

Defluoridation of Water by Schwertmannite

Aparajita Goswami, and Mihir K Purkait

Abstract—In the present study Schwertmannite (an iron oxide hydroxide) is selected as an adsorbent for defluoridation of water. The adsorbent was prepared by wet chemical process and was characterized by SEM, XRD and BET. The fluoride adsorption efficiency of the prepared adsorbent was determined with respect to contact time, initial fluoride concentration, adsorbent dose and pH of the solution. The batch adsorption data revealed that the fluoride adsorption efficiency was highly influenced by the studied factors. Equilibrium was attained within one hour of contact time indicating fast kinetics and the adsorption data followed pseudo second order kinetic model. Equilibrium isotherm data fitted to both Langmuir and Freundlich isotherm models for a concentration range of 5-30 mg/L. The adsorption system followed Langmuir isotherm model with maximum adsorption capacity of 11.3 mg/g. The high adsorption capacity of Schwertmannite points towards the potential of this adsorbent for fluoride removal from aqueous medium.

Keywords—Adsorption, fluoride, isotherm study, kinetics, schwertmannite.

I. INTRODUCTION

WATER contains many organic and inorganic ions in dissolved state. Every ion has some specific limit in water and beyond that limit the water is considered as contaminated water and likely to be treated so that it should be in the safe range for drinking purpose. Among all the contaminants, fluoride is considered as the most harmful inorganic pollutant present in water. Naturally, fluoride is present in rocks and minerals and due to weathering of such rocks, fluoride contaminates the ground water. Apart from natural source, fluoride contamination is due to the effluents coming from fertilizer industry, glass industry and semiconductor industry. These effluents increase the level of fluoride in surface water making the water unfit to drink. Small amount (1 mg/L) of fluoride is necessary to human in the growth of teeth and bones, but its excess quantity causes both dental and skeletal fluorosis [1]. Due to harmful nature of excess fluoride, World Health Organization (WHO) recommended that water containing 1.5 mg/L fluoride is considered as safe for drinking purposes [2]. This permissible limit value varies according to the temperature and climatic condition of a place. Hence Bureau of Indian Standard (BIS) recommended that water containing 1 mg/L fluoride is considered safe for drinking purpose [3].

To maintain this permissible limit, different techniques are used for defluoridation of contaminated water. Chemical coagulation precipitation [1], ion exchange [4], adsorption [5],

membrane separation [6] are the major techniques of defluoridation. Literature said that each technique has some advantages and disadvantages. Based on the comparative study, adsorption is considered as the most efficient, easy operating and cheap method of defluoridation of water. The cost of the adsorption process is mainly depends on the cost of the adsorbent. The adsorbents like acidic alumina [7], granular red mud [8], pyrophyllite [5], hydrated cement [9], LDH [10], γ -alumina [11] and other sorbents are employed for fluoride removal. These materials show unsatisfactory level of fluoride adsorption capacity. Hence researchers are more interested in finding of a new and alternate adsorbent with distinct advantages with respect to higher selectivity and better fluoride adsorption capacity.

Schwertmannite which is an iron oxide hydroxide exists naturally as geomaterial can also be synthesized in laboratory. Synthetic schwertmannite has a probable formula of $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$. Presence of OH^- group in schwertmannite considers it as a fluoride adsorbing adsorbent as fluoride ion replaces hydroxyl ion.

In the present work, schwertmannite was used as an adsorbent for fluoride removal. The adsorption process was studied with the process parameters such as contact time, initial fluoride concentration, adsorbent dose and pH. The nature of this adsorption system was described by reaction kinetics. The most common adsorption isotherm viz., Langmuir and Freundlich isotherm models were used to observe the equilibrium behavior of the system.

II. MATERIALS AND METHODS

A. Preparation and Characterization of Schwertmannite

Schwertmannite was prepared by wet chemical process where urea was used as a neutralizing agent [12]. The urea solution was prepared by dissolving 75 g of urea into 250 mL of distilled water, and $\text{Fe}_2(\text{SO}_4)_3$ solution was made by dissolving about 12.5 g of $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ in 250mL of distilled water. The $\text{Fe}_2(\text{SO}_4)_3$ solution was preheated at 70°C in a beaker and urea solution was added drop wise for about 2–4 hrs. Precipitates were formed and dried at temperatures less than 40°C. After preparing schwertmannite, characterization was done by using BET, XRD and SEM analysis.

The surface area of schwertmannite was measured by BET surface area analyzer (SA 3100, Beckman Coulter, USA). The BET surface area, total pore volume, average pore radius, micropore area were obtained from the adsorption isotherm and reported in Result and discussion section. Structural analysis of schwertmannite was done by X-ray diffractometer (D8 ADVANCE, Bruker Axs). The spectroscopic studies were performed by using a scanning electron microscopy (Oxford,

Mihir K Purkait is with the Indian Institute of Technology Guwahati, Guwahati 781039 India (phone: 91-361-2582262; fax: 91-361-2582291; e-mail: mihir@iitg.ernet.in).

Aparajita Goswami is with the Indian Institute of Technology Guwahati, Guwahati 781039 India (e-mail: aparajita@iitg.ernet.in).

Leo 1430VP) to detect the surface morphology of schwertmannite.

B. Experimental Methods

Batch adsorption experiments were carried out using 100 mL fluoride solution in 250 mL conical flasks at ambient temperature. The contact time effect on fluoride adsorption using schwertmannite was observed by agitating different concentrations (5, 10 and 15 mg/L) of fluoride solution with 3 g/L of adsorbent (0.3 g/ 100 mL fluoride solution), separately at room temperature, 30°C. Different amounts of adsorbent (1–4 g/L) were used to observe its effect on fluoride adsorption. Effect of initial pH of the solution on fluoride adsorption was studied with initial fluoride concentration of 5 mg/L in the pH range of 2.71 to 11.43. Samples were collected at certain time intervals and filtered. The residual fluoride concentrations were measured with fluoride ion electrode. For equilibrium study, 100 mL solution of different fluoride concentrations (5 mg/L to 30 mg/L) were equilibrated in a shaker for 24 hrs at a fixed adsorbent loading of 1 g/L at ambient temperature. After 24 hrs, the solution attains equilibrium and the amount of fluoride adsorbed (mg/g) on the surface of the adsorbent was determined by the difference of the two concentrations. Duplicate experiments were carried out for all the operating variables studied and only the average values were taken into consideration. A common adsorbent dose of 3 g/L, stirring speed of 150 rpm and initial fluoride concentration of 5 mg/L was used for adsorption experiments.

III. RESULTS AND DISCUSSIONS

A. Characterization of Schwertmannite

The specific surface area of schwertmannite determined from BET surface area analyzer was 314.55 m²/g. Fig. 1a showed the pore size distribution curve of adsorbent based on the nitrogen equilibrium adsorption isotherm at 77 K. It was found from the figure that schwertmannite exhibited a wide distribution of pores. About 83.53% of total pores were in the range of pore diameter below 40 nm with total pore volume of 0.10824 mL/g.nm, indicating a very high mesopore volume. The second fraction of pores appeared in the field from 50 to 150 nm. In this range, the pore volume was 0.00095 mL/g.nm with only 16.47% of the total pore volume indicating the existence of the macropores. The XRD pattern of schwertmannite was presented in Fig. 1b. No specific peak was observed in the XRD pattern which indicated that the prepared adsorbent was amorphous in nature. Fig. 1(c) showed the scanning electron microscope (SEM) picture of schwertmannite. The schwertmannite is known as a poorly crystalline iron oxide hydroxide that consists of spherical to ellipsoidal particles with hedge-hog like aggregates and several mm in size. The needle-like structures with average width and thickness of 2–4 nm and length of 60–90 nm radiate from the particle surfaces to devote “pincushion” morphology to this material.

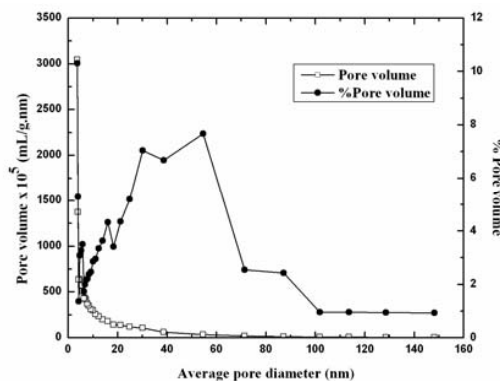


Fig. 1a Pore size distribution of schwertmannite

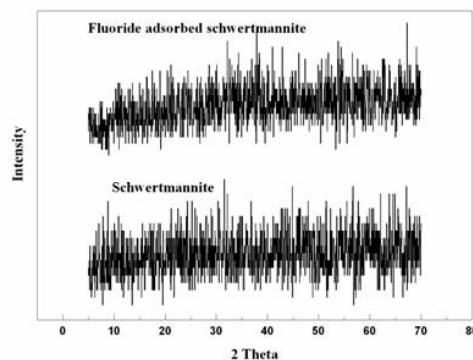


Fig. 1b XRD of schwertmannite

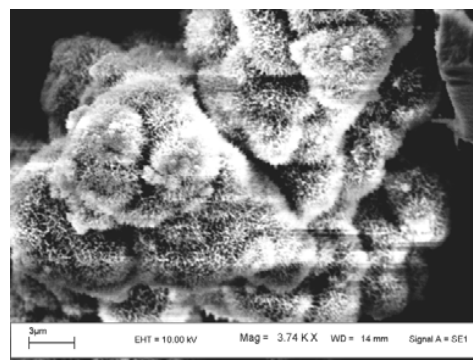


Fig. 1c SEM image of schwertmannite

B. Contact Time Effect

Fig. 2 showed the variation of residual fluoride concentration of the solution with time during the adsorption process. It was observed from the figure that rapid adsorption of fluoride took place within 10 minutes of adsorption and then adsorption became slow and almost reached equilibrium within 60 min. Initially adsorbent active sites were vacant and fluoride was adsorbed into the active sites rapidly. As time proceeds, the numbers of active sites of the adsorbent were decreased and then adsorption became slow and equilibrium was reached slowly. With an increase in contact time up to 24 hrs, the residual fluoride concentration in the solution was not decreased by less than 1%. Therefore, further experiments were conducted with a contact time of 180 minutes.

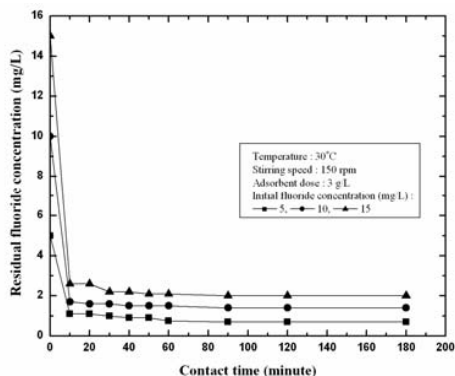


Fig. 2 Contact time effect of fluoride adsorption on schwertmannite

C. Adsorbent Dose Effect

Adsorbent dose is an important parameter for fluoride removal. With increase in schwertmannite dose (varying from 1 g/L to 4 g/L), the residual fluoride concentration was decreased gradually. The variation of residual fluoride concentration with different adsorbent dose was plotted in Fig. 3. From the figure, it was observed that 3 g/L schwertmannite was required to maintain the BIS permissible limit for 5 mg/L initial fluoride concentration. Initially, the residual fluoride concentration was decreased sharply with increase in adsorbent dose (upto 3 g/L) and thereafter it was almost constant. The sharp decrease in fluoride concentration was due to the greater surface area and availability of more adsorption sites of adsorbent. With increase in time, the number of active sites on the adsorbent and the bulk fluoride concentration were decreased and reached in equilibrium. Therefore, the amount of residual fluoride concentration was stagnant with further increase in adsorbent dose.

D. pH Effect

The change in residual fluoride concentration with pH was shown in Fig. 4. To determine the optimum pH for maximum removal of fluoride, equilibrium sorption of fluoride with

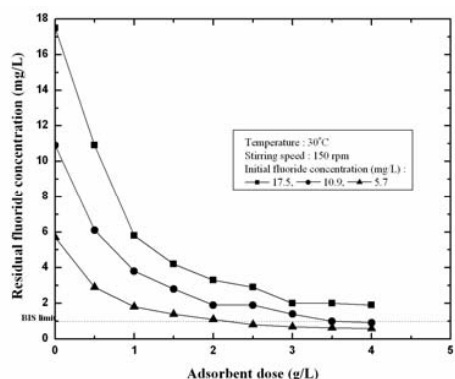


Fig. 3 Adsorbent dose effect of fluoride adsorption on schwertmannite

initial fluoride concentration of 5mg/L was investigated over a pH range of 2.71 - 11.43. From the figure, it was observed that maximum adsorption take place at pH 3.58. Above pH 3.58, an

increase in pH causes increase in residual fluoride concentration. To understand the fluoride adsorption behavior under different pH values, the following reactions are considered [12]



where $\equiv SOH$, $\equiv SOH_2^+$ and $\equiv SO^-$ are the neutral, protonated and deprotonated sites on schwertmannite and $\equiv SF$ is the active site-fluoride complex. Equation (1) expresses the ionization of HF in solution at low pH. Because HF is weakly ionized (pKa = 3.2) in solution at low pH values, the corresponding uptake of fluoride is reduced when $pH \leq 3.58$, since a fraction of fluoride becomes unavailable for adsorption. When the adsorption system (fluoride solution / schwertmannite) is operated at $pH > 3.58$ the reaction sites become deprotonated according to (3) leading to a reduction in fluoride adsorption due to increased repulsive forces between the negatively charged fluoride ions and the deprotonated sites. According to (5), 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.

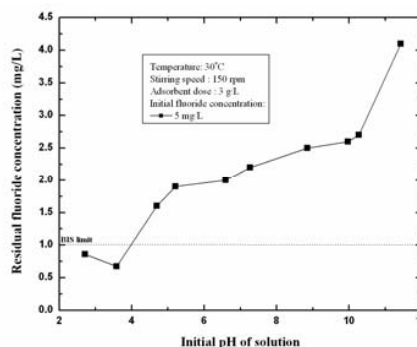


Fig. 4 pH effect of fluoride adsorption on schwertmannite

E. Adsorption Kinetics Modeling and Mechanism

1) Pseudo-first-order kinetic model

The adsorption reaction preceded by diffusion through a boundary, the kinetics follows pseudo-first-order rate equation. In this model, rate of solute uptake with time was directly proportional to difference in saturation concentration and the adsorbed amount with time [13]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

q_t and q_e are the amount of fluoride adsorbed (mg/g) at contact time t (min) and at equilibrium, k_1 is the pseudo-first-order rate constant (min^{-1}).

After integrating with the boundary conditions at $t=0$, $q_t=0$ and at $t=t$, $q_t=q_t$ and rearranging (6), the rate law for a pseudo-first-order reaction became

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

The plot of $\log(q_e - q_t)$ versus t gave a straight line with slope of $-\frac{k_1}{2.303}$ and intercept $\log q_e$. Adsorption rate constants were calculated from slope and intercept and were summarized in Table I. The values of Table I indicated that the kinetics of fluoride adsorption on schwertmannite was not diffusion controlled.

2) Pseudo-Second-Order Kinetic Model

Adsorption process with chemisorptions being the rate-control follows pseudo second-order model. The pseudo-second-order model [14] was

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (8)$$

k_2 is the equilibrium rate constant for pseudo-second-order sorption (g/mg min). Integrating (8) with the boundary conditions at $t=0$, $q_t=0$ and at $t=t$, $q_t=q_t$ and rearranging, we received

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

The plot of $\frac{t}{q_t}$ versus t gave a straight line with slope of $\frac{1}{q_e}$ and intercept $\frac{1}{k_2 q_e^2}$. The calculated value of k_2 , q_e and their corresponding regression coefficient (R^2) values were presented in Table I. Among these models the criterion for their applicability is based on judgment on the respective correlation coefficient (R^2) and agreement between experimental and calculated value of q_e . The high values of R^2 (~ 1) and good agreement between two q_e values indicate that the understudy adsorption system followed pseudo-second-order kinetic model (Table I).

TABLE I
KINETICS PARAMETERS AT 30°C

| | Initial fluoride concentration (mg/L) | | |
|------------------------------|---------------------------------------|-------|-------|
| | 5 | 10 | 15 |
| Pseudo first order kinetics | | | |
| $q_{e, \text{expt}}$ (mg/g) | 1.44 | 2.87 | 4.33 |
| $q_{e, \text{cal}}$ (mg/g) | 0.38 | 0.12 | 0.32 |
| k_1 (min^{-1}) | 0.047 | 0.023 | 0.041 |
| R^2 | 0.90 | 0.86 | 0.89 |
| Pseudo second order kinetics | | | |
| $q_{e, \text{cal}}$ (mg/g) | 1.45 | 2.88 | 4.35 |
| k_2 (g/mg. min) | 0.40 | 0.71 | 0.43 |
| R^2 | 0.99 | 1 | 1 |

F. Equilibrium Study

Adsorption isotherms are essential to understand the nature of the interaction between adsorbate and the applied adsorbent. Two important isotherms viz Langmuir and Freundlich isotherms were investigated in this study.

The well-known expression of Langmuir isotherm model is [15] presented as

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (10)$$

Where C_e (mg/L) and q_e (mg/g) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, respectively, and Q_0 (mg/g) and b (L/mg) are the Langmuir isotherm constants.

The expression for Freundlich isotherm model was given as [16]

$$q_e = K_F C_e^{n_F} \quad (11)$$

Where K_F is the Freundlich isotherm constant [(mg/g) (L/g) $^{1/n_F}$] related to the bonding energy, and n_F is the heterogeneity factor. n_F is a measure of deviation from linearity of the adsorption. The value of n_F varies with the heterogeneity of the adsorbent and for favorable adsorption process; the value of n_F should be less than unity. The experimental isotherm values were fitted with both Langmuir and Freundlich isotherm equations using Curve Expert 4 software and all the isotherm constants and their correlation coefficients were calculated and reported in Table II.

TABLE II
EQUILIBRIUM ISOTHERM CONSTANTS

| Langmuir isotherm constant | | | Freundlich isotherm constants | | |
|----------------------------|----------|----------------|---|----------------|----------------|
| Q _o (mg/g) | b (L/mg) | R ² | K _F [mg.g (L/mg) ^{1/n}] | n _F | R ² |
| 11.3 | 0.17 | 0.99 | 2.73 | 0.47 | 0.95 |

The adsorption of fluoride on schwertmannite followed Langmuir isotherm with high correlation coefficients ($R^2 \sim 0.99$). Hence, it can be concluded that Langmuir isotherm is the best isotherm to predict the adsorption of fluoride over schwertmannite. The plot of calculated values of Langmuir and Freundlich isotherm models with experimentally obtained data also concluded that Langmuir is the best fitted curve for this system and shown in Fig. 5.

The fluoride adsorption on schwertmannite in aqueous medium followed chemisorption rather than physical adsorption which were discussed in section E.2. Since the adsorption is supposed to be the chemisorption in nature, it may be proposed that mono layer coverage of fluoride ion is taking place over the schwertmannite surface. Therefore, adsorption process should be better represented physically by Langmuir isotherm model than Freundlich isotherm model.

In order to estimate the efficiency of present adsorbent for the removal of fluoride, a comparison among various adsorbents were made and shown in Table III. From the table, it was concluded that the adsorption capacity of schwertmannite was more than that of other adsorbents. Hence, schwertmannite was considered as an effective adsorbent for fluoride removal from water.

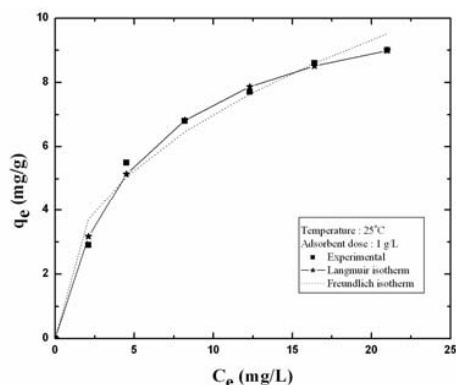


Fig. 5 Equilibrium study of fluoride adsorption on schwertmannite

TABLE III
COMPARISON OF DIFFERENT ADSORBENTS

| Adsorbent | Experimental conditions | Adsorption capacity (mg/g) | References |
|------------------|--|----------------------------|------------|
| Granular red mud | Adsorbent dose: 5 g/L; Concentration range: 5-150 mg/L; pH: 4.7; Temperature: 25 ± 1°C | 0.85 | [8] |
| Pyrophyllite | Adsorbent dose: 4 g/L; Concentration range: 2-12 mg/L; pH: 4.9; Temperature: 24°C | 2.2 | [5] |

| | | | |
|-----------------------|---|-------------|----------------------|
| Hydrated cement | Adsorbent dose: 10 g/L; Concentration range: 5.3-14.8 mg/L; pH: 6.7 | 2.68 | [9] |
| LDH | Adsorbent dose: 4 g/L; Concentration range: 10-100 mg/L; Temperature: 25°C | 4.10 | [10] |
| γ - alumina | Adsorbent dose: 12 g/L; Concentration range: 20-250 mg/L; pH: 6; Temperature: 30°C | 6.36 | [11] |
| Acidic alumina | Adsorbent dose: 4.5 g/L; Concentration range: 2-15 mg/L; pH: 4.4; Temperature: 25°C | 8.40 | [7] |
| Schwertmannite | Adsorbent dose: 3 g/L; Concentration range: 5-30 mg/L; Temperature: 30°C | 11.3 | Present study |

IV. CONCLUSION

The current study highlighted that schwertmannite which is basically a iron oxide hydroxide had a considerable potential for fluoride removal from aqueous medium. Both the permissible limit (WHO and BIS) was achieved by schwertmannite at pH 3.58 with an adsorbent dose of 3 g/L. Kinetic study revealed that fluoride adsorption process was controlled by pseudo-second-order rate equation. The equilibrium data was fitted with Langmuir and Freundlich isotherm models. Langmuir isotherm model was fitted well to this system with an adsorption capacity of 11.3 mg/g of adsorbent.

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