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The Adsorption of Hydrogen Fluoride and Fluoride Ion on a Water Treatment Sludge

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The hydrogen fluoride (HF) and fluoride ion (F^-) adsorption potentials of a water treatment sludge were investigated in a batch mode as a function of pH, contact time, initial fluoride concentrations, and other co–existing anions. The maximum removal of total fluoride was apparently observed at pH 5.1, whereas HF or F^- adsorptions showed nearly 100% in pH range from 2.2 to 4.3. The HF or F^- adsorption by the water treatment sludge has occurred rapidly during the initial 5–60 min and thereafter slowly increased until 48 h. The other anions such as SO_4^{2-}, NO_3^- and Cl^- have not adversely affected on extent of HF or F^- adsorption by the water treatment sludge.

INTRODUCTION

Fluoride in drinking water is known to have both beneficial and detrimental effects on animal health depending upon its concentration. For human beings, intake of 1.0–1.5 mg L^{-1} fluoride prevents dental and skeletal problems. However, the chronic ingestion above this level might cause the disease of mottling teeth, many types of bone diseases, and the lesions of endocrine glands, thyroid, liver, and other organs. The World Health Organization (WHO) proposed that the maximum concentration of fluoride in drinking water should not exceed 1.5 mg L^{-1} (WHO, 2006). High concentration of fluoride in water sources has been critical problems in much areas of the world where the fluoride concentration is of 0.01 to 3 mg L^{-1} in fresh water and of 1.0 to 35 mg L^{-1} in ground water. For example, a certain hot spring water in Korea contained 12.7 mg L^{-1} of fluoride (Lee, 2007) and the ground water in Japan, 2.3 mg L^{-1} (Tominaga *et al*., 2002).

There are a number of techniques for fluoride removal from water such as adsorption (Srimurali *et al*., 1998; Reardon and Wang, 2001), ion exchange (Vaaramaa and Lehto, 2003), and precipitation (Singh *et al*., 1999). Among these methods, the adsorption technique is most widely used for removing fluoride. Adsorbents have been used for defluoridation including activated alumina (Ghorai and Pant, 2004), activated carbon (Ramos *et al*., 1999), bone char (Bhargava and Killedar, 1992), and zeolites (Mayadevi, 1996). However, these adsorbents have some disadvantages in terms of removal efficiency, limited availability of materials, and disposal of treatment chemicals. Therefore, recent researches are focused on the development of lower cost agents and highly effective materials for fluoride removal (Fan *et al*., 2003).

Water treatment sludge is an inescapable by–product generated during the processing of drinking water. The sludge typically contains mineral and humic substances from water, together with any treatment chemicals used as coagulants. The water treatment sludge contains appreciable amounts of hydrous oxides with significant P–sorbing capacity (Elliott *et al*., 1990; Novak and Watts, 2004). The sludge with a rugged surface has shown a superior adsorption capability for fluoride (Sujana *et al*., 1998), copper and lead (Wu *et al*., 2004). The water treatment sludge has a potential adsorption capacity of fluoride. It can be utilized as a "low–cost" and potentially recyclable adsorbent. However, there is little information on the removal of fluoride by the water treatment sludge.

In this study, we investigated the water treatment sludge as an adsorbent for removing aqueous fluoride in respect of pH, contact time, concentration, and other anions.

MATERIALS AND METHODS

Sludge sample

The water treatment sludge was supplied from a drinking water treatment plant located at Kurume, Fukuoka, Japan. The sludge was air–dried and then sieved (<425 μm.). The chemical composition of the sludge was analyzed by the X–ray fluorescence analysis (Shimadzu, EDX –800) in the Analytical Center of Kyushu University, listed in Table 1. Aluminum oxide as Al_2O_3 was the dominant component (49.9%).

Reagents

The fluoride solution was prepared sodium fluoride (NaF) supplied from Wako Chemicals. Alfusone, which is a mixed powder of 2.5% (w/w) La–ALC (mole ratio, 1:1) chelate with potassium hydrogen phthalate, and hexamethylenetetramine buffer, was purchased from Dojindo Laboratories (Kumamoto, Japan) for the chromogenic reagent of fluoride. The 1% alfusone solution was prepared by dissolving in distilled water (DW) at each analysis. The chemicals used in the all experiments were in analytical grade.

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Table 1. Principal chemical compositions of the water treatment sludge

Composition	Al_2O_3	SiO_2	Fe_2O_3	CaO	K_2O	TiO_2	SO_3	P_2O_5	MnO	Total
(%)	49.9	40.0	5.6	1.4	1.4	0.6	0.4	0.4	0.3	100.0

Determination of HF or F^- concentration

The HF or F^- concentration of the synthetic solutions was determined according to the method reported by Okumura *et al.* (2003). One milliliter of the 1% alfusone solution, 0.25 mL of filtrated solutions, 0.4 mL of buffer solution (CH_3COONa), and 2 mL of acetone were added to a test tube. The final volumes were made up to 10 mL with DW. After 60 min, 620 nm absorbances of the mixtures were measured by a spectrophotometer (Perkin–Elmer, Lambda 10). The adsorption of fluoride was calculated from the difference between added fluoride and the final concentration in the solution.

Effect of pH on adsorption

The removal of fluoride ions is highly dependent on the pH. The water treatment sludge contains mainly oxides of aluminum, iron and silica (Table 1). These oxides of the adsorbent in the aqueous medium would be hydroxylated to develop surface charge. In particular, the alumina, a main component of the sludge, has a good capacity for fluoride removal (Bahena *et al.*, 2002). The removal of HF or F^- by the sludge was investigated at pH ranging from 2.0 to 9.0, which was prepared by adjusting pH with 0.1 mol L^{-1} (M) $HClO_4$ or 0.1 M NaOH solution in a 10 mL polyethylene centrifuge tube. Two milliliters of 0.5 M $NaClO_4$, 2 mL of 5 mM NaF solution and 0.1 g of the sludge also were placed in the tube. The final volumes were made up to 10 mL with distilled water. The suspensions were agitated for 24 hours in an air–conditioned room at 298±1 K. Thereafter, the suspensions were centrifuged at 2,100× *g* for 15 min and filtered through a 0.2 μm Millipore filter. The sample obtained by filtrating was used for colorimetry analysis. In the addition of the HF or F^- determination, total fluoride concentrations were measured with the method modified by the addition of acetylacetone as a demasking agent (Okumura *et al.*, 2003).

Effect of contact time on adsorption

Adsorption experiments were conducted from 0 to 2880 min. The sludge of 2.5 g and 50 mL of 0.5 M $NaClO_4$ were placed into a plastic beaker. Then, a fluoride solution was added and was made up to 250 mL with adding distilled water. The initial concentration was 1 mM. After the pre–determined time intervals, the suspensions filtered and analyzed for the residual concentrations of HF or F^-.

Adsorption isotherm

Langmuir and Freundlich equations are the most widely used isotherm models. Since the dried and ground sludge had heterogenic granulometria (Babatunde and Zhao, 2007; Tor, 2006), adsorption isotherm for the water treatment sludge was plotted using the Freundlich equation :

$$X=KC^{1/n} \tag{1}$$

where C is equilibrium fluoride concentration (mg L^{-1}), X is the adsorbed fluoride (mg Kg^{-1}), K is a coefficient, and n is the degree of linearity. To determine the coefficients K and n, the equation (1) may be linearized by taking the logarithm of both sides. The linear form of Freundlich isotherm can be given as

$$\log X=1/n \log C + \log K \tag{2}$$

A plot of log X versus log C should be linear and the K (intercept) and $1/n$ (slope) are the Freundlich coefficients related to adsorption capacity and adsorption intensity, respectively. A smaller value of $1/n$ lying in the range of 0 to 1 indicates a stronger bond between adsorbate and adsorbent, while a higher value for K showed more adsorption of adsorbate from a synthetic solution (Rao and Bhole, 2001; Raji and Anirudhan, 1997).

One gram of the sludge, 20 mL of $NaClO_4$ and 50 mL of distilled water were placed in a 200 mL plastic beaker. The suspension was adjusted to pH 5.0 with 0.1 M $HClO_4$ or 0.1 M NaOH during 24 h. Then, 20 mL of the fluoride solutions from 0 to 100 mM was added the plastic beaker and DW was added to 100 mL. The suspensions were stirred for 24 hours and centrifuged at 2,100× *g* for 15 min, then passed through 0.22 μm Millipore filter. The filtrate was analyzed for HF or F^- concentrations by the same methods as above. The experiments were conducted in 298±1 K.

Effect of other anions on adsorption

Fluoride adsorption experiments were conducted in the mixed solution of fluoride and other anions like chloride, sulfate, and nitrate. The concentrations of 0, 1.0, 10.0, and 100 mM for anions of SO_4^{2-}, NO_3^- and Cl^- were prepared respectively by dissolving of their sodium salts in 1 mM fluoride solution. The prepared solutions were placed in the polyethylene tube with 0.15 g of the water treatment sludge. The solution was agitated for 24 h at 298±1 K and filtered. The concentration of HF or F^- in the filtrate was determined by the same methods as above.

RESULTS AND DISCUSSION

Effect of pH on adsorption

The effect of pH on the adsorption of fluoride may be attributed to factors such as the activation of the adsorbent species (Çengeloglu *et al.*, 2002). The results are shown in Fig. 1. The adsorption percentage of total fluoride species apparently increased with increasing pH and reached a maximum of 84.58% at pH 5.1. Then the adsorption of total fluoride species decreased sharply

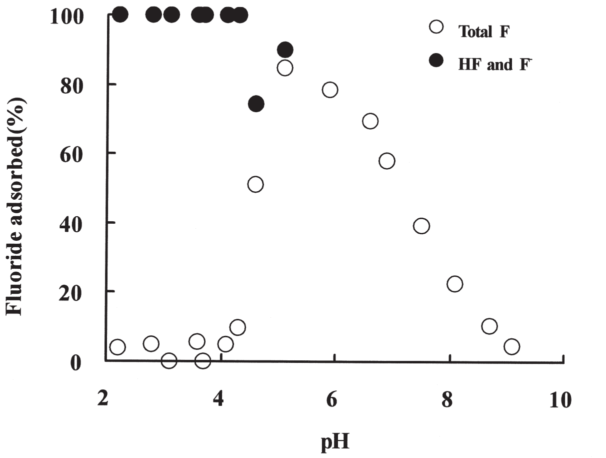

Fig. 1. Adsorption of fluoride as a function of pH.
Conditions: adsorbent 0.1 g, fluoride concentration (NaF) 1 mM, time 24 h, $NaClO_4$ 0.1 M, final volume 10 mL.

and only 4.41% was adsorbed at pH 9.0. The adsorption percentage of HF or F^- showed nearly 100% within the pH range from 2.2 to 4.3. It meant that fluoride at pH < approximately 4.3 existed with soluble metal–fluoride such as fluoro–aluminates complexes (AlF_n^{3-n}). Also, it was found that metal–fluoride complexes have been dissociated from adsorbent surface and then the fluoride separated from the metal–fluoride complexes by acetylacetone existed with conformations such as HF or F^-. The hydroxyl groups on the adsorbent surface in high pH range negatively charged with increasing pH, written as :

$$AlOH + OH^- = AlO^- + H_2O \qquad (3)$$

Consequently, the less adsorption capacity in solution of the range more than pH 5.1 would be due to the F^- ions cannot be adsorbed with AlO^-.

Effect of contact time on adsorption

The variation of HF or F^- adsorbed with contact times is shown in Fig. 2. The removal of HF or F^- increased significantly in the early period within 5–60 min and thereafter slowed, but continuously increased until 48 h. The adsorption percentage of HF or F^- was found to be 86.84% after 48 h (2880 min). The result is in good agreement with the literatures by other workers, which reported that the removal of fluoride by alum–impregnated activated alumina was rapid, that is, most of the fluoride was removed within 10–60 min (Tripathy *et al.*, 2006) and fluoride removal of 72% by the magnesia–amended activated alumina granules took place in first 60 min (Maliyekkal *et al.*, 2007).

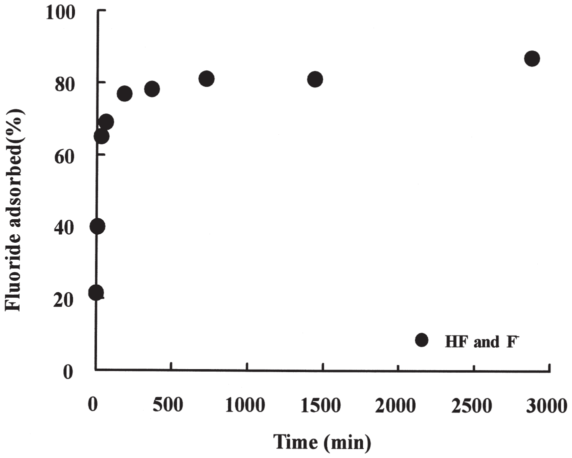

Fig. 2. Adsorption of fluoride as a function of contact time (min).
Conditions: adsorbent 2.5 g, fluoride concentration (NaF) 1 mM, $NaClO_4$ 0.1 M, final volume 250 mL.

Adsorption isotherm

Analysis of isotherm data is important for predicting adsorption capacities of adsorbents, which is one of the main parameter required for the design of an adsorption system (Maliyekkal *et al.*, 2007). The adsorption isotherm experiments were carried out to determine maximum fluoride adsorption by the sludge, shown in Fig. 3. The isotherm showed that the adsorption of HF or F^- increased with increasing equilibrium concentration of fluoride, thereafter, became flat at higher equilibrium concentrations. The correlation coefficient (R^2) values (0.982) showed that the Freundlich isotherm fitted well with the experimental data of the sludge.

The values of K and $1/n$ in the adsorption of HF or F^-, determined from the intercept and the slope, were 4.396 and 0.822 (n=1.216), respectively. Raji and Anirudhan (1997) reported that a smaller value of $1/n$ lying in the range of 0–1 and value of n lying in the range of 1–10 confirms the favorable conditions for adsorption. Therefore, the adsorption of HF or F^- onto the sludge indicated a favorable conditions because of the $1/n$ values lower than 1. Also, the higher value of n indicated that the surface of the sludge was heterogeneous and potential adsorbent for fluoride adsorption.

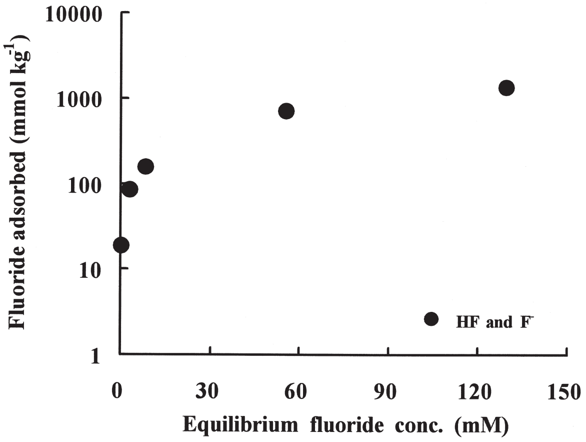

Fig. 3. Adsorption isotherm of fluoride.
Conditions: adsorbent 1 g, pH 5.0, time 24 h, $NaClO_4$ 0.1 M, temperature 298±1 K, final volume 100 mL.

Effect of other anions on adsorption

The adsorption percentage of HF or F^- in the solutions added SO_4^{2-}, NO_3^- and Cl^- increased 18.3, 26.2, and 20.9%, respectively (Table 2). We found that the co–existing anions such as SO_4^{2-}, NO_3^-, and Cl^- have not

Table 2. Effect of co–existing anions on fluoride adsorption by the sludge

Co–existing anions	Concentration of anions (mM)			
	0	1	10	100
	Fluoride adsorbed (%)			
Na_2SO_4	65.3	67.1	75.8	83.6
$NaNO_3$	64.0	66.5	78.6	90.2
NaCl	70.1	73.2	83.6	91.0

adversely effected on removal efficiency of HF or F^- onto the sludge. It was in an agreement with to the similar works done by other workers (Maliyekkal *et al.*, 2007; Lv *et al.*, 2006; Lv *et al.*, 2007; Shen *et al.*, 2003), especially Karthikeyan *et al.* (1997) was found that the fluoride adsorption efficiency onto activated alumina is not significantly affected by the presence of the other anions like SO_4^{2-}, NO_3^- and Cl^-.

CONCLUSIONS

In the present study, a water treatment sludge has been investigated as adsorbent for utilization in removing fluoride from the solutions. The optimum adsorption of total fluoride species from sample solution was apparently occurred at pH 5.1, but HF or F^- adsorbed nearly 100% at the range less than pH 4.3. Fluoride adsorption by the sludge was found to be very rapid during the initial period, namely, most of the HF or F^- was removed during 5–60 min and thereafter slowed, continuously increased until 48 h. The adsorption data were fitted well by the Freundlich equation with higher correlation coefficient values. We found that the increase of co–existing anions such as SO_4^{2-}, NO_3^-, and Cl^- to 100 mM have not adversely effected on the adsorption efficiency of HF or F^- onto the sludge. The water treatment sludge, an inescapable by–product of water treatment processes, can be expected to be reused as a adsorbent removal capacity for fluoride.

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