

## Removal of fluoride ions from aqueous solution at low pH using schwertmannite

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### Abstract

Wastewater containing fluoride requires polishing after precipitation/coagulation treatment in order to meet stringent environmental legislation. Accordingly, adsorption characteristics of fluoride onto schwertmannite adsorbent were studied in a batch system with respect to changes in initial concentration of fluoride, equilibrium pH of sample solution, adsorbent dosage and co-existing ions. Equilibrium adsorption data were obtained at 295.6, 303 and 313 K, and are interpreted in terms of two-site Langmuir, Freundlich, Langmuir–Freundlich, Redlich–Peterson, Tóth and Dubinin–Radushkevitch isotherm models. The experimental and equilibrium modeling results revealed that the capacity of schwertmannite for fluoride is high but insensitive to changes in solution temperature. An increase in equilibrium pH of sample solution reduced significantly the fluoride removal efficiency. In binary component systems, inner-sphere complex forming species had negative effects on fluoride adsorption while outer-sphere complex forming species improved slightly the fluoride removal efficiency. The schwertmannite adsorbent was regenerable and had the ability to lower the fluoride concentration to acceptable levels.

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### 1. Introduction

Management of health hazardous ions such as fluoride is of public health interest since fluoride is responsible for teeth mottling and bone fluorosis. Wastewater from hydrofluoric, metal plating, soldering, glass, phosphate fertilizer, semi-conductor and other electronic industries are low in pH and contain high levels of fluoride. Due to strict environmental policies, however, industrial concerns are bound by law to treat waste streams to acceptable discharge standards. The current discharge standards for wastewater containing fluoride vary from country to country. For instance, Japan recommends a value below 5–15 mg F/L [1], which vary from one prefecture to another, Poland legislation recognizes discharge standard of 25 mg F/L [2], in India the standard varies from 1.5 to 10 mg F/L [3], 15 mg F/L in Taiwan [4] and 10 mg F/L in China [5]. Treatment of wastewater containing

fluoride ions requires a robust and an effective technique. Due to the high concentration of fluoride in the industrial effluent, the most popularly applied separation technology for removing fluoride from wastewater is the precipitation/coagulation technique. However, achieving low concentration using precipitation technique seems to be impossible or requires use of excess amount of precipitating agent. Moreover, the technique generates a lot of water containing very small particles that poses disposal problems. Recently, innovative techniques such as membrane filtration [3,6], electrocoagulation–flotation [4,7], electrochemical [5], fluidized-bed precipitation [8], ion exchange [9] and adsorption [1,10–12] have been studied for the fluoride removal from wastewater.

Among the potential separation technologies mentioned above, adsorption is arguably one of the most suitable techniques for polishing wastewater streams, especially after precipitation/coagulation process. By polishing waste streams using adsorption technique, it is possible to meet the permissible levels of fluoride defined by most legislations. Furthermore, the technique is relatively low in cost, robust, environmentally benign

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and simple [13]. A starting point in the development of an adsorption unit is the choice of an adsorbent among the various adsorbent candidates. Hundreds of adsorbents for fluoride adsorption have been presented in literature. Among these, only a few such as surface-tailored zeolites [14], activated aluminas [15],  $\text{La}^{3+}$ -impregnated cross-linked gelatin [10], alumina supported on carbon nanotubes [16] have appreciable capacity for fluoride. The authors of most previous works of fluoride adsorption had interest in applying their adsorbents in treating drinking water. Actually, the materials showed good performances near neutral pH values. It is probable that most of those materials would not be stable at extreme pH values and therefore may not have application value to polishing industrial wastewaters containing fluoride unless the pH is adjusted. Schwertmannite on the other hand is stable at low pH and has magnetic properties. It exists naturally as geomineral but can also be synthesized. Synthetic schwertmannite has a probable formula of  $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ . If used in powdered form, it can easily and simply be separated using the external magnetic field and thus the adsorbent can easily be reused [17]. It has also been shown to have strong affinity for chromate and arsenate anions [18].

Successful and cost-effective removal of contaminants from wastewater by adsorption requires optimal operation of the adsorption units. To achieve this, design parameters must first be obtained through performance of adsorption equilibrium and kinetic experiments. The equilibrium data, which forms the backbone of this study, is normally generated in a simple batch experimental set up. Once such data is generated, it is a common practice to validate various isotherm models in an attempt to choose a model(s) that gives the best description of the experimental results. The frequently tested isotherm models are the Langmuir, two-site Langmuir, Freundlich, Langmuir–Freundlich, Redlich–Peterson, Tóth and Dubinin–Radushkevich isotherms. The details of these models are easily available in literature. These isotherms can be grouped into two- or three-parameter models.

This work is part of a wider project in which we apply schwertmannite in removing health and environmentally hazardous inner-sphere complex forming species from water. Previously, we showed that schwertmannite has a very high capacity for phosphate ions [17]. In the current study, the fluoride adsorption characteristics of schwertmannite at low solution pH are studied in equilibrium adsorption experiments, with specific interest to apply this adsorption media to polish wastewater. Two- and three-parameter equilibrium isotherm models are validated using equilibrium adsorption data. In other sets of experiments, the effect of equilibrium pH, the ability to achieve permissible levels and the ability to regenerate and reuse the adsorbent are tested. Finally, binary component systems are used to study the effect of co-existing ions on fluoride removal efficiency.

## 2. Materials and methods

### 2.1. Preparation and characterization of schwertmannite

Schwertmannite sample was prepared, using a wet chemical process whereupon urea was used as a neutralizing agent [17].

The urea solution was made by dissolving 150 g of urea into 500 mL of distilled water, and  $\text{Fe}_2(\text{SO}_4)_3$  solution was made by dissolving about 25 g of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  in 500 mL of distilled water. The urea solution was added drop wise for about 2–4 h into the  $\text{Fe}_2(\text{SO}_4)_3$  solution preheated at 343 K in a beaker. The precipitates formed were dried at temperatures less than 313 K. After preparing schwertmannite, measurements of zeta potentials at various pHs were carried out using an electrophoretic light scattering spectrophotometer and XRD pattern of the schwertmannite sample was obtained by using  $\text{Cu K}\alpha$  radiation at 40 kV and 40 mA over the  $2\theta$  range of 15–50°. For structural characterization, a scanning electron microscope (SEM) was used while the internal surface area was determined by the BET method.

### 2.2. Batch equilibrium adsorption experiment

Data for sorption isotherm were generated by contacting 0.05 g of schwertmannite with fluoride-containing aqueous solutions at  $\text{pH}_e$  3.8. Samples of 50 mL of the fluoride ion solutions at concentrations ranging from 10 to 90 mg/L were pipetted into 100-mL plastic bottles. The bottles were placed in a thermostatic shaker and shaken for 1 day at 295.6, 303 and 313 K. The shaking speed was set at 150 strokes per minute (spm). At the end of the experiment, samples were withdrawn from the test bottles and filtered through a 0.2- $\mu\text{m}$  syringe filter and residual fluoride concentration was measured by a fluoride-ion-selective electrode (Horiba, Japan). The equilibrium sorption capacity was determined from

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where  $C_0$  (mg F/L) is the initial concentration,  $C_e$  (mg F/L) the concentration at equilibrium,  $q_e$  (mg F/g) the amount adsorbed at equilibrium,  $m$  (g) the adsorbent mass and  $V$  (L) is the solution volume.

### 2.3. Effect of equilibrium pH

Experiments were carried out by varying initial solution pH values within the range of 3–11, using either 0.1 M NaOH or 0.1 M HCl, according to the same procedure and analytical technique used to generate adsorption isotherm data. Accordingly, adsorption was done by adding 0.05 g of schwertmannite to 50 mL of 10 mg/L fluoride solution contained in plastic bottles. The bottles were placed in a thermostatic shaker and operated for 1 day under the same conditions described above. The equilibrium pH ( $\text{pH}_e$ ) was measured and assumed to be the pH at which adsorption was done.

### 2.4. Test for regulatory compliance

The ability of schwertmannite to reduce fluoride to acceptable levels at  $\text{pH}_e$  3.8 was tested by varying the amount of the adsorbent from 0.025 to 0.10 g. A given amount of the adsorbent was added to 50 mL of 10 mg/L fluoride solution contained in plastic bottles at  $\text{pH}_e$  3.8. The bottles were placed in a thermo-

static shaker and were agitated at 150 rpm for 1 day. At the end of the experiment, samples were withdrawn from the test bottles and filtered through a 0.2- $\mu\text{m}$  syringe filter and residual fluoride ion concentration was measured by a fluoride-ion-selective electrode.

### 2.5. Binary component system

The effect of co-existing ions was explored at  $\text{pH}_e$  3.8 in binary components adsorption. The ions considered were chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), sulfate ( $\text{SO}_4^{2-}$ ) and phosphate ( $\text{PO}_4^{3-}$ ). To obtain data for fluoride sorption at equilibrium in  $\text{F}^-/\text{Cl}^-$ ,  $\text{F}^-/\text{NO}_3^-$ ,  $\text{F}^-/\text{SO}_4^{2-}$  and  $\text{F}^-/\text{PO}_4^{3-}$  binary component systems, 0.05 g of schwertmannite adsorbent was contacted with aqueous solutions containing 10 mg/L fluoride at 295.6 K. The concentrations of coexisting ions were varied from 0 to 80 mg/L. Samples of 50 mL solution containing fluoride and a co-existing ion were pipetted into 100 mL plastic bottles. The bottles were placed in a thermostatic shaker and shaken for 1 day. At the end of the experiment, samples were withdrawn from the test bottles and filtered through a 0.2- $\mu\text{m}$  syringe filter and the residual fluoride concentration measured by fluoride ion selective electrode. By carrying appropriate material balance, the quantities of fluoride adsorbed were determined.

### 2.6. Adsorption–desorption cycle

A single adsorption–desorption cycle was tested. Initially, using a similar procedure described in Section 2.2, 7.9 mg F/g was loaded onto schwertmannite adsorbent. The desorption of fluoride loaded on schwertmannite particles and the regeneration of the adsorption media were done at pH 2. After the regeneration, the ability of schwertmannite adsorbent to remove fluoride from solution was again tested in an adsorption experiment, using a similar procedure to that described in Section 2.2.

### 2.7. Analyses

The residual fluoride concentration was measured by Horiba (Japan) fluoride-ion-selective electrode according to the Japanese Standard Method (JIS K0102). Accordingly, a calibration curve was initially prepared by recording potential values for a range of known fluoride concentration, mostly 0.1–5.0 mg/L. To ensure that other ions did not interfere with the fluoride measurements [5], total ionic adjustment buffer solution (TISAB, pH 5.3) containing 58 g NaCl, 1 g diammonium hydrogen citrate, 50 mL acetic acid and an appropriate amount of 5 M NaOH all in a volume of 1 L was prepared and used during fluoride ions concentration measurements.

## 3. Results and discussion

### 3.1. Adsorption media characterization

Schwertmannite is an iron oxide hydroxide material with a poorly crystalline structure, high specific surface area ( $162 \text{ m}^2/\text{g}$ )

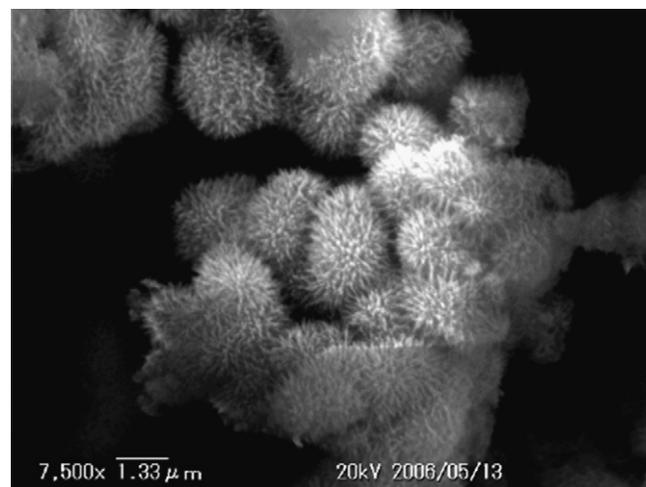


Fig. 1. SEM map of schwertmannite showing microparticles of size of  $\approx 2 \mu\text{m}$ .

and is brownish yellow in color. In water, it has a pH of about 2.9. Because of its poor crystallinity and meta-stability, it was unknown as a mineral until a few years ago. The scanning electron microscope (SEM) map (see Fig. 1) shows that schwertmannite is characterized by near spherical, hedge-like, crystal aggregates in which needle-like structures with average width and thickness of 2–4 nm and length of 60–90 nm radiate from the particle surfaces to form a “pincushion” morphology. Fig. 2 shows the XRD pattern of the schwertmannite sample used in this study. The material is poorly crystalline with some broad peaks especially between  $30.00^\circ$  and  $40.00^\circ$ . Such observation was reported by Fukushi et al. [19]. The electrokinetic property of schwertmannite was explored by measuring its zeta potential at various pH values. The result shows that the isoelectric point of schwertmannite particles is about 4.2 (see Fig. 3). At pH below 4.2, the particles are positively charged while negative charge is retained on the particles at pH above 4.2. In Fig. 3 typical active sites; protonated, neutral and deprotonated, that may be found in schwertmannite in the positive and negative zeta potential regimes are also included.

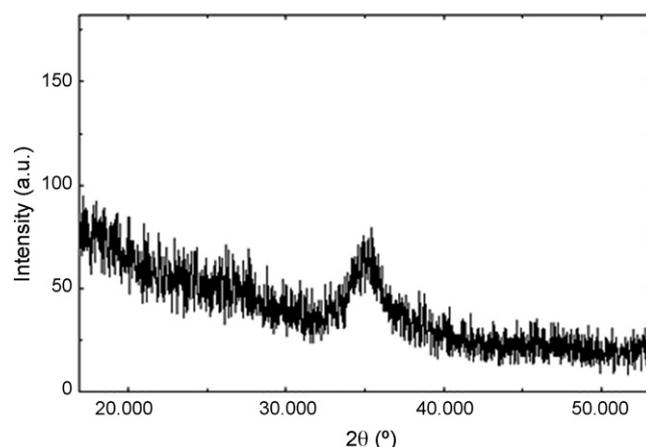


Fig. 2. XRD pattern of the schwertmannite sample.

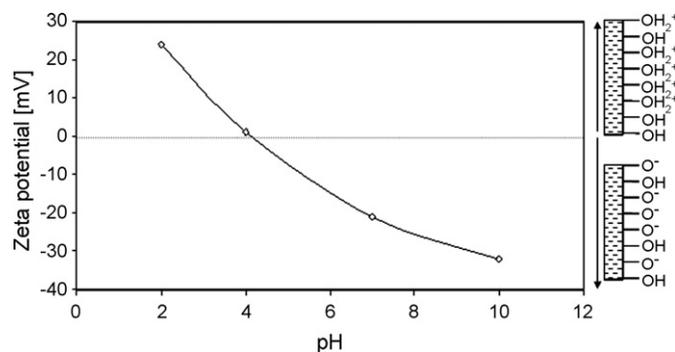


Fig. 3. Zeta potential measurements of the schwertmannite sample. Illustrations showing the nature of the active sites in the positive and negative zeta potential regions are also included.

### 3.2. Batch adsorption equilibrium

Equilibrium data is important in evaluating the adsorption capacity of an adsorbent for a given adsorbate. Information derived from such data is important also in comparing different adsorption media. In Fig. 3, it was shown that schwertmannite is amphoteric in nature. This is a common phenomenon with iron-based adsorbents, which has also been reported by Wang and Reardon [20] and Hiemstra and van Riemsdijk [21]. At low pH, the active sites, being positively charged, have a strong binding power for anionic ligands through the formation of inner-sphere complexes. In this section, fluoride adsorption results at low pH are presented in the form of equilibrium isotherms. If the effective active sites are assumed to consist of protonated and neutral sites, which are distributed non-uniformly, then it is justifiable to describe the equilibrium data with the two-site Langmuir, Freundlich, Langmuir–Freundlich, Redlich–Peterson, Tóth and Dubinin–Radushkevitch isotherms summarized in Table 1. The fitting procedure of these models was presented in details in an earlier publication [14].

Table 1  
Summary of equilibrium isotherms

Isotherm	Equation
Two-site Langmuir	$q_e = \frac{q_1 b_1 C_e}{1 + b_1 C_e} + \frac{q_2 b_2 C_e}{1 + b_2 C_e}$ (2)
Freundlich	$q_e = K_F C_e^{1/n}$ (3)
Langmuir–Freundlich	$q_e = \frac{K_{LF} C_e^{1/n}}{1 + a_{LF} C_e^{1/n}}$ (4)
Redlich–Peterson	$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{1/n}}$ (5)
Tóth	$q_e = \frac{q_m C_e}{[a_t + C_e^t]^{1/t}}$ (6)
Dubinin–Radushkevitch	$\frac{q_e}{q_m} = \exp(-K \varepsilon^2)$ (7)

$K_F$ ,  $K_{LF}$ ,  $K_{RP}$ : Freundlich, Langmuir–Freundlich, and Redlich–Peterson constants (L/g);  $b_1$ ,  $b_2$ ,  $a_{LF}$ ,  $a_{RP}$ : affinity coefficients (L/mgF);  $1/n$  and  $t$ : heterogeneity coefficient [–];  $q_m$ : maximum adsorption capacity (mg F/g);  $q_e$ ,  $q_1$ , and  $q_2$ : uptake at equilibrium (mg F/g); 1 and 2: high- and low-energy sites;  $\varepsilon$ : Polanyi potential (kJ/mol);  $K$ : constant ( $\text{mol}^2/\text{kJ}^2$ );  $C_e$ : equilibrium concentration (mg F/L);  $a_t$ : adsorptive potential constant ((mg F/L) <sup>$t$</sup> ).

The interactions between schwertmannite and fluoride at 295.6, 303 and 313 K resulted in fluoride removal from water, and are presented in the form of equilibrium data (experimental data points) in Fig. 4. From the experimental data, the fitting of several equilibrium models was tested. During the fitting, normalized standard deviation (Eq. (8)) was used as the objective function to be minimized:

$$\phi = 100 \sqrt{\frac{\sum ((q_{\text{exp}} - q_{\text{cal}})/q_{\text{exp}})^2}{N_i - 1}} \quad (8)$$

where  $q_{\text{exp}}$  (mg F/g) is the experimental fluoride uptake,  $q_{\text{cal}}$  (mg F/g) the calculated amount of fluoride ion adsorbed and  $N_i$  is the number of data points. Table 2 summarizes the isotherm parameters. The two-site Langmuir capacity ( $q_m$ ) of the adsorption media is 50.2–55.3 mg F/g. Modeling results show further

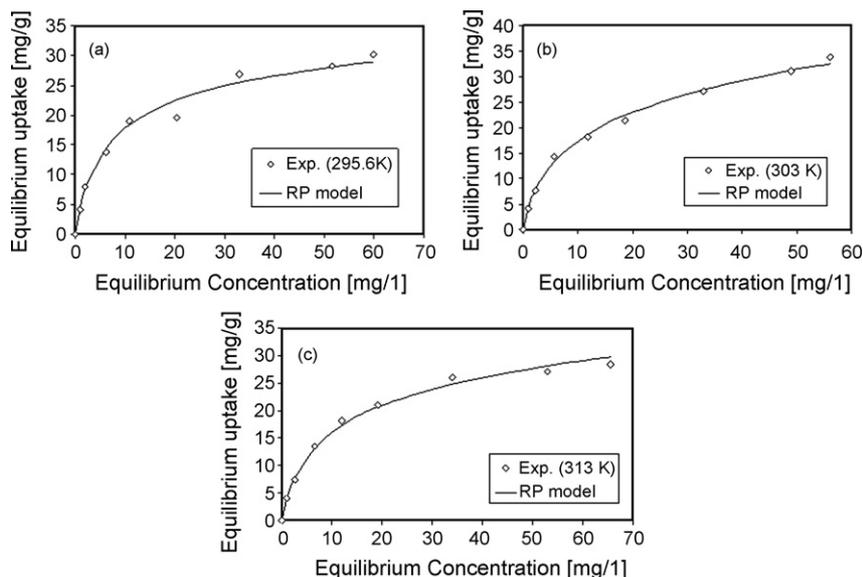


Fig. 4. Fluoride uptake by schwertmannite at different temperatures: (a) 295.6 K, (b) 303 K and (c) 313 K. Solid lines represent the Redlich–Peterson model simulation: adsorbent dose, 1 g/L;  $\text{pH}_c$  3.8; agitation speed, 150 rpm.

Table 2  
Summary of equilibrium isotherm parameters

Temperature (K)	Two-site Langmuir isotherm					
	$q_1$	$q_2$	$q_m$	$b_1$	$b_2$	$\phi$
295.6	33.3	22.0	55.3	0.12	$5.7 \times 10^{-4}$	10.1
303.0	27.2	23.0	50.2	0.19	$3.4 \times 10^{-3}$	7.9
313.0	31.8	23.0	54.8	0.12	$3.4 \times 10^{-3}$	5.8
Temperature (K)	Freundlich isotherm					
	$K_F$	$1/n$		$R^2$	$\phi$	
295.6	5.2	0.45		0.958	14.5	
303.0	5.1	0.48		0.979	10.4	
313.0	4.7	0.47		0.955	15.2	
Temperature (K)	Langmuir–Freundlich isotherm					
	$K_{LF}$	$1/n$	$a_{LF}$	$R^2$	$\phi$	
295.6	5.3	0.77	0.14	0.995	4.9	
303.0	5.1	0.67	0.09	0.994	5.3	
313.0	4.2	0.91	0.13	0.997	2.7	
Temperature (K)	Redlich–Peterson isotherm					
	$K_{RP}$	$1/n$	$a_{RP}$	$R^2$	$\phi$	
295.6	5.6	0.89	0.28	0.994	6.9	
303.0	6.8	0.76	0.50	0.997	4.0	
313.0	5.1	0.82	0.33	0.997	4.0	
Temperature (K)	Tóth					
	$q_m$	$t$	$a_t$	$R^2$	$\phi$	
295.6	64	0.40	1.81	0.993	8.2	
303.0	69.5	0.44	2.32	0.997	4.4	
313.0	64	0.42	1.92	0.994	7.7	
Temperature (K)	Dubinin–Radushkevich isotherm					
	$q_m$	$K$	$E$	$R^2$	$\phi$	
295.6	89.1	$5.0 \times 10^{-3}$	10.0 (ion exchange)	0.981	9.9	
303.0	97.7	$5.2 \times 10^{-3}$	9.80 (ion exchange)	0.993	6.0	
313.0	86.6	$5.1 \times 10^{-3}$	9.90 (ion exchange)	0.981	9.8	

that the adsorption capacity of fluoride ions for the higher energy sites,  $q_1$ , was >50% of the total sorption capacity ( $q_m$ ) for the three temperatures studied. When the predicted affinity parameter of the two kind of sites were considered, the higher energy sites had a significantly large affinity coefficient, i.e.  $b_1 \gg b_2$  (see Table 2). This implies that, within the range of concentration considered in this study, fluoride was mostly adsorbed on the high-energy sites. Meanwhile, the adsorption capacity of schwertmannite is higher than the fluoride carrying capacity of novel materials such as surface tailored aluminas, zeolites and carbon nanotubes [14–16].

Experimental data was further fitted to the Freundlich model (Eq. (3)) by a non-linear regression technique to determine the isotherm parameters. The Freundlich parameters are summarized in Table 2. The constant related to the adsorption capacity,  $K_F$ , is 5.24, 5.10 and 4.74 for 295.6, 303 and 313 K, respectively. The heterogeneity coefficient,  $1/n$ , on the other hand is 0.45, 0.48

and 0.47 for 295.6, 303 and 313 K, respectively. The  $1/n$  values are less than 1 and suggest that the schwertmannite adsorbent was heterogeneous in nature. Based on the values of regression coefficients and normalized standard deviation, the Freundlich isotherm seems not to fit data well. In order to improve data fitting, three-parameter models were also considered.

The three-parameter models, Langmuir–Freundlich (Sips isotherm) and Redlich–Peterson, were both linearized and their fitting validity tested against the experimental data. As an example, Fig. 5 shows the linear plots of the Redlich–Peterson model, for various operating temperatures. The regression coefficients and normalized standard deviations obtained during data fitting suggest that both the isotherms describe the present adsorption system sufficiently well. From the plots, the isotherm parameters were extracted and are summarized in Table 2. The parameters do not show any particular trend with a variation in solution temperature. The heterogeneity coefficient,  $1/n$ , is

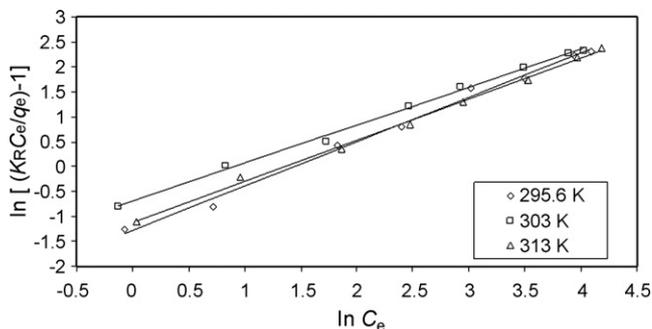


Fig. 5. Fitting equilibrium experimental data presented in Fig. 4 to the linear form of Eq. (5).

less than 1 suggesting that the equilibrium results deviate from the classical Langmuir isotherm. The Tóth isotherm is also a three-parameter model that describes adsorption on heterogeneous surfaces. Its fitting validity was tested and the parameters are summarized in Table 2 for the three temperature values used in this study. In agreement with the experimental data, the Tóth isotherm parameters are insensitive to changes in solution temperature. The predicted adsorption capacity for schwertmannite is 64–69.5 mg F/g. The predicted capacity is higher than that predicted by two-site Langmuir isotherm.

To determine the Dubinin–Radushkevich parameters, linear plots (not shown) of  $\ln q_e$  versus  $\varepsilon^2$ , for the uptake of fluoride by schwertmannite at 295.6, 303 or 313 K were constructed. From the linear plots, the negative slope and intercept were used to determine the numerical values of  $K$  and  $q_m$ , respectively. The  $K$  values are 0.005, 0.0052, 0.0051 mol<sup>2</sup>/kJ<sup>2</sup> and the  $q_m$  values are 89.1, 97.7 and 86.6 mg/g for 295.6, 303 and 313 K, respectively. To evaluate the nature of interaction between fluoride and the binding sites, mean free energy of adsorption ( $E = (2K)^{-0.5}$ ) per mole of the adsorbate, which is the energy required to transfer one mole of fluoride to the schwertmannite surface from infinity in solution, was determined. If the magnitude of  $E$  is between 8 and 16 kJ/mol, the adsorption process proceeds by ion exchange, while for values of  $E < 8$  kJ/mol, the adsorption process is of a physical nature [14,22]. The free energies of adsorption of fluoride onto schwertmannite were 10.0, 9.80 and 9.90 for operation at 295.6, 303 and 313 K, respectively, suggesting that the interaction between fluoride and the schwertmannite proceeded by ion exchange. This mechanism is widely reported for fluoride adsorption [14,23–25]. A critical assessment of the predicted adsorption capacity of fluoride gives an impression that the Dubinin–Radushkevich model over-predicts the capacity values and thus is not suitable for the present adsorption system.

As mentioned previously, the objective function that was considered in comparing the various models was the normalized standard deviation,  $\phi$ . Low values of  $\phi$  suggest good fit. Assessment of the  $\phi$  values alone summarized in Table 2 suggests that all the isotherms, except the Freundlich isotherm, predicted the experimental data satisfactorily well. This is because the computed  $\phi$  values for the Freundlich isotherm are relatively high and moreover, the regression coefficients are low. Among the best-fitting isotherms, the Dubinin–Radushkevich isotherm is

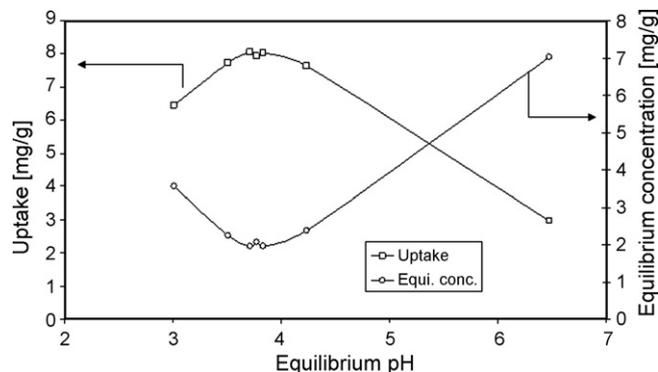
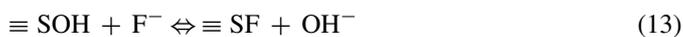
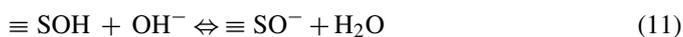


Fig. 6. Effect of equilibrium pH on fluoride removal from aqueous solution: adsorbent dose, 1 g/L; initial concentration, 10 mg F/L; agitation speed, 150 spm; temperature, 296.5 K.

not logically suitable since it predicts high adsorption capacity values. To give an indication of how good the models fitted the data set, the Redlich–Peterson (RP) model fitting is included in Fig. 4.

### 3.3. Effect of equilibrium pH

Fig. 6 shows a plot of fluoride uptake (left) and removal (right) from solution against equilibrium pH. Only acidic pH range is considered, as would be expected of fluoride-containing industrial wastewater. Between the pH 3.0 and pH 3.7, the uptake of fluoride increases with an increase in pH. Maximum adsorption occurs at pH 3.7. Above pH 3.7, an increase in pH causes the fluoride removal efficiency to decrease sharply. To understand the fluoride adsorption behavior under different pH values, the following reactions are considered [14,23].



where  $\equiv \text{SOH}$ ,  $\equiv \text{SOH}_2^+$  and  $\equiv \text{SO}^-$  are the neutral, protonated and deprotonated sites on schwertmannite and  $\equiv \text{SF}$  is the active site-fluoride complex. Eq. (9) expresses the ionization of HF in solution at low pH. Because HF is weakly ionized ( $\text{p}K_a = 3.2$ ) in solution at low pH values, the corresponding uptake of fluoride is reduced when  $\text{pH} \leq 3.7$ , since a fraction of fluoride becomes unavailable for adsorption. When the adsorption system (fluoride solution/schwertmannite) is operated at  $\text{pH} > 3.7$  the reaction sites become deprotonated according to Eq. (11) leading to a reduction in fluoride adsorption due to increased repulsive forces between the negatively charged fluoride ions and the deprotonated sites. Similar trend was observed by Hingston et al. [26] in an adsorption system involving fluoride and goethite (ferric oxyhydroxides). In their case a sharp maximum in fluoride adsorption on ferric oxyhydroxide was observed at a pH 3. According to Eq. (13), fluoride adsorption on active sites is expected to cause an increase in solution

pH. This was not observed in our case since schwertmannite adsorbent had a strong tendency to lower the pH of solution. If hydroxyl ions were released, they may have competed fluoride for the adsorption sites.

### 3.4. Regulatory compliance

In assessing a given technique for wastewater purification, regulatory compliance is a key factor to consider in the screening strategy. The present work considers, as an example, a fluoride level below 5 mg/L, for the lower end Japanese standard, to be acceptable for discharge to receiving water bodies. Adsorption is only economical when applied to remove low-concentration health and environmental hazardous contaminants. In line with this, it is prudent to first apply a precipitation method to lower fluoride levels in wastewater then apply adsorption technique for further polishing [27]. Consequently, the ability of schwertmannite adsorbent to remove fluoride to acceptable level was tested by varying the masses of the schwertmannite adsorbent at fixed initial fluoride concentration of 10 mg/L. The 10 mg/L value [7] was tentatively chosen as a value below which application of a technique such as the precipitation technique will not environmentally and economically be viable in fluoride removal from wastewater. The results of the residual fluoride concentration against amounts of schwertmannite adsorbent are shown in Fig. 7. The residual fluoride concentration decreased with an increase in the amount of adsorbent due to an increase in the number of active sites. From an initial concentration of 10 mg/L, the schwertmannite was able to remove fluoride to concentrations below 5 mg/L (Japanese standard for wastewater (ww)) and 1.5 mg/L (WHO standard for drinking water and Indian standard for wastewater).

### 3.5. Binary component systems

This section of the study assesses fluoride adsorption behavior in the presence of two kinds of co-existing ions: those that form outer-sphere complexes (chloride, nitrate, sulfate) and those that form inner-sphere (sulfate, phosphate) complexes with binding surfaces. The concentration of fluoride ions was fixed at 10 mg/L while the co-existing ions concentration was varied from 0 to 80 mg/L. Fig. 8 presents the results of fluoride uptake

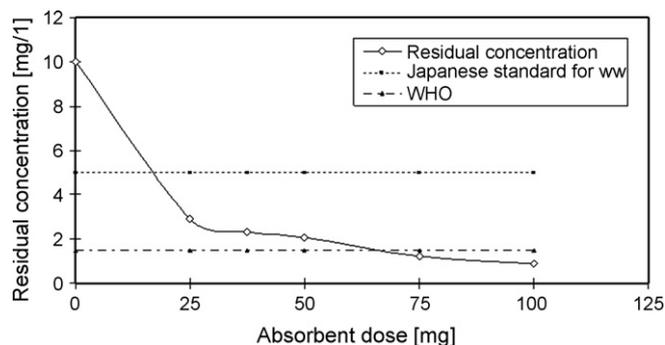


Fig. 7. Test for regulatory compliance: adsorbent dose, 1 g/L; initial concentration, 10 mg F/L, pH<sub>e</sub> 3.8; agitation speed, 150 spm; temperature, 296.5 K.

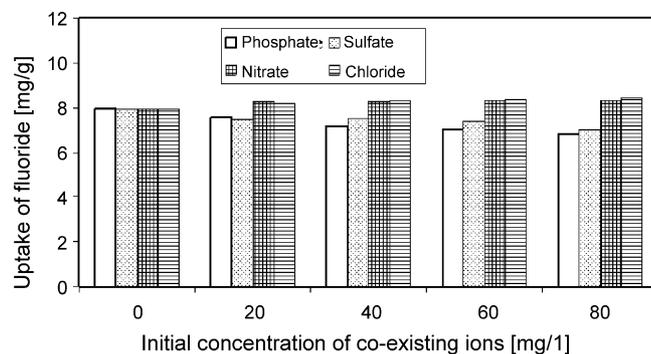


Fig. 8. Effect of co-existing anions on fluoride adsorption: adsorbent dose, 1 g/L; initial concentration, 10 mg F/L; pH<sub>e</sub> 3.8; agitation speed, 150 spm; temperature, 296.5 K.

by schwertmannite adsorbent as a function of initial concentration of the co-existing ions. On the one hand, the uptake of fluoride shows a slight increase in the presence of monovalent ions of chloride and nitrate. On the other hand, a decrease in fluoride uptake is observed in the presence of divalent ion (sulfate) or trivalent ion (phosphate).

Nitrate and chloride ions are low-affinity ligands. Their adsorption mechanism is via formation of weaker bonds with the active sites at the outer Helmholtz plane, i.e. outer-sphere complexation. Thus, their presence in solution would have no effect on fluoride adsorption since fluoride adsorbs through formation of strong bonds with active sites at the inner Helmholtz plane, i.e. inner-sphere complexation. The slight improvement in fluoride removal efficiency in the presence of nitrate and chloride could be due to an increase in the ionic strength of the solution and/or a weakening of lateral repulsion between adsorbed fluoride ions, which in turn lead to an increase in fluoride adsorption. Similar observation, though explained differently, has been reported by Onyango et al. [23] and Moreno-Castilla [28]. Another interesting observation in Fig. 8 is that at any given concentration of the nitrate and chloride ions, both give an almost the same equilibrium uptake of fluoride. It is known that ionic size of background electrolytes has effects on adsorption [29]. The latter observation is due to the fact that both Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> have the same ionic size, which is approximately 0.3 nm. Sulfate ions partially form outer-sphere complexes or inner-sphere complexes [14]. In the present adsorption system, the sulfate ion reduces the fluoride adsorption slightly. There are two possible causes for this observation. One, sulfate ion may have competed fluoride ion for the same adsorption sites since sulfate ion is partially inner-sphere complex forming species. Two, the presence of sulfate ion, a divalent anion, in solution may have increased the coulombic repulsive forces leading to reduced probability of fluoride interaction with the active sites. Of all the co-existing ions, phosphate presence in the reaction system had the largest effect on fluoride adsorption. A plausible explanation to this observation is that both the fluoride and phosphate ions competed for the same active site. This argument is bolstered by the fact that in our earlier study, we showed that schwertmannite adsorbent has high affinity and capacity for phosphate [17].

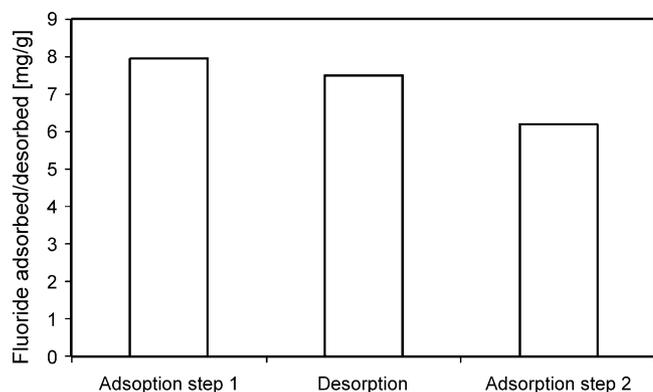


Fig. 9. Fluoride adsorption–desorption cycle: initial concentration 10 mg F/L; adsorbent dose 1 g/L, desorption/regeneration pH 2; agitation speed, 150 spm; temperature, 296.5 K.

### 3.6. Adsorption–desorption cycle

Wastewater purification by adsorption technology is economical if the adsorbent is regenerable. Moreover, reuse of adsorbent helps reduce environmental impacts of disposing used adsorbent. Initially, the schwertmannite adsorbent was loaded (adsorption step 1) with 7.9 mg F/g (see Fig. 9). Then, desorption of fluoride from the adsorbent and regeneration of the adsorbent were done at pH 2. About 94% of the loaded fluoride was desorbed, giving an indication that fluoride adsorption was somewhat reversible in nature. The small fraction of adsorbed fluoride that was not desorbable represented fluoride ion tightly bound to the schwertmannite particles. Upon application of the regenerated schwertmannite in fluoride adsorption, the adsorption capacity from a solution containing 10 mg F/L was found to be 6.2 mg/g (see Fig. 9 for adsorption step 2), representing 78% of the original capacity. The reduction in fluoride adsorption capacity was due to the fact that not all loaded fluoride could be desorbed. In addition the adsorption–desorption cycle was not optimized at this stage. The optimization is proposed for further studies, especially in column dynamic studies, to improve the adsorption–desorption cycle.

## 4. Conclusions

Fluoride adsorption onto schwertmannite was studied in the temperature range 295.6–313 K and was found to be insensitive to changes in solution temperature. Equilibrium solution pH had a remarkable effect on fluoride adsorption, suggesting that electrostatic coulombic attractive/repulsive forces played a major role in fluoride uptake. In simulating equilibrium data, simple models such as the two-site Langmuir, Freundlich, Langmuir–Freundlich, Redlich–Peterson, Tóth and Dubinin–Radushkevich isotherms were used. The model parameters were obtained and discussed. All the models gave satisfactory description of equilibrium data except the Freundlich isotherm. The Dubinin–Radushkevich isotherm though fitting the equilibrium data very well was logically inadmissible since it overestimated the adsorption capacity. The experimentally determined fluoride adsorption capacity of

schwertmannite was larger than those previous reported for other adsorbents. In a binary component system consisting of fluoride and either an inner-sphere or an outer-sphere complex forming species, it was found that fluoride adsorption reduced in the presence of the former and increased slightly in the presence of the latter. The schwertmannite adsorbent had the ability to lower the fluoride concentration to acceptable levels and was regenerable, and therefore can be applied to polish wastewater after a precipitation/coagulation process.

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