Preparation and characterization of porous granular ceramic containing dispersed aluminum and iron oxides as adsorbents for fluoride removal from aqueous solution

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ABSTRACT

Porous granular ceramic adsorbents containing dispersed aluminum and iron oxides were synthesized by impregnating with salt solutions followed by precipitation at 600 °C. In the present work detailed studies were carried out to investigate the effect of contact time, adsorbent dose, initial solution pH and co-existing anions. Characterization studies on the adsorbent by SEM, XRD, EDS, and BET analysis were carried out to clarify the adsorption mechanism. The adsorbents were sphere in shape, 2–3 mm in particle size, highly porous and showed specific surface area of 50.69 sq m/g. The fluoride adsorption capacity of prepared adsorbent was 1.79 mg/g, and the maximum fluoride removal was obtained at pH 6. Both the Langmuir and Freundlich isotherm models were found to represent the measured adsorption data well. The experimental data were well explained with pseudo-second-order kinetic model. Results from this study demonstrated potential utility of Al/Fe dispersed in porous granular ceramics that could be developed into a viable technology for fluoride removal from aqueous solution.

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1. Introduction

Fluoride element is essential as well as detrimental for the dental and skeletal growth of human beings. Deposited fluoride contaminations are found in water mostly due to natural processes (e.g., geochemical reactions and volcanic emissions) and industrial activities (e.g., semiconductor, electroplating, steel and fertilizer industries) [1,2]. The WHO recommended the tolerance limit for fluoride in drinking water is 1.5 mg/L [3]. It has been reported that higher fluoride concentrations in water can lead to various diseases (e.g., dental caries, skeletal fluorosis, osteoporosis and arthritis) [4,5]. Moreover, some serious effects were also observed in different countries, such as India, Mexico, Africa and China [6–9]. For these reasons, the removal of the excess fluoride from water is important in terms of protection of public health and environment.

Existing methods to remove fluoride from water includes adsorption, ion exchange, membrane processing (such as reverse osmosis), Donnan dialysis, and electrodialysis [10–17]. Among these different traditional methods, adsorption is one of the most popular separation and purification method due to its high selectivity, low operating cost, easy handling and effective reducing

quantity [18]. Several adsorbents were tried for the removal of fluoride from aqueous solution namely activated alumina, red mud, chitosan beads, carbonaceous materials, calcite, and hydrated cement [10,19–23]. However, most of these adsorbents were not applicable in rural areas due to their financial and technological constraints. Therefore, it is desirable to develop a novel adsorbent which is robust, inexpensive, porous and able to effectively remove fluoride in subsequent operations and also can avoid clogging during field applications.

Due to its high electronegativity and small ionic size, the fluoride ion is classified as a hard base, which has a strong affinity towards metal ions including Al^{3+} and Fe^{3+} [24]. Dispersing a mixture of these metals in a porous material would limit the total dissolved solids in treated water as well as would provide high fluoride adsorption capacity [25]. Porous granular ceramics could be the good candidate to be a metal-support material due to its large surface area and continuous porosity structure. In the present study, we have successfully developed a new adsorbent by impregnation of porous granular ceramics with aluminum and iron salts to remove fluoride form aqueous solution. Batch studies are conducted using these novel adsorbents with optimization of various experimental conditions, including contact time, adsorbent dose, initial pH and co-existing ions in solutions. The nature and morphology of the adsorbents are therefore discussed on the basis of SEM, XRD, EDS, and BET studies. The Langmuir and Freundlich

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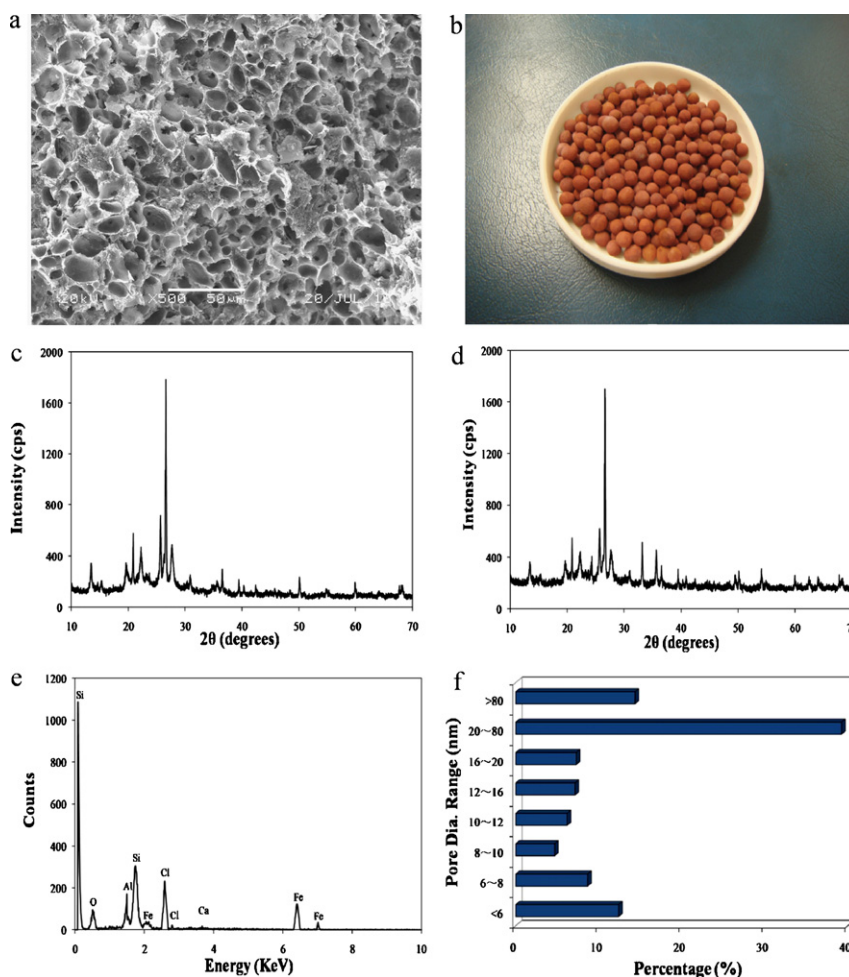
Fig. 1. SEM images of (a) cross section of pristine granular ceramics and (b) Photo of pristine granular ceramics, Powder XRD patterns of (c) pristine granular ceramics and (d) adsorbed granular ceramics, EDS spectra of (e) pristine granular ceramics, BJH (Barrett–Joyner–Halenda) pore-size distribution of (f) pristine granular ceramics.

isotherm models are used to explain the mechanism of fluoride removal by these novel adsorbents. Various kinetic models are also included to describe the adsorption process.

2. Experimental

2.1. Material preparation

Knar clay (particle size was less than 75 μm) was purchased in the Isehisa Store (Japan), zeolite (particle size was less than 100 μm) was supplied by the Azuwan Cement Factory (Japan), wheat starch was supplied by the Wako Pure Chemical Industries, Ltd (Japan). Knar clay, zeolite and starch (with mass ratio 1:1:1) were mixed by ultra pure water (resistivity 18.2 MΩ cm at 25 °C) to prepare the porous granular ceramic based on simple co-precipitation method by manual. Detailed procedure was given in previous publication [11]. Then the prepared porous granular ceramics were impregnated in a boiling mixture of 1 M AlCl₃ and 1 M FeCl₃ aqueous solution for 2 h. After the heating, the samples remained to be immersed in the salt solution for 2 h. The impregnated granules were removed from the solution, then exposed in the open air for 2 h and afterwards dried in an oven at 105 °C for 24 h. The obtained samples were calcined at 600 °C for 1 h in a muffle furnace. Finally, samples were cooled to room temperature and transferred to airtight glass bottles for further study. The specific surface areas of adsorbents were determined by the BET

method with N_2 gas (Coulter SA3100, Japan). The mineralogy of supported metal-oxide was characterized by powder XRD techniques (Rigaku RINT2200, Japan). The surface morphology and spot elemental analysis of ceramic adsorbents were carried out using the scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) detector (JEOL, SEM-EDS-6700F, Japan), respectively.

2.2. Adsorption experiments

A stock solution (100 mg F/L) was prepared by dissolving 0.221 g anhydrous sodium fluoride in 1 L of ultra pure water. This was diluted to obtain the required concentration for further use. The fluoride adsorption experiments were carried out by a batch method at room temperature (25 ± 1 °C). The pH of the fluoride solution in the experiment was adjusted using 0.1 M NaOH and HCl solutions. 100 mL of fluoride solution and 2 g of coated ceramic adsorbents were placed in a shaker at a speed of 100 rpm (Tai Tec Thermo Minder Mini-80, Japan). The effect of experimental procedure for adsorption isotherms and kinetics, adsorption at different adsorbent dose, initial pH and interference of other co-existing anions has been described in a batch study. Fluoride analysis was carried out using a fluoride reagent spectrophotometer (Hach, DR/4000U, Japan) at 620 nm wavelength according to SPADNS (APHA, Standards Method for the Examination of Water and Waste Water, 1998) [26].

Table 1
Chemical analysis and surface area characterization of Al/Fe dispersed in porous granular ceramics.

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	MnO	pH_{zpc}
Chemical analysis of Al/Fe dispersed in porous granular ceramics (oxides)							
Composition (wt.%)	49.78	17.70	19.20	2.36	4.70	0.24	6.5 ± 0.1
	BET surface area (m²/g)		Langmuir surface area (m²/g)		T-plot surface area (m²/g)		Pore volume (cm³/g)
Surface area and pore volume analysis of Al/Fe dispersed in porous granular ceramics							
Granular ceramics	50.69		39.89		35.12		0.1108

3. Results and discussion

3.1. Characterization of adsorbent

The prepared Al/Fe dispersed in porous granular ceramic adsorbent is reddish brown colored and 2–3 mm in diameter (shown in Fig. 1b). As can be seen from Fig. 1a, the adsorbents have the expected large numbers of porous structures in the cross section which indicates the adsorbent may have a high adsorption capacity. This microcosmic pore texture can be attributed to the sintering of certain inorganic and organic substances (such as starch) during the calcination process. The EDS spectrum of Fig. 1e shows the presence of Fe, Al, Si, O and Cl in the surface of adsorbent, which can be attributed to the impregnation process with $AlCl_3$ and $FeCl_3$ salt solutions. It is difficult to establish the accurate chemical composition of the inorganic compounds which were formed in granular ceramics, because of the possible existence of some amorphous compounds and the complexity of the knar clay. However, it appears that there would be mainly iron and aluminum oxides on the surface of ceramics. The chemical composition (oxides) of Al/Fe dispersed in porous granular ceramic adsorbent that was determined by EDS is presented in Table 1. The XRD patterns of the ceramic adsorbents that contain iron and aluminum oxides are shown in Fig. 1c and d. It is observed from Fig. 1c that diffraction peaks attributed to crystalline iron oxide, aluminum oxide, hematite and maghemite. The peaks of Fe and Al in Fig. 1c are due to the granular ceramics coated by $AlCl_3$ and $FeCl_3$ salt solutions. It is clear that the crystal and amorphous structures of adsorbent had significantly changed after the adsorption process (Fig. 1d). The diffraction peaks are attributed to crystalline iron and aluminum fluoride hydroxide hydrate and iron zinc oxide fluoride. This may suggest that the uptake of fluoride ions is partly by chemical adsorption. The specific surface area of Al/Fe dispersed in porous granular ceramic adsorbent (Table 1) further confirmed its porous nature. The specific surface area of ceramic adsorbent is found to be 50.69 sq m/g, and the pore volume is 0.1108 ml/g. The pore-size distributions (Fig. 1f) indicate that the observed pore sizes mostly varied between 6 and 80 nm (73.23%). As the radius of fluorine (1.33 Å) is much smaller than this value (6–80 nm), which may increase the possibility of F^- ions dispersing into the inner layer of the granular adsorbents.

3.2. Effect of adsorbent dose

The effect of adsorbent dose on the fluoride removal was studied at pH 6.9 ± 0.1, room temperature and 10 mg/L of fluoride. The results obtained are shown as percent adsorption and loading capacity in Fig. 2a. It was observed that the percentage removal of fluoride increased from 69.4% to 95.7% with an increase in adsorbent dose from 10 to 30 g/L. However, after a dose of 20 g/L, the amount removed per unit of adsorbent declined. The increase in fluoride removal with increase of adsorbent dose is the consequence of a greater amount of available binding sites for fluoride. The distribution coefficient (K_D) for fluoride on adsorbent was calculated

by [27]:

$$K_D = \frac{[F^-]_{ads}}{[F^-]_{diss}(1/C_p)} \tag{1}$$

where C_p is the solid concentration in kg/L and K_D has the units of L/kg. A distribution coefficient reflects the binding ability of the surface for an element. The K_D value of a system mainly depends on pH and the type of surface. It was found that the K_D values increased with increase of adsorbent dose (Fig. 2b), which is very similar to the results investigated by Sujana and Anand [28]. It is clearly revealed the binding ability of the surface, as reflected in the K_D values, decreased with the adsorbent dose increased. If the surface is homogeneous the K_D value should not change with adsorbent dose at constant pH, so the increase of K_D values indicated the heterogeneous in nature of adsorbent surface [28,29].

3.3. Effect of solution pH

The initial pH of solution is one of the important parameters that could obviously affect the extent of fluoride adsorption. As shown in Fig. 3a, the amount of adsorbed fluoride enhances significantly with increasing pH and it attains a maximum at pH 6, thereafter it declines. The maximum fluoride removal was found to be 89.3%, with a fluoride adsorption capacity of 0.4464 mg/g. Fig. 3b demonstrates the variation of equilibrium pH (pH_f) from the initial
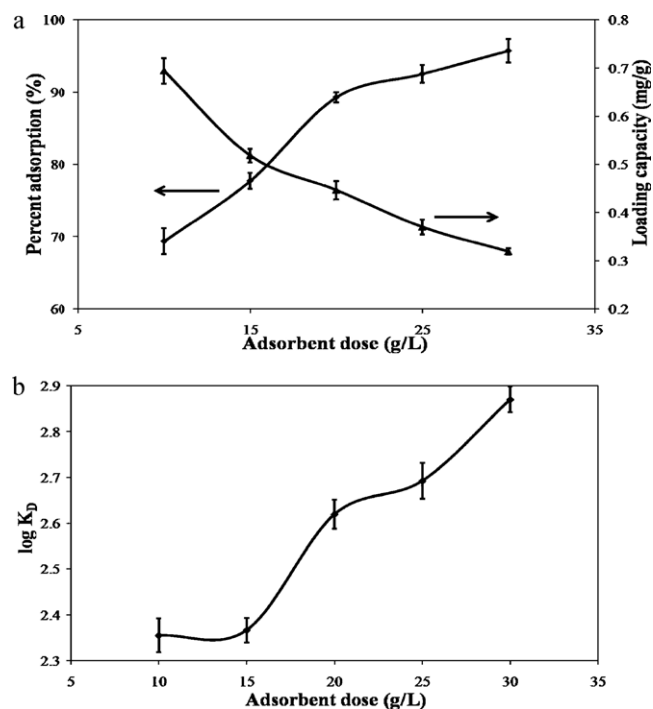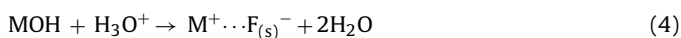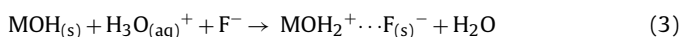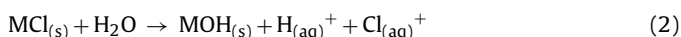
Fig. 2. (a) Effect of prepared adsorbent dose variation on fluoride removal (initial pH 6.9 ± 0.1, initial fluoride concentration 10 mg/L, equilibrium contact time 48 h and temperature $25 \pm 1\,°C$). (b) The plot of log K_D value as a function of prepared adsorbent dose (data corresponding to (a)).
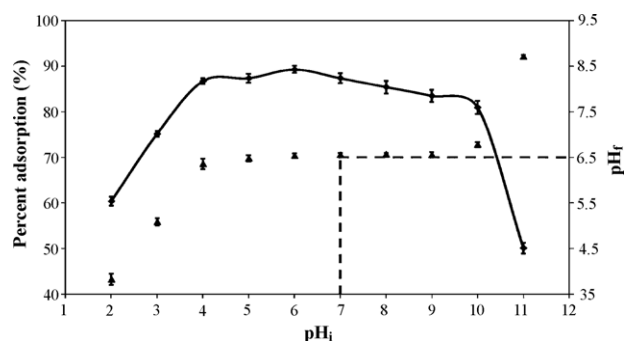
Fig. 3. (a) Effect of initial pH (pH$_i$) variation on fluoride removal (adsorbent dose 20 g/L, initial fluoride concentration 10 mg/L, equilibrium contact time 48 h and temperature 25 ± 1 °C). (b) The variation of final pH (pH$_f$) against initial pH (pH$_i$).

pH (pH$_i$) during experiments. Horizontal portion at pH$_f$ ranged in 6.5–6.6 should be the pH$_{zpc}$ of prepared adsorbent. Therefore, the surface characteristic of the mixed oxide is (i) positive at pH$_f$ < 6.5, (ii) neutral at pH$_f$ = 6.5–6.6, and (iii) negative at pH$_f$ > 6.6.

The mechanism involved in the fluoride adsorption process using Al/Fe dispersed in porous granular ceramics can be described by the following equations, where M is Al^{3+} and Fe^{3+} bound to porous granular ceramics.

$$MCl_{(s)} + H_2O \rightarrow MOH_{(s)} + H_{(aq)}^+ + Cl_{(aq)}^+ \tag{2}$$

$$MOH_{(s)} + H_3O_{(aq)}^+ + F^- \rightarrow MOH_2^+ \cdots F_{(s)}^- + H_2O \tag{3}$$

$$MOH + H_3O^+ \rightarrow M^+ \cdots F_{(s)}^- + 2H_2O \tag{4}$$

It was evident from our results that the granular ceramics exhibited significantly fluoride removal in the acidic pH range (the fluoride removal is 86.7% at pH 4, which is similar to the maximal value 89.3% at pH 6). This may be due to the fact that for pH$_i$ < pH$_{zpc}$, the positive adsorbent surface adsorbed fluoride with electrostatic force of attraction (Eq. (3)) or by exchange of hydroxyl ion on the solid surface (Eq. (4)). The minimal fluoride removal at pH < 4 may be attributed to the formation of HF, which would reduce the coulombic attraction between fluoride and the adsorbent surface [1]. The decrease in the amount of fluoride adsorbed at pH > 6 is probably due to competition for adsorption sites between fluoride and hydroxyl ions even though the oxide surface is positively charge [30]. The mechanism as suggested are found to be similar to that had been reported for fluoride adsorption by iron (III)–aluminum (III)–chromium (III) ternary mixed oxide [31], concrete materials [32] and activated cerium (IV) oxide/SiMCM-41 adsorbent [33].

3.4. Effect of co-existing anions

The fluoride-contaminated water may contain several other anions which may compete with fluoride ions in the adsorption process. The present study assessed fluoride adsorption behavior in the presence of 200 mg/L chloride, nitrate, sulfate, carbonate, and phosphate ions, with initial fluoride concentration of 10 mg/L. As can be seen from Fig. 4, it was observed that carbonate and phosphate showed extremely negative effect, nitrate showed slightly positive effect while chloride and sulfate really did not affect the fluoride removal. The slight increase in fluoride removal in the presence of nitrate ion could be due to an increase in the ionic strength of the solution or a weakening of lateral repulsion between adsorbed fluoride ions. While the carbonate and phosphate ions decreased the fluoride adsorption may attribute to the high coulombic repulsive forces, which reduce the probability of fluoride interactions with the active sites. Besides, the pH of the fluoride solutions was 6.15, 6.45, 6.57, 10.34 and 10.78, respectively, for Cl$^-$, NO$_3^-$, SO$_4^{2-}$,
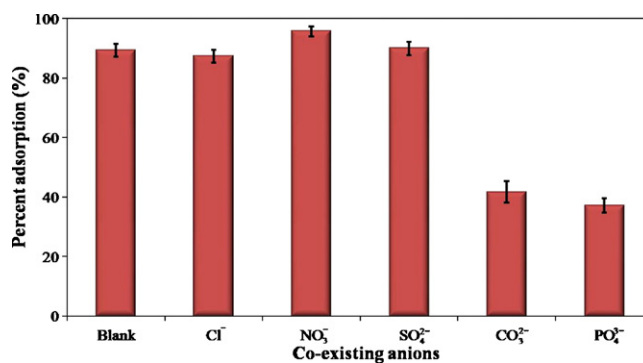
Fig. 4. Effect of co-existing anions on fluoride removal (adsorbent dose 20 g/L, initial fluoride concentration 10 mg/L, equilibrium contact time 48 h and temperature 25 ± 1 °C).

CO$_3^{2-}$ and PO$_4^{3-}$, while the initial pH of the fluoride solution was 6.9 without the addition of salt/anions. It was also confirmed from the experiment on the effect of pH (Section 3.3), that fluoride removal decreases in highly alkaline pH. Similar observations have been reported by Eskandarpour et al. and Kagne et al. [34,23].

3.5. Adsorption isotherms

The distribution of fluoride ion between the liquid and solid phase is a measure of the position of equilibrium in the adsorption process which can be expressed by the Freundlich and Langmuir isotherm models.

Freundlich equation is derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces. The linearized form of Freundlich model is formulated as [35]:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{5}$$

where C_e is equilibrium concentration, q_e is equilibrium adsorption capacity, K_F and $1/n$ are Freundlich constants, related to minimum adsorption capacity and adsorption intensity, respectively. The values of K_F and $1/n$ were obtained from the slope and intercept of the linear Freundlich plot of log q_e versus log C_e, and the results were shown in Table 2. It was found that the value of adsorption intensity ($1/n$ = 0.468) is less than unity, which indicates favorable in the fluoride adsorption process [36].

Langmuir adsorption isotherm models the monolayer coverage of the adsorption surfaces and assumes that adsorption take places on a structurally homogeneous surface of the adsorbent. The linear form of the Langmuir model can be presented as [37]:

$$\frac{1}{q_e} = \frac{1}{q_{max} b C_e} + \frac{1}{q_{max}} \tag{6}$$

where C_e is the concentration of fluoride at equilibrium, q_e is the adsorption capacity at equilibrium, q_{max} is the monolayer capacity of the adsorbent and b is the Langmuir adsorption constant. The values of Langmuir parameters, q_{max} and b were calculated from the slope and intercept of the linear plots of $1/q_e$ versus $1/C_e$ and were found to be 1.788 mg/g and 0.313 L/mg, respectively, with regression coefficient (R^2) of 0.995.

Table 2
Langmuir and Freundlich isotherm parameters for the adsorption of fluoride on Al/Fe dispersed in porous granular ceramics.

Langmuir isotherm		Freundlich isotherm	
q_{max} (mg/g)	1.788	$1/n$	0.468
b (L/mg)	0.313	K_F (mg/g)	0.386
R^2	0.995	R^2	0.976

Table 3
Kinetics parameters for adsorption of fluoride onto Al/Fe dispersed in porous granular ceramics.

Initial F⁻ conc. (mg/L)	Pseudo-first order			Pseudo-second order			Intra-particle diffusion	
	k_1 (min⁻¹)	q_e (mg g⁻¹)	R^2	k_2 (g(mg⁻¹ min⁻¹))	q_e (mg g⁻¹)	R^2	k_i (mg g⁻¹ min¹ᐟ²)	R^2
10.00	0.055	0.231	0.975	0.371	0.483	0.995	0.034	0.987

The essential characteristic of the Langmuir isotherm can be denoted by the dimensionless constant called equilibrium parameter, R_L, defined by [38]:

$$R_L = \frac{1}{1 + bC_o} \tag{7}$$

where b is the Langmuir constant and C_o is the initial fluoride concentration (mg/L). The value of $R_L < 1$ represents favorable adsorption and $R_L > 1$ represents unfavorable adsorption [39]. The value of R_L for an initial fluoride concentration of 10 mg/L is found to be 0.242, which indicates that this system is favorable for adsorption.

3.6. Adsorption kinetics

The effect of contact time was studied up to 72 h at initial fluoride concentration of 10 mg/L, adsorbent dose of 20 g/L, initial solution pH of 6.9, temperature of 25 °C. The results showed that loading capacity was 0.4464 mg/g, and the equilibrium was attained within 48 h. According to the kinetic data obtained from the experiments, pseudo-first-order and pseudo-second-order kinetic models were used to elucidate the mechanisms of adsorption and potential rate controlling steps [40,41].

$$\log(q_e - q_t) = \frac{\log q_e - k_1 t}{2.303} \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

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. The adsorption rate constant k_1 was determined from the slope of the linear plot of $\log(q_e - q_t)$ versus t (Fig. 5a), and k_2 was obtained by plotting t/q_t versus t (Fig. 5b). The adsorption kinetic constants obtained from the pseudo-first and pseudo-second order models are shown in Table 3. The kinetic data indicates that the fluoride adsorption on Al/Fe dispersed in porous granular ceramics obeys the pseudo-second order kinetic model ($R^2 = 0.995$) more than pseudo-first order kinetic model ($R^2 = 0.975$), which suggests a chemisorption process in this experiment.

The possible contribution of intra-particle diffusion on fluoride adsorption process was described by using Weber–Morris model. The linear form of intra-particle diffusion model is given by [42]:

$$q_t = k_i t^{1/2} + C \tag{10}$$

where k_i can be calculated from the slope of the plot of q_t versus $t^{1/2}$. As shown in Fig. 5c, the linear portion of plot is not passing through the origin, which indicates the fluoride adsorption on Al/Fe dispersed in porous granular ceramics is a complex procedure. Both the surface adsorption as well as intra-particle diffusion contributes to the rate determining step [28,38]. Since the pore size of adsorbent is larger than fluorine radius (Section 3.1), it is conductive to the penetration of F⁻ ion inside the pore structure of granular ceramic adsorbents.

3.7. Adsorbent recoating

Regeneration of any exhausted adsorbent is a crucial factor in any sorption process for improving the process economics. In

the present study, 0.1 M HCl and NaOH were used as an eluent to check its eluting potential. From the results, it was observed that 0.1 M HCl could elute nearly 85% adsorbed fluoride from porous granular ceramics. Then the adsorption study was carried out using 20 g/L fluoride-desorbed adsorbents with initial fluoride concentration of 10 mg/L. The results showed that a considerable reduction in adsorption efficiency after the regeneration, which may be attributed to the gradual dissolution of coated layer from the surface during vigorous washing of the adsorbent. Hence, a new recycle protocol was developed by recoating the exhausted adsorbent before adsorption. For this, after desorption process using 0.1 M HCl, the exhausted granular ceramic adsorbents were dipped in 1 M AlCl₃ and FeCl₃ solutions for 2–3 h. The mixture were dried and calcined at 600 °C and used for next adsorption cycle. After the
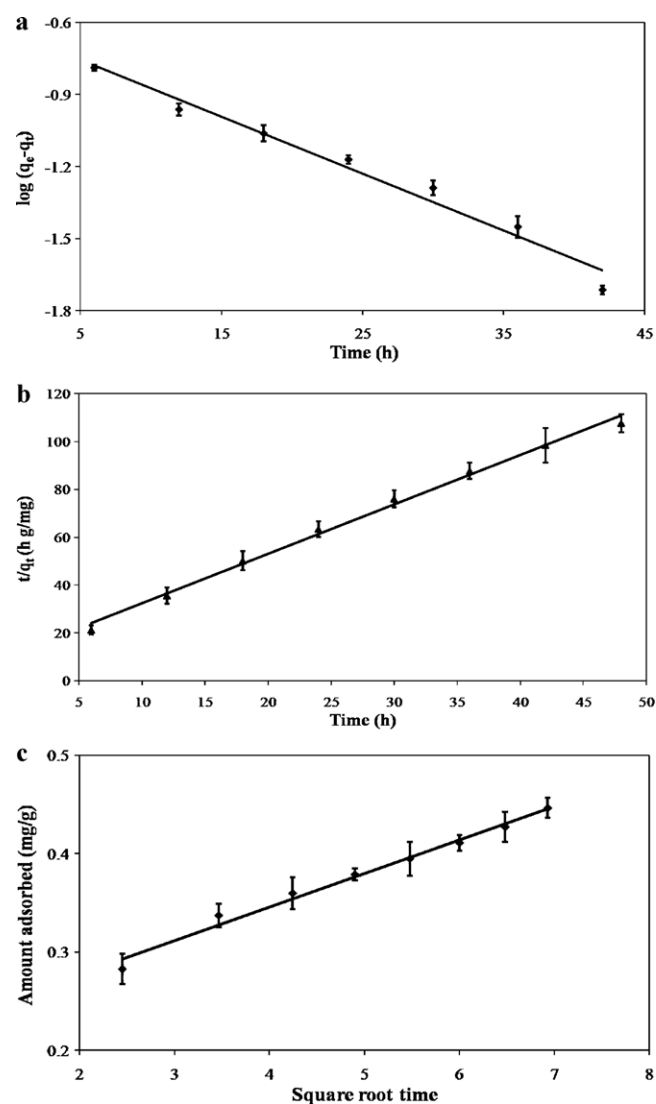
Fig. 5. (a) Pseudo-first-order kinetic plot for fluoride removal. (b) Pseudo-second-order kinetic plot for fluoride removal. (c) Intra-particle diffusion plot for fluoride removal. (adsorbent dose 20 g/L, initial pH 6.9 ± 0.1, initial fluoride concentration 10 mg/L, equilibrium contact time 48 h and temperature 25 ± 1 °C).

adsorption experiment, it was found that adsorption efficiency of adsorbent after recoating was no reduction.

4. Conclusion

In the present study, Al and Fe dispersed in porous granular ceramics were prepared by the impregnation with aluminum and iron chloride salts followed by a precipitation process. These low-cost adsorbents showed a good efficiency in fluoride removal from aqueous solution and could be useful for environmental protection purposes. The loading capacity of these prepared adsorbents for fluoride was 1.79 mg/g at room temperature. The optimum fluoride removal was observed at pH ranges of 4.0–9.0 indicating that the adsorbent has promising potential utility in practical application. Carbonate and phosphate ions showed extremely negative effect, nitrate ion showed slightly positive effect while chloride and sulfate ions really did not affect the fluoride removal capacity. The adsorption process was fitted well with both the Freundlich and Langmuir isotherm models. Kinetic study results indicated that the adsorption process followed a pseudo-second-order kinetic model. Therefore, the elaborated porous granular ceramics with mixed aluminum and iron oxides have a good potential by promising environmental materials for fluoride removal from aqueous solution.

Acknowledgements

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