking [mmol·L^{-1}], W is weight of sample [g] , L is volume of solution [L] and R is the removal percentage of fluoride [%].

2.3 Fluoride Adsorption

The fluoride adsorption ability of the product obtained by mechanochemical treatment for 10 min using ϕ 5 mm balls was investigated.

The pH dependence of the fluoride adsorption for the product was investigated, in comparison with that of raw zircon sand. 0.1 mmol·L^{-1} KF solution with pH 1 - 7 was adjusted using HCl. 0.1 g of the raw sand or the product was added into the KF solution with different pHs, and shaken for 12 h at room temperature. After shaking, the mixture was centrifuged, the pH of the supernatant was measured with a pH meter, and the fluoride concentration in the supernatant was measured by a fluoride ion meter to calculate the fluoride adsorption amount using the equations (1).

The amount of fluoride adsorption in diluted seawater was examined for fluoride selective adsorption of the product and raw sand. 0.1 g of the product or raw sand was added into 10 mL of diluted seawater, which diluted 10 – 1000 times, with 0.1 mmol·L^{-1} F^-, and shaken for 12 h. After shaking, the mixture was centrifuged, the pH (equilibrium pH) of the supernatant was measured with a pH meter, and the fluoride concentration in the supernatant was measured by a fluoride ion meter to calculate the fluoride adsorption amount using equations (1).

Fluoride adsorption isotherm was examined using KF solution with pH 2, adjusted by HCl solution. 0.1 g of the product or raw zircon sand was added into 0.05 – 4.0 mmol·L^{-1} KF solution, and shaken for 12 h. After shaking, the mixture was centrifuged, the pH (equilibrium pH) of the supernatant was measured with a pH meter, and the fluoride concentration in the supernatant was measured by a fluoride ion meter to calculate the fluoride adsorption amount using equations (1).

Fluoride adsorption kinetics of the product in KF solution was examined. 1.0 g of the product was added into 200 mL of 0.1 mmol·L^{-1} KF solution, and was stirred for 1.5 h at 20, 30 and 40 °C. During stirring, a part of the solution (2 mL) was collected at each time, and was filtered using a membrane filter. The fluoride concentration in the filtrate was determined by a fluoride ion meter to calculate the fluoride adsorption amount using (1).

3. RESULTS AND DISCUSSION

3.1 Fluoride Adsorption Ability

The amount of fluoride adsorption of the product obtained by mechanochemical treatment is shown in Fig. 1. With increasing the mechanochemical treatment time to 10 minutes, the fluoride adsorption of the product increased, and then became almost constant, regardless of the ball diameter. It would be considered that effect of mechanochemical treatment on adsorption ability depends on volume of filling ratio.

The fluoride adsorption amount of the product after 10 minutes mechanochemical treatment is 0.004 mmol · g^{-1}, which is almost 2 times as that of raw zircon sand (0.002 mmol · g^{-1}). The removal of fluoride was about 50%. It is noted that the amount of fluoride adsorption of the product was about 1/29 of the amount of fluoride adsorption of magnesia (0.114 mmol · g^{-1}) [7], and 1/250 of the amount of fluoride adsorption of zirconia (1.0 mmol · g^{-1}) [8].

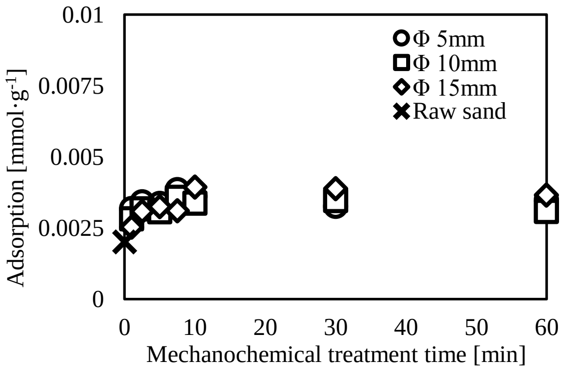

Fig. 1 Fluoride adsorption amount of the product after mechanochemical treatment using the ball with various diameter.

The pH dependence of the fluoride adsorption of the product and raw sand is shown in Fig. 2. The fluoride adsorption of the product increased with decreasing pH, and the adsorption amount at pH 3.5 was 0.008 mmol · g^{-1}, which was about 2 times higher than that at pH 7, while adsorption of raw zircon sand at pH 3.2 was 0.007 mmol · g^{-1}. The product and zircon sand indicate the highest adsorption capacity at pH 2 – 3. It is reported that the fluoride adsorption amount of Zr adsorbent with Zr-OH on the surface increases as the pH decreases [9]. It is considered that Zr-O-H is increased on the surface of the product by mechanochemical treatment.

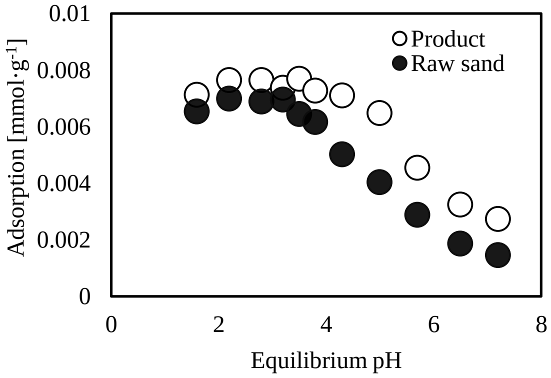

Fig. 2 Effect of pH on fluoride adsorption amount of the product.

The fluoride adsorption amounts of the product and zircon sand in diluted seawater were shown in Fig. 3. The product indicates higher fluoride adsorption than raw sand and almost same adsorption amount in 1/10 – 1/1000 diluted seawater as in distilled water. This result shows that product can selectively adsorb fluoride in high saline water.

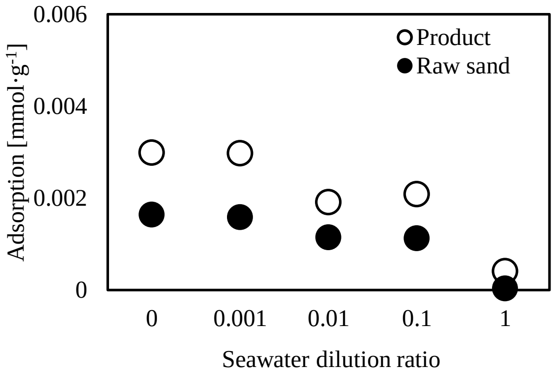

Fig. 3 Fluoride adsorption amount of the product and raw sand in seawater.

Fig. 4 shows the adsorption isotherms of the product and raw sand in fluoride solution at pH 2. As the equilibrium concentration increased, the fluoride adsorption increased sharply up to the equilibrium concentration of 0.11 mmol · L^{-1} and 0.12 mmol · L^{-1} for the product and raw sand, respectively, and then gradually increased. The product has higher adsorption amount at low fluoride concentration than that of raw zircon sand, because the fluoride adsorption amount of Zr adsorbent with Zr-OH on the surface is more effective at low fluoride concentration [8]. Therefore, mechanochemical treatment promotes the fluoride adsorption of low fluoride adsorption, indicating the different behavior at low fluoride concentration in Fig. 4.

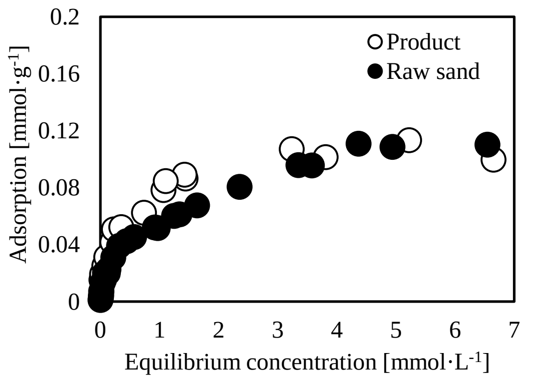

Fig. 4 Fluoride adsorption isotherm of the product at pH 2.

The experimental results obtained in Fig. 4 for the product and raw sand are analyzed using the Langmuir adsorption model and the Freundlich adsorption model to estimate the fluoride adsorption behavior of the product. The liner equations of Langmuir adsorption model and Freundlich adsorption model are as follow:

$$C \cdot q^{-1} = (q_{max} \cdot K_L)^{-1} + C \cdot (q_{max})^{-1} \qquad (3)$$

$$\ln q = \ln K_F + n^{-1} \cdot \ln C \qquad (4)$$

where q is adsorption amount [mmol · g^{-1}], C is fluoride concentration [mmol · L^{-1}], $q_{\max}$ is the maximum adsorption amount [mmol · g^{-1}], K_L is adsorption equilibrium constant of Langmuir, K_F and n are constant of Freundlich.

The results are shown in Table 2. According to the correlation coefficient, Langmuir equation (correlation coefficient: R^2 = 0.99) could be more realistic than that Freundlich's equation (R^2 = 0.30). The calculated maximum adsorption capacity of the product using Langmuir equation is 0.11 mmol · g^{-1} which is almost same as that of raw sand.

Table 2 The results of parameter from adsorption isotherm of the product and raw sand.

	Langmuir			Freundlich		
	q_{max}	K_L	R^2	n	K_F	R^2
Product	0.11	3.28	0.99	1.92	0.33	0.30
Raw sand	0.12	1.30	0.97	1.41	0.34	0.54

The important feature of the Langmuir isotherm can be written in form of a dimensionless quantity known as separator factor (R_L) which is given by (5).

$$R_L = \left(1 + K_L \cdot C_{0,max}\right)^{-1} \qquad (5)$$

where K_L and $C_{0,\max}$ are the adsorption equilibrium constant of Langmuir model and maximum initial concentration, respectively.

The value of R_L determines nature of the isotherm shape. It can either be favorable ($0 < R_L < 1$), unfavorable adsorption ($R_L > 1$), liner ($R_L = 1$) or irreversible adsorption ($R_L = 0$). The obtained values of R_L to be 0.038 for fluoride adsorption by the product suggest that the process is favorable.

The value of the Freundlich constant (n) indicates the affinity between the adsorbent and the adsorbate. The adsorbate is easily adsorbed ($0.1 < n^{-1} < 0.5$), or difficulty adsorbed ($n^{-1} > 2$) [10]. The value of n^{-1} obtained to be 0.52 for fluoride adsorption by the product suggest that the process has not affinity.

Figure 5 shows the fluoride adsorption of product after mechanochemical treatment in fluoride solution at various temperatures. As the stirring time increased, the fluoride adsorption increased, and then be almost constant. As the temperature decreased, the fluoride adsorption amount increased.

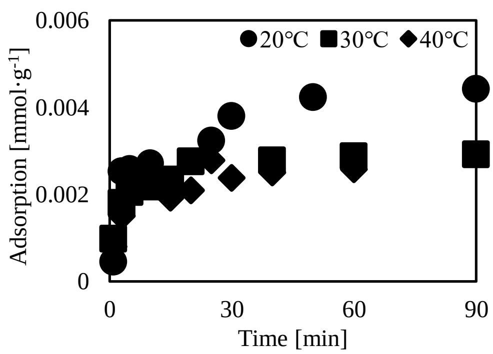

Fig. 5 Fluoride adsorption of the product at various temperatures.

The experimental results obtained in Fig. 5 were analyzed by pseudo-first-order and pseudo-second-order kinetics models to estimate the fluoride adsorption behavior of the product in fluoride solution. The linearized equations of pseudo-first-order and pseudo-second-order kinetics models are as follows;

$$ln(q_e - q_t) = ln\, q_e - k_1 \cdot t \quad (6)$$

$$t \cdot {q_t}^{-1} = (k_2 \cdot q_e^2)^{-1} + t \cdot {q_e}^{-1} \quad (7)$$

where q_e, q_t, k_1, k_2 and t are the maximum adsorption amount (mmol · g^{-1}), the adsorption amount at time (mmol · g^{-1}), the pseudo-first-order adsorption kinetics constant (min^{-1}), the pseudo-second-order adsorption kinetics constant (g · mmol^{-1} · g^{-1}), and time (min), respectively.

The results analyzed are shown in Table 3. According to the correlation coefficient (R^2), the data fit much better to pseudo-second-order model than to pseudo-first-order model. It was found that the product has higher adsorption amount at lower temperature, while reaction rates decrease.

Table 3. The results of parameters from adsorption kinetics.

	Pseudo-first-order			Pseudo-second-order		
Temp.	q_e	k_1	R^2	q_e	k_2	R^2
20 ℃	0.003	0.034	0.92	0.005	41	0.99
30 ℃	0.002	0.025	0.83	0.004	72	0.98
40 ℃	0.002	0.023	0.82	0.003	91	0.98

The activation energy for fluoride adsorption was calculated by the Arrhenius equation as follows;

$$k_2 = A \cdot exp(-\Delta E \cdot (R \cdot T)^{-1}) \quad (8)$$

where ΔE is the activation energy [kJ · mol^{-1}], A is the frequency factor, T is the absolute temperature [K], and R is the gas constant. From the plot of ln(k_2) vs. 1/T (Fig. 6), the activation energy for fluoride adsorption was found to be 7.53 kJ · mol^{-1}.

The magnitude of ΔE indicates the type of adsorption, which can be physical or chemical. The physical adsorption process has lower ΔE values (5 - 40 kJ · mol^{-1}) [11], while the chemical adsorption has higher ΔE values (40 - 800 kJ · mol^{-1}) [12]. The activation energy of ordinary physical adsorption supports the high F$^-$ affinity of the product and the feasibility of the reaction.

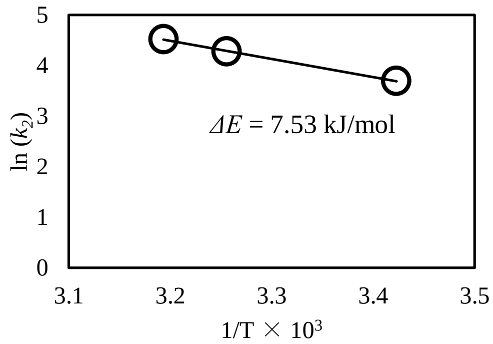

Fig. 6 Arrhenius plot for fluoride adsorption on the adsorbent.

3.2 Fluoride Adsorption From Hot Spring Water

Figure 7 shows the fluoride ion concentration and the fluoride removal from the hot spring water after treatment for 3 h by adding various amounts of the product. It is noted that the Japanese fluoride effluent standard value is 8.0 mg L^{-1}. With increasing the addition of the product, fluoride concentration decreases, and be lower than effluent standard. The removal was 34 % with more than 100 g L^{-1} addition.

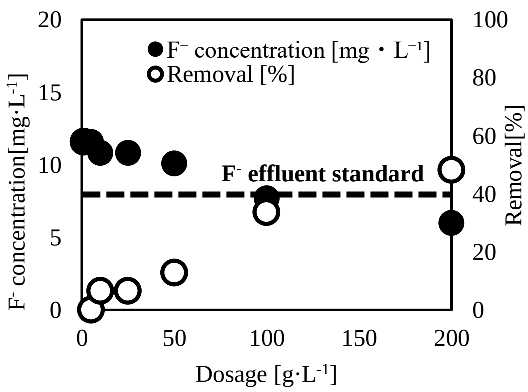

Fig. 7 Concentration and removal of fluoride from hot spring water.

Figure 8 shows the fluoride concentration and the fluoride removal at each shaking time when the product was added at 100 g L^{-1}. With increasing the reaction time, the fluoride concentration gradually decreased to Japanese effluent standard, and the removal reached to 49%, which indicates that fluoride in the hot spring water can be removed to below the effluent standard value by treating at 100 g L^{-1} for 180 min.

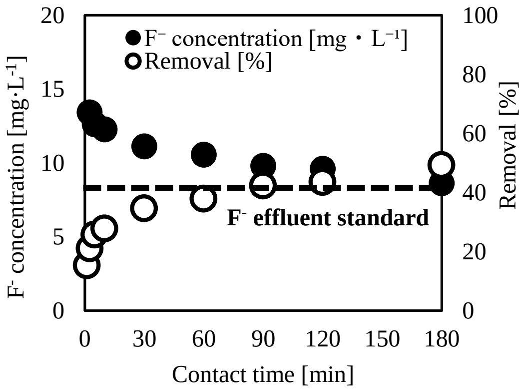

Fig. 8 Concentration and removal of fluoride during the treatment.

The chemical composition of hot spring water and treated water with 100 g·L^{-1} addition for 3 h is shown in Table 4. While 35 % of F^- was removed in the hot spring water after the treatment, other elements were removed less than 16 %. It suggests that fluoride in hot spring water can be selectively removed using mechanochemically treated zircon sand.

Table 4 pHs and chemical compositions of hot spring water and treated water (mg·L^{-1}).

	Hot spring water	Treated water
pH	1.6	1.7
F^-	11.6	7.6
Cl^-	5101	5167
SO_4^{2-}	12720	10739
Na^+	210	221
K^+	140	117
Mg^{2+}	103	105
Ca^{2+}	24.7	27.8
Fe^{2+}	149	151
Al^{3+}	122	125

4. CONCLUSION

Highly selective fluoride adsorbent was attempted to be prepared from zircon sand by mechanochemical treatment using a planetary ball mill, and the fluoride adsorption ability of the product, such as fluoride adsorption amount, pH dependence, fluoride adsorption isotherms and kinetics, was investigated. The results are as follows;

1. The amount of fluoride adsorption of zircon sand can be increased rapidly within 10 min of mechanochemical treatment.
2. The amount of fluoride adsorption of the product increased with decreasing pH.
3. The fluoride adsorption of the product in high saline water was higher than raw sand.
4. The adsorption isotherm at pH 2 was fitted to Langmuir model better than Freundlich model, and the calculated maximum adsorption amount is 0.09 mmol·g^{-1}.
5. The adsorption kinetics of the fluoride in the fluoride solution fit to pseudo-second-order model better than pseudo-first-order model. The product indicates higher adsorption amount at lower temperature, while the reaction kinetics decrease.
6. Fluoride can be adsorbed selectively from hot spring water below Japanese effluent standard for fluoride (8.0 mg·L^{-1}).

These results indicate that a novel product with high selective fluoride adsorption ability can be prepared by simple mechanochemical treatment, and can be applied to remove fluoride from hot spring water.

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