1. Introduction

Management of ions hazardous to health, such as fluoride, is of interest for public health. Excess intake of fluoride is responsible for dental caries, bone fluorosis, and lesions of the thyroid, endocrine glands, and brain. Fluoride is a naturally occurring element in minerals, geochemical deposits, and natural water systems and enters food chains through either drinking water or eating plants and cereals [1]. According to the World Health Organization (WHO), the tolerance limit of fluoride content of drinking water is 1.5 mg/L [2]. High fluoride levels in groundwater are a worldwide problem, including various regions in Africa and Asia, as well as China [3]. Many provinces in China, including Shanxi, Inner Mongolia, Shandong, Henan, and Xinjiang, reported fluoride concentrations in water above the permissible limits. The available statistics indicate that more than 30 million people are seriously affected by fluorosis and another 100 million are exposed to it in China [4].

Treatment of wastewater containing fluoride ions requires a suitable and effective method. Membrane filtration [5], precipitation [6], nanofiltration [7], ion-exchange [8], electrocoagulation flotation [9], and adsorption [10] have been used for fluoride removal. Among these methods, adsorption is the most effective and widely used method because it is universal, has a low maintenance cost, and is applicable for the removal of fluoride even at low concentrations. In recent years, considerable attention has been focused on the study of fluoride removal using natural, synthetic, and biomass materials such as activated alumina [11], fly ash [12], alum sludge [13], chitosan beads [14,15], red mud [16], zeolite [17], calcite [18], hydrated cement [19], attapulgite [20], and acid-treated spent bleaching earth [21]. These adsorbents have shown a certain degree of fluoride adsorption capacity but some of them can only be used in a narrow pH range (5–6) and some of them are too expensive to be considered for full-scale water treatment. Furthermore, most of them are fine particles or powders which would be suspended in water, making separation difficult and blocking flumes. Therefore, an effective and low-cost adsorbent with coarse particles is desired as an efficient treatment technology for fluoride in large-scale water samples.

The present study focused on the development of ceramic materials which are robust, porous, and able to effectively remove fluoride in subsequent operations and also avoid clogging during field applications. We successfully combined Kanuma mud, which is widespread in Japan, with starch, zeolite, and FeSO₄·7H₂O to calcine ceramic materials and investigated the fluoride adsorption capability of this adsorbent. Hence, a batch study was conducted into using this novel adsorbent with optimization of various experimental conditions, including pH, different initial fluoride concentrations, influence of competitor anions, and the effect of temperature on fluoride sorption. The mechanism of fluoride removal by ceramic materials is reasonably explained by adsorption isotherms. The nature and morphology of the adsorbents are therefore discussed on the basis of BET, SEM, and EDS studies. Various kinetic models were also used to describe the adsorption process. A new type of granular adsorbent was prepared, with high stability and adsorption capacity, suitable for use in practice.

A new medium, granular ceramic, has been developed for fluoride removal from water. Granular ceramic is a solid-phase medium that produces a stable Al–Fe surface complex for fluoride adsorption. BET, SEM, and EDS were used to characterize the physical attributes (particle size, pore size and distribution, surface roughness) of the granular ceramic. Fluoride adsorption characteristics were studied in a batch system with respect to changes in initial concentration of fluoride, pH of solution, and coexisting ions. Fluoride adsorption was found to be pH dependent and the maximum removal of fluoride was obtained at pH 5.0–8.0. Equilibrium adsorption data were obtained at 293, 303, and 323 K, and interpreted in terms of the Langmuir and Freundlich isotherm equations. The experimental data revealed that the Freundlich isotherm equation gives a more satisfactory fit for fluoride removal. The adsorption process was observed to follow a pseudo-second-order kinetic model and intraparticle diffusion was indicated to play a major role in fluoride uptake. Fluoride adsorption was reduced in the presence of phosphate and sulfate ions and increased slightly in the presence of chloroide and nitrate ions.

Keywords:
Granular ceramic
Fluoride removal
Adsorption isotherms
Adsorption kinetics


Fluoride removal from water by granular ceramic adsorption
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ABSTRACT

A new medium, granular ceramic, has been developed for fluoride removal from water. Granular ceramic is a solid-phase medium that produces a stable Al–Fe surface complex for fluoride adsorption. BET, SEM, and EDS were used to characterize the physical attributes (particle size, pore size and distribution, surface roughness) of the granular ceramic. Fluoride adsorption characteristics were studied in a batch system with respect to changes in initial concentration of fluoride, pH of solution, and coexisting ions. Fluoride adsorption was found to be pH dependent and the maximum removal of fluoride was obtained at pH 5.0–8.0. Equilibrium adsorption data were obtained at 293, 303, and 323 K, and interpreted in terms of the Langmuir and Freundlich isotherm equations. The experimental data revealed that the Freundlich isotherm equation gives a more satisfactory fit for fluoride removal. The adsorption process was observed to follow a pseudo-second-order kinetic model and intraparticle diffusion was indicated to play a major role in fluoride uptake. Fluoride adsorption was reduced in the presence of phosphate and sulfate ions and increased slightly in the presence of chloroide and nitrate ions.

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2. Experimental

2.1. Synthesis of the granular ceramic

Kanuma mud was supplied by the Makino Store (Japan) (the grain size of the Kanuma mud was mainly 99% less than 100 μm), zeolite (particle size was less than 150 μm) was supplied by the Azuwan Cement Factory (Japan), starch and FeSO₄·7H₂O were supplied by the Wako Pure Chemical Industries, Ltd. (Japan). The amounts of 4 g of Kanuma mud, 4 g of zeolite, 1.5 g of starch, and 0.5 g of FeSO₄·7H₂O were mixed to homogeneity. Deionized water was then added into the mixture to make a paste and the granulation procedure was carried out manually. The obtained granules were then dried at 105 °C for 24 h and calcined at 600 °C for 1 h. Finally, the granular ceramic product was cooled to room temperature and sieved to 2–3 mm for further studies. The specific surface areas of adsorbents were determined by the BET method with N₂ gas (Coulter SA3100, Japan). The morphology of the adsorbents was determined by scanning electron microscopy (SEM) using an ESEM-6700F (JEOL, Japan). Spot elemental analysis of the ceramic adsorbents was carried out using the energy dispersive X-ray spectroscopy (EDS) technique with JSM-6700F (JEOL, Japan).

2.2. Fluoride adsorption experiments

A stock solution (100 mg/L) was prepared by dissolving 0.221 g NaF (analytical grade) in 1 L of deionized water. All the solutions for fluoride removal experiments and analysis were prepared by an appropriate dilution from the stock solution. Adsorption studies were carried out for each desired initial fluoride concentration solution in a polypropylene conical flask immersed in a temperature-controlled water bath and shaken with a mechanical shaker (Tai Tec, Thermo Minder Mini-80, Japan) for the required time at a rate of 120 cycles/min. Fluoride analysis was carried out with a Hitachi-DR/4000U (Japan) UV–visible spectrophotometer using the SPADNS indicator at 620 nm [22]. The adsorption isotherm at pH 6.90 ± 0.10 was studied by varying the initial fluoride concentration from 5 to 50 mg/L. The effect of pH was investigated by adjusting the pH from 2 to 12 using 0.1 M NaOH and HCl solutions under an initial fluoride concentration of 10 mg/L. A kinetic study at pH 6.90 ± 0.10 was carried out at different time intervals with an initial fluoride concentration of 10 mg/L. Finally, the effects of a number of competing ions (Cl⁻, NO₃⁻, SO₄²⁻, PO₄³⁻, Ca²⁺, and Mg²⁺) were observed using 20–200 mg/L solutions at pH 6.90 ± 0.10 over 72 h.

3. Results and discussion

3.1. Characterization of granular ceramic

The samples of granular ceramic were brown-colored particles, indicating the presence of iron in the form of insoluble oxides. The
EDS results (Table 1) show that the atomic proportion of Al to Fe at the surface was about 3.8:1. The surface morphology of the granular ceramic was examined by SEM (Fig. 1a), clearly revealing a flocced and porous surface texture, which indicates that the adsorbents were highly porous, with a high adsorption capacity. Fig. 1a and b compare the surface features of adsorbents before and after fluoride adsorption at a magnification of 3000×. The aluminum and iron oxides on the granular ceramic surfaces initially formed a rough surface structure (Fig. 1a) but with extensive flowthrough exposure (for 72 h) during fluoride adsorption changed to smooth, polyhedron, and stretched cubic structures (Fig. 1b). Fluoride adsorption occurred at the surface of the media, presumably including the inside surface area of the pores in the adsorbent granules. EDS (Fig. 1c) detection indicated that the adsorbent consisted mainly of Fe, O, and F, implying that the F was bound with iron oxide. The granular ceramic size was between 2 and 3 mm. The typical surface of the granular ceramic particle was highly porous, with pore diameters ranging from 20 to 80 nm (Fig. 2). As the radius of fluorine is nano-scale and much smaller than this value, this pore size range is conducive to the penetration of fluorine into the inner layer of the adsorbents. The BET specific surface area of the granular ceramic was 73.67 m²/g and the total pore volume was 0.14 cm³/g. These properties impart the granular ceramic media with high permeability and adsorptive potential.

3.2. Effect of solution pH

The effect of pH on fluoride removal from aqueous solution by the granular ceramic was studied at various pH values (ranging from 1 to 12). Fig. 3 shows the effect of pH on fluoride adsorption onto the granular ceramic and the shifts in pH after adsorption. The granular ceramic exhibited strong adsorption of fluoride when the pH was between 5.0 and 8.0, which is more suitable for practical applications in household systems compared with red mud, which can only be used at pH 4.7 [16]. This may be due to the electrostatic attraction between the positively charged aluminum and iron oxide surface and the fluoride anions. Removal efficiency fell sharply as pH decreased below 5.0 or increased above 8.0. The sharp decrease in the amount of fluoride adsorbed under alkaline pH conditions is probably due to competition for adsorption sites between fluoride and hydroxyl ions even though the oxide surface is positively charge [23]. On the other hand, under acidic conditions, the decrease may be attributed to the formation of weakly ionized hydrofluoric acid [13] or the combined effects of chemical and electrostatic interactions between the oxide surface and the fluoride ions. The equilibrium pH (pHf) increased at the initial acid pH range, while it decreased when the initial solution was alkaline. However, it was observed that granular ceramic had a significant capacity to buffer highly acidic and alkaline solutions. No Al³⁺, Fe²⁺, or Fe³⁺ were released into the final solutions when the pH of initial solutions was ranked from 5.0 to 10.0, indicating that no harmful metal ions were leached into the treated water.

3.3. Adsorption isotherm analysis

The experimental data for the equilibrium isotherm of fluoride adsorption on granular ceramic were fitted to the Langmuir and Freundlich isotherm models that are frequently used to describe equilibrium adsorption data [24,25].

\[
\frac{1}{q_e} = \left( \frac{1}{q_0 B C_e} \right) + \frac{1}{q_0}
\]

(1)

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

(2)

where \( q_e \) is the amount of solute adsorbed per unit weight of material (mg/g), \( q_0 \) is the maximum adsorption capacity (mg/g), \( B \) is the Langmuir constant, \( K_f \) is the minimum sorption capacity (mg/g), \( n \) is the adsorption intensity of the Freundlich isotherm, and \( C_e \) is the equilibrium concentration of fluoride (mg/L). The isotherm parameters are shown in Table 2. The applicability of the isotherm equation was compared by evaluating the correlation coefficients \( R^2 \). From this, both the Langmuir and the Freundlich isotherm models could fit the fluoride adsorption process on granular ceramic, but the Freundlich isotherm equation gave a more satisfactory fit. The Freundlich isotherm gives a minimum adsorption capacity of 12.12 mg/g (20 °C) for granular ceramic, which is much higher than for granular red mud, at 0.85 mg/g [16]. The estimated value of \( K_f \) for fluoride adsorption decreased with a rise in temperature. This could be interpreted that fluoride adsorption is exothermic.
3.4. Adsorption kinetic studies

3.4.1. Kinetic rate parameters
According to the kinetic data obtained from the experiment, pseudo-first-order and pseudo-second-order mechanisms have been used to elucidate the mechanisms of adsorption and potential rate-controlling steps [26,27].

\[ \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3) \]

\[ \frac{t}{q_t} = \frac{1}{(k_{f2} q_e^2)} + \frac{1}{q_e} \quad (4) \]

where \( q_t \) and \( q_e \) are the amount of adsorbed fluoride (mg/g) at time \( t \) and at equilibrium time, respectively. \( k_1 \) and \( k_f \) are first-order and second-order rate constants for adsorption.

The results are shown in Table 3. The correlation coefficient value for the pseudo-second-order adsorption model \( (R^2 = 0.9989) \) is higher than that obtained from the first-order kinetics \( (R^2 = 0.9463) \). The calculated equilibrium adsorption capacity \( q_e (0.4915 \text{ mg/g}) \) is consistent with the experimental value \( (0.4432 \text{ mg/g}) \). Therefore, it is possible to conclude that the granular ceramic adsorption process followed a second-order kinetic model.

3.4.2. Surface mass transfer coefficient
Mass transfer analysis for the removal of fluoride was carried out using the kinetic model proposed by McKay et al. [28], which describes the transfer of adsorbate in solution. The model is expressed as

\[ \ln\left( \frac{C_t}{C_0} \right) = \ln\left( \frac{1}{1 + mk_L} \right) - \frac{1 + mk_L}{mk_L} \beta_S t \quad (5) \]

where \( C_t \) is the concentration after time \( t \) (mg/L), \( C_0 \) is the initial concentration (mg/L), \( m \) is the mass of adsorbent per unit volume of particle-free adsorbate solution (g/L), \( \beta_S \) is the mass transfer coefficient (cm/s), \( k_L \) is the constant obtained from the Langmuir isotherm equation (L/mg), and \( S_L \) is the outer surface of adsorbent per unit volume of particle-free solution (cm\(^{-1}\)), given as

\[ S_L = \frac{6m}{D_0 d (1 - e)} \quad (6) \]

where \( D_0 \) is the particle mean diameter (cm), \( d \) is the density of the adsorbent (g/cm\(^3\)), and \( e \) is the porosity of the adsorbent.

The results are shown in Fig. 4. The plot of \( \ln(C_t - C_0) - (1/1 + mk_L) \) versus \( t \) for fluoride gives a straight line and thus confirms the validity of the diffusion model for the F\(^-\) granular ceramic system. The value of the mass transfer coefficient \( \beta_S \) was calculated from the slope of the straight line plot and was found to be \( 1.32 \times 10^{-5} \text{ cm/min for fluoride. This value indicates that} \)

\[ q_t = k_0 t^{0.5} \quad (7) \]

where \( q_t \) is the amount adsorbed (mg/g) at a given time \( t \) (h) and \( k_0 \) (mg/g h\(^{0.5}\)) is the intraparticle diffusion rate constant.

A plot of the quantity of the fluoride adsorbed against the square root of time is shown in Fig. 5. If intraparticle diffusion is a rate-controlling step, then the plot should be linear and pass through the origin. However, the plot is not linear over the whole time range and the graphs of this figure reflect a three-stage nature, with an initial linear portion followed by an intermediate linear portion and a plateau. This implies that the external surface adsorption (stage 1) was fast during the first 12 h and a stage of intraparticle diffusion (stage 2) was attained and continued up to 36 h. Finally, an equilibrium adsorption (stage 3) began after

### Table 2
Characteristic parameters of Langmuir and Freundlich models for the adsorption of fluoride onto granular ceramic.

<table>
<thead>
<tr>
<th>Temperature (^{\circ}\text{C})</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_e^* ) (mg/g)</td>
<td>( B ) (L/mg)</td>
</tr>
<tr>
<td>20</td>
<td>0.929</td>
<td>1.133</td>
</tr>
<tr>
<td>30</td>
<td>0.989</td>
<td>1.344</td>
</tr>
<tr>
<td>50</td>
<td>0.941</td>
<td>3.240</td>
</tr>
</tbody>
</table>

### Table 3
Kinetics constant for adsorption of fluoride onto granular ceramic.

<table>
<thead>
<tr>
<th>( C ) (mg/L)</th>
<th>Measured ( q_{exp} ) (mg/g)</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_e ) (mg/g)</td>
<td>( k_1 ) (1/min)</td>
<td>( q_e ) (mg/g)</td>
</tr>
<tr>
<td>10.00</td>
<td>0.4432</td>
<td>0.0615</td>
<td>0.6464</td>
</tr>
</tbody>
</table>

Fig. 4. Mass transfer plot for the adsorption of fluoride on granular ceramic (adsorbent 20 g/L, initial fluoride concentration 10 mg/L, equilibrium contact time 72 h, initial pH 6.90 ± 0.10, and temperature 20 °C).

Fig. 5. Intraparticle diffusion modeling of fluoride adsorption on granular ceramic (adsorbent 20 g/L, initial fluoride concentration 10 mg/L, equilibrium contact time 72 h, initial pH 6.90 ± 0.10, and temperature 20 °C).
36 h. The fluoride ions were therefore slowly transported via intraparticle diffusion into the particles and finally retained in the internal pores. A similar behavior of the intraparticle diffusion curve with an initial linear portion was found for adsorption of fluoride by mechanochemically activated kaolinites [31]. Moreover, the rate constant of intraparticle diffusion was calculated to be 0.0374 mg/g h$^{0.5}$ for fluoride.

3.5. Possible mechanism of fluoride adsorption

Several researchers have reported that the possible adsorption mechanism of fluoride on metal oxides was either by surface complexation [32] or electrostatic adsorption [33] or a combination of both. In the present study, the possible reaction mechanism for adsorption of fluoride onto granular ceramic can be hypothesized as below. In aqueous solution, the coated FeSO$_4$·7H$_2$O would hydrate to Fe(OH)$_3$ according to the reaction:

$$2\text{FeSO}_4\cdot7\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_4^{2-} + \text{SO}_3^{2-} + 14\text{H}_2\text{O}$$  

(8)

$$\text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + \text{Fe(OH)}_3$$  

(9)

$$\text{Fe(OH)}_3 + \text{F}^{-} \rightarrow \text{Fe(OH)}_3\cdot\text{F}_x$$  

(10)

During the formation of iron hydroxide, the fluoride ions present in the aqueous solution would replace the hydroxyl ions in the iron crystal lattice without disturbing the crystal structure of the compound. A similar process would occur in the presence of iron crystal lattice without disturbing the crystal structure of the compound.

3.6. Effect of co-ions on fluoride adsorption

Actually, fluoride contaminated water contains several other ions that may influence the adsorption process. This study assessed fluoride adsorption behavior in the presence of 200 mg/L salt solutions of chloride, sulfate, nitrate, and phosphate, independently, at an initial fluoride concentration of 10 mg/L. The effect of these coexisting ions on F$^{-}$ removal is shown in Fig. 6. It was observed that fluoride removal decreased from 88.6% to 77.1% in the presence of sulfate and to 52.7% in the presence of phosphate but slightly increased in the presence of chloride and nitrate ions. It is expected that some anions would enhance coulombic repulsion forces and some would compete with fluoride for the active sites [17]. Generally, multivalent anions are adsorbed more readily than monovalent anions [35]. Fluoride removal in the presence of anions increased in the order PO$_4^{3-}$ < SO$_4^{2-}$ < Cl$^{-}$ < NO$_3^{-}$. This correlates with the $Z/r$ (charge/radius) values of the anions, which varies in the order PO$_4^{3-}$ (3/3.40) > SO$_4^{2-}$ (2/2.40) > Cl$^{-}$ (1/1.81) > NO$_3^{-}$ (1/2.81). The effects of calcium and magnesium ions on fluoride removal were also studied by varying their concentrations from 20 to 200 mg/L. It was observed the fluoride removal increased with increasing Ca$^{2+}$ and Mg$^{2+}$ and this may due to the formation of insoluble CaF$_2$ and MgF$_2$.

4. Conclusions

A new medium, granular ceramic, has been developed for fluoride removal from aqueous solution. Several advantages of the granular ceramic make the adsorbent a highly effective medium for removing fluoride at normal pH, including (a) its granular structure, (b) its high surface area, and (c) the low cost of the granular ceramic preparation process from clay materials. The efficiency of adsorption increased with increased pH up to 5.0–8.0 but further increases in pH showed a negative trend. The adsorption process followed both the Langmuir and the Freundlich isotherm equations but the latter was more suitable, as assessed by the correlation coefficient values. The adsorption process was observed to follow a pseudo-second-order kinetic model and intraparticle diffusion was indicated to play a major role in fluoride uptake. The fluoride adsorption was reduced in the presence of phosphate and sulfate ions and increased slightly in the presence of chloride and nitrate ions. It was shown that the granular ceramic used as a media in fluoride removal procedures maintained the water quality and no aluminum or ferric ions were leached out from the adsorbents. Therefore, the new granular ceramic is a promising material for fluoride removal from aqueous solution.

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