



## An excellent fluoride sorption behavior of ceramic adsorbent

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### ARTICLE INFO

#### Article history:

Received 2 May 2010

Received in revised form 8 July 2010

Accepted 10 July 2010

Available online 21 July 2010

#### Keywords:

Ceramic adsorbent

Fluoride removal

Sorption isotherms

Kinetic modeling

### ABSTRACT

A new material, ceramic adsorbent, has been developed and undertaken to evaluate the feasibility for fluoride removal from aqueous environment. Batch experiments were performed to study the influence of various experimental parameters such as contact time (0–48 h), initial fluoride concentration (20–100 mg/L), pH (2–12) and the presence of competing anions on the adsorption of fluoride on ceramic adsorbent. The experimental data revealed that both the Langmuir and Freundlich isotherm models fitted well with the fluoride sorption process. The maximum adsorption capacity of ceramic adsorbent for fluoride removal was 2.16 mg/g. The optimum fluoride removal was observed between pH ranges of 4.0–11.0. The sorption process was well explained with pseudo-second-order kinetic model. The fluoride adsorption was decreased in the presence of phosphate followed by carbonate and sulfate. Results from this study demonstrated potential utility of ceramic adsorbent that could be developed into a viable technology for fluoride removal from aqueous environment.

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## 1. Introduction

Fluoride has been known for centuries as a toxic element. The main source of fluoride in aqueous solution is fluoride-rich rocks through which the water has percolated. Fluoride may also be derived from mining or industrial activity in some areas [1]. According to the World Health Organization (WHO) guidelines, the upper limit of fluoride concentration in drinking water is 1.5 mg/L [2]. High level of fluoride in aqueous solution is a world-wide problem. Many people from North Africa, China, Mexico and India have been suffering from fluoride poisoning [3,4]. In China, for example, more than 1.34 million patients have suffered from skeletal fluorosis due to high fluoride drinking water and another 30 million are exposed to it [5,6].

The most commonly used methods for the defluoridation of water are adsorption, ion-exchange, precipitation, nano-filtration and electro dialysis [7–15]. Among these methods, adsorption has been found to be superior to other techniques for fluoride removal based on initial cost, flexibility and simplicity of design, and ease of operation and maintenance [16]. A large number of adsorbents have been studied for the removal of fluoride ions, including activated alumina, calcite, fly ash, charcoal, amberlite resin, layered double hydroxides and spent bleaching earth [17–23]. Among these adsorbents, activated alumina seems to be widely used because of

its efficiency and low cost [17]. However, the main disadvantage of activated alumina is its residual aluminum and soluble aluminum fluoride complexes, the generation of sludge and narrow available pH range (5.0–6.0) [24–26]. In addition, most of these materials are available only as fine powders that are difficult to separate from liquid after adsorption.

This study has developed a novel ceramic adsorbent for removal of fluoride from aqueous solution in order to overcome these obstacles. This ceramic adsorbent is the solid phase of a spherical shape, with high fluoride removal efficiency and sufficient mechanical strength to retain its physical integrity after long-time adsorption. Ceramic adsorbents were prepared by cost-effective mixture materials consisting of Kanuma mud, which is widespread in Japan, with zeolite, starch, and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . The major objective of this study was to develop and investigate the ceramic material as a feasible fluoride adsorbent. Kinetic, equilibrium and effects of solution pH studies of fluoride removal by the optimized ceramic were discussed in batch experiments.

## 2. Experimental

### 2.1. Preparation of ceramic adsorbent

Kanuma mud, a common, inexpensive deposit of volcanic ash, was provided by Makino Store, Kiyosu, Japan. Kanuma mud was sieved to obtain less than 100  $\mu\text{m}$  and then dried at 105 °C for 2 h to use for developing the ceramic adsorbent. Zeolite (the grain size was less than 75  $\mu\text{m}$ ) was supplied by the Azuwan Cement Fac-

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**Table 1**  
Chemical analysis of Kanuma mud, zeolite and ceramic adsorbent by SEM–EDS test.

Composition (wt.%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	MnO	pH <sub>ZPC</sub>
Kanuma mud <sup>a</sup>	56.20	38.70	2.20	0.36	2.00	0.54	6.1 <sup>b</sup>
Zeolite	63.48	28.79	1.33	2.81	1.24	2.35	–
Ceramic adsorbent	44.91	37.28	12.24	1.27	1.93	2.37	5.8 ± 0.2

<sup>a</sup> The effect on LOI (600 °C) has been neglected.

<sup>b</sup> Information supplied by the manufacturer.

tory, Japan. Starch and FeSO<sub>4</sub>·7H<sub>2</sub>O were supplied by the Wako Pure Chemical Industries, Ltd, Japan. 4 g of Kanuma mud, 3 g of zeolite, 2 g of starch and 1 g of FeSO<sub>4</sub>·7H<sub>2</sub>O were mixed to homogeneity. Ultra pure water (resistivity 18.2 MΩ cm at 25 °C) 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 110 °C for 48 h and calcined at 600 °C for 1 h in a muffle furnace. Finally, the developed ceramic material was allowed to cool to room temperature in the furnace and then used for adsorption experiment.

### 2.2. Characterization of ceramic adsorbent

The developed optimized ceramic adsorbent was analyzed in order to determine its physicochemical properties. The specific surface area and pore-size distributions were determined with a Brunauer–Emmett–Teller (BET) method by gas adsorption (Coulter SA3100, US). The morphological images were acquired by scanning electron microscope (SEM) (JSM-6700F, JEOL, Japan). The spot element analysis of the ceramic adsorbent was carried out using the energy dispersive X-ray spectroscopy (EDS) detector (SEM-EDS, JEOL, Japan). The mineralogy of supported metal-oxide was characterized by powder XRD techniques (Rigaku RINT2200, Japan). Fluoride analysis was performed by a UV–visible spectrophotometer (Hitachi, DR/4000U, Japan). The determination of leached iron and aluminum was carried out by an inductively coupled plasma atomic emission spectrometer (ICP–AES, ICP–7500, Shimadzu, Japan).

### 2.3. Batch sorption studies

The adsorption of fluoride on ceramic adsorbent was studied at room temperature (30 °C) by batch experiments. The adsorbent used for this study was sieved to obtain uniform particle size of 2–3 mm. About 2 g ceramic adsorbent was added into 100 mL of 10 mg/L sodium fluoride solution with a desired pH value. The mixture was shaken in a shaker at a speed of 100 rpm (Tai Tec, Thermo Minder Mini-80, Japan). The effect of contact time (0–48 h) was examined at pH 6.9 ± 0.1 with initial fluoride concentration of 10 mg/L. The adsorption isotherm was studied by varying the initial fluoride concentration from 5 to 50 mg/L at pH 6.9 ± 0.1. The effect of pH was investigated by adjusting solution pH from 2 to 12 using 0.1 M HCl and 0.1 M NaOH under an initial fluoride concentration of 10 mg/L. The effect of competing anions (chloride, nitrate, carbonate, sulfate and phosphate) on fluoride adsorption was investigated by performing fluoride adsorption under a fixed fluoride concentration (10 mg/L), with initial competing anion concentrations of 20–200 mg/L at pH 6.9 ± 0.1 over 48 h.

### 2.4. Sorption–desorption cycle

In order to test the regenerative ability of the ceramic adsorbent, a single sorption–desorption cycle was tested. Initially, the sorption study was conducted using 20 g/L of ceramic adsorbent and 10 mg/L of fluoride concentration (see Section 2.3). Then desorption of flu-

oride loaded on ceramic adsorbent was carried out with 0.1 M HCl and 0.1 M NaOH as the eluent. After the regeneration, the ability of ceramic adsorbent to remove fluoride from solution was again tested in a sorption experiment, using a similar procedure to that described in Section 2.3.

## 3. Results and discussion

### 3.1. Characterization of ceramic adsorbent

The surface morphology of the ceramic adsorbent was examined by SEM (Fig. 1a), clearly revealing a flocced and porous surface texture, which indicates the adsorbents were highly porous, with a high adsorption capacity. After extensive flow-through exposure (for 48 h) during fluoride adsorption, the surface changed to be smooth, polyhedron and stretched cubic structures (Fig. 1b). Fluoride adsorption may not only occur at the surface of the adsorbent but also inside of the pores. The EDS (Table 1) results showed that the iron content of ceramic adsorbent accounted for 12.24%, comparing with Kanuma mud, the proportion increased 5.5 times due to the addition of FeSO<sub>4</sub>·7H<sub>2</sub>O. 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 specific surface area of ceramic adsorbent was found to be 80.94 sq m/g, and the pore volume was 0.1176 mL/g. The pore-size distributions (Fig. 1d) revealed that the observed pore sizes mostly varied between 6 and 80 nm (69.47%). The result also indicated that a large percentage of the pores (17.86%) were under 6 nm. According to IUPAC classification, this ceramic adsorbent is a typical mesoporous material. The XRD patterns of the ceramic adsorbents that contain Fe oxide are shown in Fig. 1e and f. It was observed from Fig. 1e that diffraction peaks attributed to crystalline iron oxide and ferrimordenite. The peaks of Fe in Fig. 1e were due to the sample support made in FeSO<sub>4</sub>·7H<sub>2</sub>O. The XRD study reveals that the amorphous structure of adsorbent showed significant changes after the fluoride adsorbed in Fig. 1f. The diffraction peaks are attributed to crystalline iron fluoride hydroxide hydrate and iron zinc oxide fluoride. This suggests that the uptake of fluoride ions by ceramic adsorbent is partly by chemical adsorption.

### 3.2. Sorption isotherms

The experimental data was validated using Freundlich and Langmuir isotherm models. The linear forms of Freundlich and Langmuir isotherm equation are as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (1)$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{Bq_m(1/C_e)} \quad (2)$$

where  $q_e$  is the amount of fluoride ion adsorbed per unit mass of the adsorbent and  $C_e$  is the amount of fluoride ion in liquid phase at equilibrium.  $K_f$ ,  $n$ ,  $q_m$  and  $B$  are Freundlich and Langmuir constants, respectively. These equation are applied to correlate the amount of

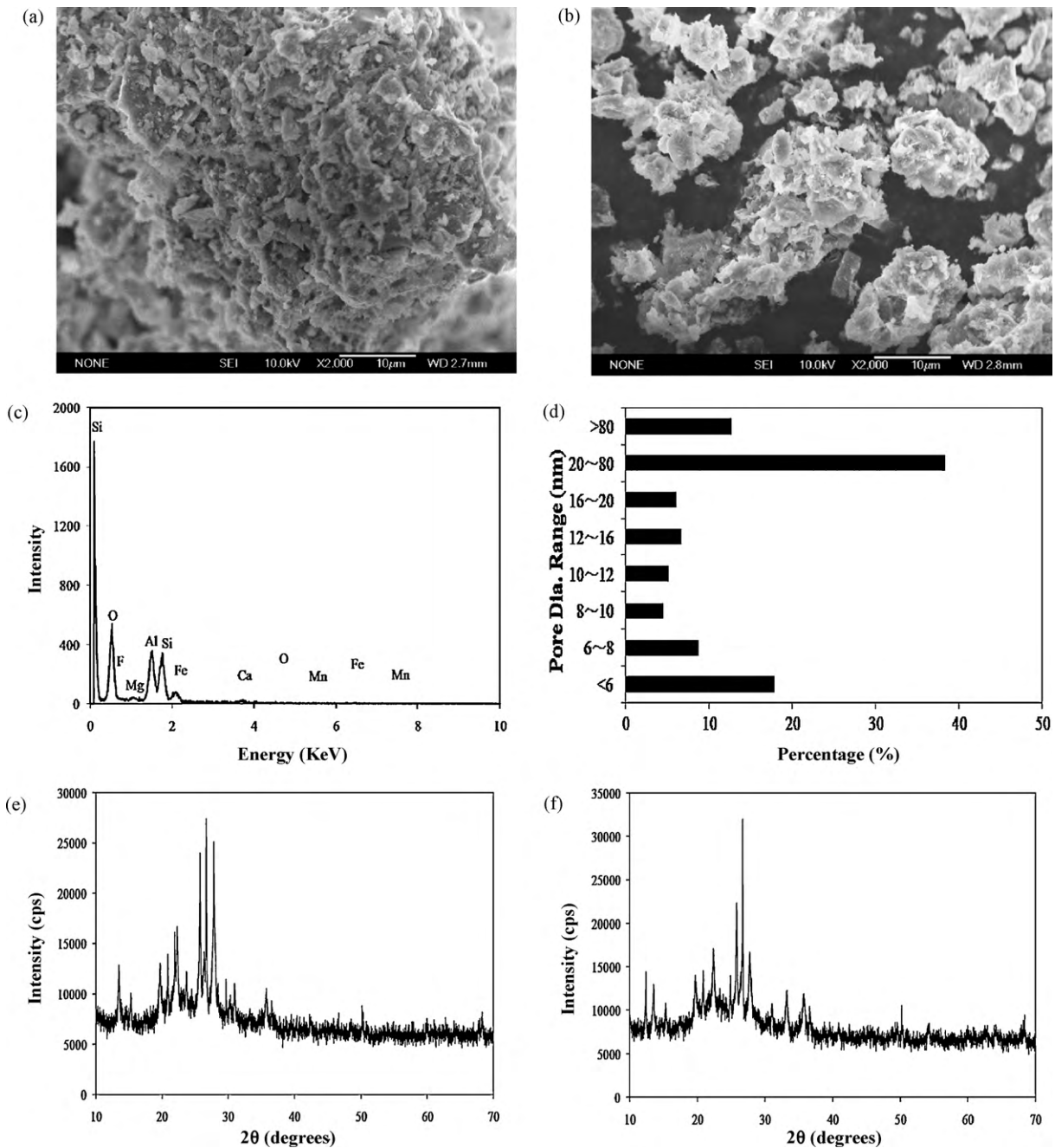


Fig. 1. SEM images of (a) ceramic adsorbent and (b) fluoride-adsorbed ceramic adsorbent, EDS spectra of (c) fluoride-adsorbed ceramic adsorbent composite, BJH (Barrett–Joyner–Halenda) pore-size distribution of (d) ceramic adsorbent, powder XRD patterns of (e) ceramic adsorbent and (f) fluoride-adsorbed ceramic adsorbent.

the fluoride adsorbed per unit amount of the adsorbent and can be calculated from slope and intercept.

Fig. 2a shows a plot of  $\log q_e$  versus  $\log C_e$ . The constants  $1/n$  and  $\log K_f$  were calculated from the slope and intercept. From the linear graph the correlation coefficient  $R^2$ -value and minimum sorption capacity were found 0.95 and 0.53 mg/g respectively. The experimental data fit well to the Freundlich isotherm model. The condition for the validity of a Freundlich type adsorption model is sorption on heterogeneous surfaces [27]. In Fig. 2b plot of  $1/q_e$  versus  $1/C_e$  yields straight line which demonstrates that sorption data followed by Langmuir sorption model well. The value of  $q_m$  is 2.16 mg/g and the Langmuir constant  $B$  is 0.3946. The essential characteristic of the Langmuir isotherm can be denoted by the dimensionless constant called equilibrium parameter,  $R_L$ , defined

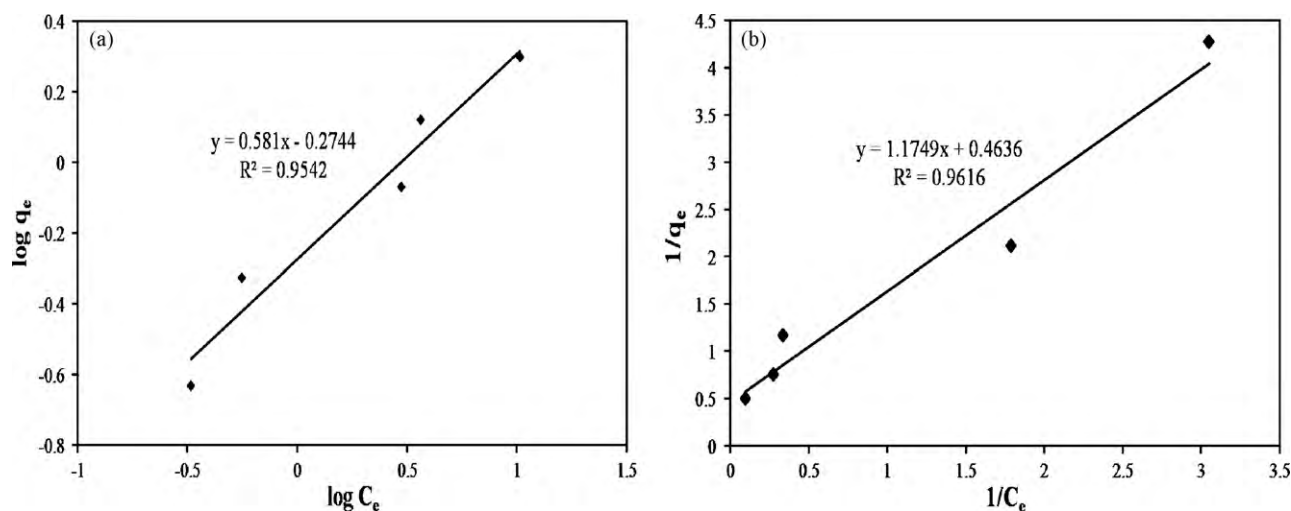
by:

$$R_L = \frac{1}{1 + BC_0} \quad (3)$$

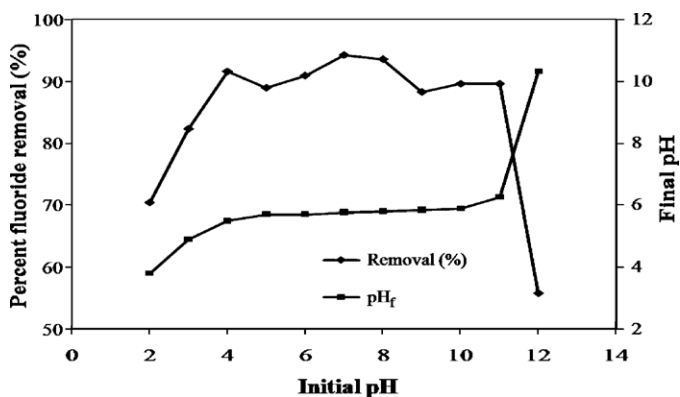
where  $B$  is the Langmuir constant and  $C_0$  is the initial adsorbate concentration (mg/L),  $R_L$  value indicate the type of isotherm to be irreversible ( $R_L = 0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) and unfavourable ( $R_L > 1$ ) [28,29]. The value of  $R_L$  0.202 indicates favourable sorption of fluoride onto the ceramic adsorbent.

### 3.3. Effect of solution pH

The results presented in Fig. 3 indicate that the percentage fluoride removal greatly depends on the solution pH. The optimal pH



**Fig. 2.** Isotherm modeling of fluoride adsorption on the ceramic adsorbent (a) Freundlich isotherm; (b) Langmuir isotherm (initial fluoride concentration 10 mg/L, equilibrium contact time 48 h, initial pH  $6.9 \pm 0.1$ , and temperature  $30^\circ\text{C}$ ).



**Fig. 3.** Effect of initial pH on fluoride removal and the equilibrium pH ( $\text{pH}_{\text{final}}$ ) by the ceramic adsorbent performed in batch study (initial fluoride concentration 10 mg/L, equilibrium contact time 48 h, adsorbent dosage 20 g/L, and temperature  $30^\circ\text{C}$ ).

for fluoride uptake appeared to be pH 7, with a removal percentage of 94.23%. The experimental data agree with the results obtained by Solangi et al. [30]. The removal ability fluctuated slightly over the pH range of 4–11, which means that this ceramic adsorbent can adapt to a wide range of pH for fluoride adsorption from water and is suitable for practical applications. The equilibrium pH ( $\text{pH}_{\text{final}}$ ) values were measured after 48 h sorption. It is clear that  $\text{pH}_{\text{final}}$  increases smoothly with increasing initial pH (Fig. 3). However, it was observed that ceramic adsorbent had a significant capacity to buffer highly acidic and alkaline solutions. The pH of zero point charge ( $\text{pH}_{\text{zpc}}$ ) of ceramic adsorbent was  $5.8 \pm 0.2$ , estimated using batch equilibrium techniques described by Chutia et al. [31]. 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 [7]. On the other hand, under acidic conditions, the decrease may be attributed to the formation of weakly ionized hydrofluoric acid [27] or the combined effects of chemical and

electrostatic interactions between the oxide surface and fluoride ions.

### 3.4. Kinetic modeling

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 [30,31].

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

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  $k_2$  are first-order and second-order rate constants for adsorption.

Kinetic constants obtained from the pseudo-first-order and pseudo-second-order models are given in Table 2. The value of correlation coefficient ( $R^2 = 0.9996$ ) for the pseudo-second-order sorption model is higher than that ( $R^2 = 0.9463$ ) obtained from the pseudo-first-order kinetic. Additionally, theoretical and experimental  $q_{e,\text{exp}}$  (0.4721 mg/g) value is in a good accordance with the calculated equilibrium adsorption capacity  $q_{e,\text{cal}}$  (0.5020 mg/g). Therefore, it is possible to suggest that the sorption of fluoride by ceramic adsorbent followed the pseudo-second-order type reaction kinetics.

### 3.5. Effect of competing anions

The fluoride-contaminated water may contain several other anions which may compete with the sorption of fluoride. The adsorption studies were carried out in the presence of 20–200 mg/L salt solutions of chloride, nitrate, sulfate, carbonate and phosphate independently at an initial fluoride concentration of 10 mg/L. The effects of these co-existing ions on fluoride removal are shown in

**Table 2**  
Kinetics constant for adsorption of fluoride onto ceramic adsorbent.

C (mg/L)	Experiment $q_{e,\text{exp}}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		$k_1$ (1/min)	$q_{e,\text{cal}}$ (mg/g)	$R^2$	$k_2$ [g/(mg min)]	$q_{e,\text{cal}}$ (mg/g)	$R^2$
10.00	0.4721	0.0930	0.2389	0.9463	0.6464	0.5020	0.9996

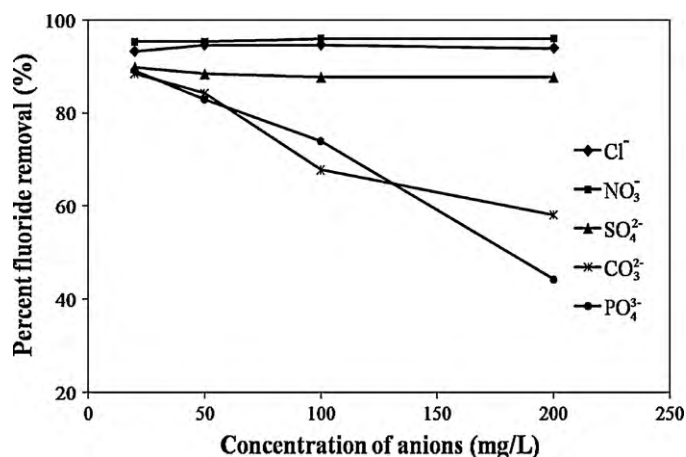
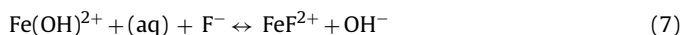


Fig. 4. Effect of different concentrations of competing anions on fluoride adsorption by the ceramic adsorbent performed in batch study (initial fluoride concentration 10 mg/L, equilibrium contact time 48 h, adsorbent dosage 20 g/L, and temperature 30 °C).

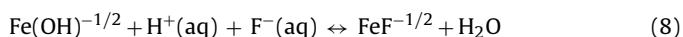
Fig. 4. It was observed that fluoride removal slightly increased in the presence of chloride and nitrate ions, which could be due to an increase in the ionic strength of the solution or a weakening of lateral repulsion between adsorbed fluoride ions. Similar observations have been reported by Eskandarpour et al. [32]. It was also observed that fluoride removal slightly decreased in the presence of sulfate, and obviously decreased in the presence of carbonate and phosphate ions. Fluoride sorption slightly decreased by sulfate ion may be attributed to the high coulombic repulsive forces, which reduce the probability of fluoride interactions with the active sites [33,34]. Carbonate and phosphate ions had the greatest effect on fluoride sorption may be explained not only in terms of the competition for the same active sites with fluoride, but also by the high affinity and capacity for carbonate and phosphate ions on ceramic adsorbent. The results are in good agreement with similar work done by Kagne et al. [35] for hydrated cement, where the fluoride removal efficiency is not significantly affected by chloride, nitrate and sulfate but is significantly affected by carbonate and phosphate.

### 3.6. Possible mechanism

The mechanism of fluoride sorption on iron oxide surfaces can be given as [36]:



Hiemstra et al. [37] investigated the adsorption of fluoride on goethite and confirmed by IR analysis that the process mainly occurred through coordination to surface FeOH groups. They formulated the formation of  $\text{FeF}^{-1/2}$  as:



It is expected that similar process occur on the present study using ceramic adsorbent. It has been reported that fluoride interacts with singly coordinated FeOH surface groups and the mechanism of fluoride adsorption on iron oxide surfaces can be described as an exchange reaction against  $\text{OH}^-$  of surface groups. The OH/F exchange further suggests that the fluoride ion can be considered as fully located in the surface [37,38].

### 3.7. Comparison of fluoride sorption with other adsorbents

A comparison has been made between ceramic adsorbent and previously reported adsorbents for fluoride removal. As can be seen

Table 3

Comparison between various adsorbents used for fluoride removal.

Name of sorbent	Adsorption capacity (mg/g)	Reference
AlFe650/C	13.64	[20]
Carbon slurry	4.86	[16]
Zn–Al layered double hydroxides	4.14	[40]
Magnesia-amended activated alumina	4.04	[24]
Activated alumina	2.41	[17]
Ceramic adsorbent	2.16	Present study
Activated carbon (Al-C300)	1.10	[39]
Calcite	0.39	[18]
Red mud	$6.28 \times 10^{-3}$	[41]
Charcoal	$7.88 \times 10^{-5}$	[42]

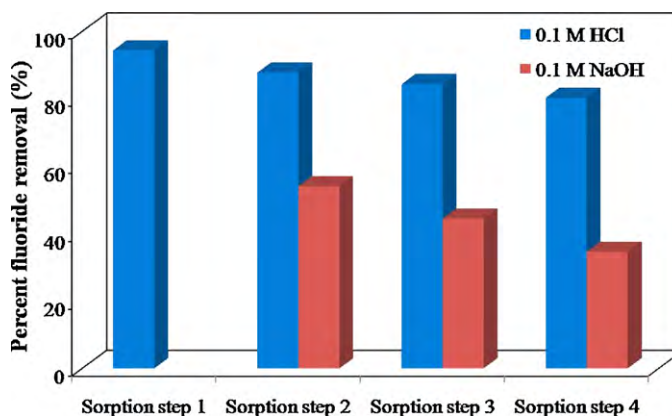


Fig. 5. Fluoride sorption–desorption cycle (initial fluoride concentration 10 mg/L, equilibrium contact time 48 h, adsorbent dosage 20 g/L, and temperature 30 °C).

in Table 3, ceramic-supported iron oxide as adsorbent is better than many other adsorbents in terms of defluoridation capacity. The high fluoride adsorption capacity obtained in this work is mainly due to the dispersion of Fe in the ceramic adsorbent. This element has a strong affinity with fluoride ions. Therefore synthesized ceramic adsorbent that is easy to implement is effective adsorbent for removing fluoride from aqueous solution.

### 3.8. Sorption–desorption cycle

Water purification by adsorption technology is economical if the adsorbent is regenerable. Moreover, reuse of adsorbent helps reduce environmental impacts of disposing used adsorbents. Initially, fluoride removal on ceramic adsorbent was calculated to be 94.4% (see Fig. 5). Then, desorption of fluoride from the adsorbent and regeneration of the ceramic adsorbent were done with 0.1 M HCl and NaOH as eluent. The results (Fig. 5) showed that a reduction in sorption efficiency occurred after the regeneration. At the end of the fourth cycle, the fluoride sorption efficiency was observed to be 80.2 and 34.7% using 0.1 M HCl and NaOH as eluent, respectively. That may indicate the eluent with 0.1 M HCl was more suitable to be used to regenerate the ceramic adsorbent. However, after the fourth sorption cycle, about 14.2% reduction in efficiency was observed using the eluent with 0.1 M HCl. This reduction in sorption efficiency may be attributed to the gradual dissolution of iron from the ceramic adsorbent surface during vigorous washing of the sorbent.

## 4. Conclusions

In this study, a novel sorbent, ferrous-amended ceramic adsorbent has been prepared and examined for its potential in removing

fluoride from aqueous environment. Its granular structure, high surface area and effective capacity of fluoride removal make the adsorbent a highly potential media to be used in purification of fluoride from water. The adsorption capacity of ceramic adsorbent for fluoride was 2.16 mg/g at 30 °C. The sorption process was fitted well with both the Langmuir and Freundlich isotherm models. Kinetic study results indicate that the adsorption process followed a pseudo-second-order kinetic model. The optimum fluoride removal was observed at pH ranges of 4.0–11.0 indicating that the ceramic adsorbent has promising potential utility in practical application. The fluoride adsorption was reduced in the presence of carbonate, phosphate and sulfate and increased slightly in the presence of chloride and nitrate ions. The ceramic adsorbent also can be regenerated several times with 0.1 M HCl as eluent. Therefore, the new ceramic adsorbent is a promising material for fluoride removal from water environment.

### Acknowledgements

The authors thank Development of Catch-Up Type Ceramics Material with Higher Pollutant Removal Efficiency and Its Application to Water Renovation of JST, the National Key Technology R&D Program in the 11th Five-year Plan of China (2006BAJ08B04, 2006BAD01B03), 863 Project (2007AA06Z351) for the financial support of this work.

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