Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1011708

57 (2016) 6624–6631
March

Taylor & Francis
Taylor & Francis Group

Adsorption of fluoride from aqueous solution by Bio-F sorbent: a fixed-bed column study

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Received 23 August 2014; Accepted 13 January 2015

ABSTRACT

In this work, the adsorption potential of Bio-F to remove fluoride from aqueous solution was investigated using fixed-bed adsorption column. The effects of inlet fluoride concentration (10–30 mg/L), feed flow rate (10–30 mL/min), and Bio-F bed height (10–20 cm) on the breakthrough characteristics of the adsorption system were determined. The highest bed capacity of 9.867 mg/g was obtained using 30 mg/L inlet fluoride concentration, 10 cm bed height, and 20 mL/min flow rate. The adsorption data were fitted to three well-established fixed-bed adsorption models namely, Adam's–Bohart, Thomas, and Yoon–Nelson models. The results fitted well to the Adam's–Bohart and Yoon–Nelson models with low sum of square errors at different conditions. The Bio-F was found to be a suitable adsorbent for adsorption of fluoride using fixed-bed adsorption column.

Keywords: Fluoride; Bio-F; Fixed-bed column; Adsorption; Breakthrough

1. Introduction

Fluoride in groundwater is mostly of geogenic origin arising from disintegration of rocks containing the fluoride ions. In addition, anthropogenic sources such as infiltration of chemical fertilizers in agricultural areas and liquid wastes from industrial entities also contribute to fluoride ions in groundwater [1]. Excess fluoride in drinking water is prevalent in 150 districts of 17 states in India [2,3]. Defluoridation of drinking water is of great concern because excessive intake of fluoride can cause various diseases. The presence of fluoride in drinking water within permissible limits is beneficial for the health; however, excessive intake of fluoride causes adverse health effects including dental fluorosis and skeletal abnormalities [4]. Hence, it becomes necessary to bring down the fluoride concentration within permissible limit of 1.5 mg/L according to Indian Standards.

The popular technologies which have been investigated for fluoride removal from water are adsorption, ion exchange, precipitation, Donnan dialysis, electrodialysis, reverse osmosis, nanofiltration, and ultrafiltration [1,5,6]. Among these methods, adsorption is still one of the most extensively used method which offers satisfactory results and seems to be a more attractive method for the removal of fluoride in terms of cost, simplicity of design, and operation [7].

Batch experiments were used to measure the efficiency of adsorption for removing specific adsorbate

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as well as to determine the maximum adsorption capacity [8]. However, the batch study fails to simulate the dynamics in a continuous mode and so, the column study seems essential to model the flow dynamics of a solution through a fixed bed [9]. A continuous packed bed adsorber does not run under equilibrium conditions and the effect of flow condition (hydrodynamics) at any cross-section in the column affects the flow behavior downstream. The flow behavior and mass transfer aspects become peculiar beyond a particular length to diameter ratio of the column.

The defluoridation feasibility of a commercially available Bio-F has been studied using batch experiments [10]. However, packed fixed-bed column study of Bio-F is not yet reported. So, the present work, herein reports the efficiency assessment of fluoride removal by Bio-F packed fixed-bed column from the fluoride spiked aqueous solution samples on lab-bench scale with modeling of the breakthrough data using theoretical models such as Adam's–Bohart, Thomas, and Yoon–Nelson models.

2. Experimental

2.1. Adsorbate

For fixed-bed column studies, Bio-F adsorbent was used for the removal of fluoride from aqueous solution, which was manufactured by HES Water Engineers (I) Pvt. Ltd (a joint venture company of water engineers, Australia). Particle size of Bio-F as estimated by sieve test was found to be ≤ 600 μm (0.06 cm). The density of Bio-F determined by pycnometer was 129.31 g/cc and the porosity of the Bio-F was 68.18%. Scanning electron micrograph of the adsorbent sample is helpful to understand its surface texture. Fig. 1 clearly reveals a flocked and porous surface texture, indicating a high adsorption capacity [10]. The stock solution of 100 mg/L fluoride was prepared by dissolving 221 mg of analytical anhydrous NaF in one liter of distilled water. Test solutions of various F concentrations were prepared from stock solution.

2.2. Experimental setup

Fixed-bed column was made up of Pyrex glass tube of 1.6 cm inner diameter and 75 cm height. As shown in Fig. 2 at the bottom of the column, glass beads were filled to prevent the loss of adsorbent. A known quantity of the Bio-F adsorbent was packed in the column to yield the desired bed height of 10, 15, and 20 cm (equivalent to 10, 15, and 20 g of Bio-F). The column was again filled up with glass beads in order to provide a uniform flow of the solution through the column. Fluoride solution of known concentrations (10, 20, and 30 mg/L) at pH 6.7 was pumped from the column at a desired flow rate (10, 20, and 30 mL/min) which is controlled by a peristaltic pump (Enertech-Victor ENPD 100). The fluoride solutions at the outlet of the column were collected at regular time intervals and the concentration was measured using an ion meter (Thermo Scientific Orion 5 Star Ion Meter). The experiments were carried out at room temperature of 28 ± 1°C without any pH adjustment.

2.3. Mathematical description

Efficiency of any fixed-bed column is described through the concept of the breakthrough curve. The time for breakthrough appearance and the shape of breakthrough curve are important characteristics for determining the operation and dynamic response of an adsorption column [8]. The breakthrough curves show the loading behavior of fluoride ion which is to be removed from solution in a fixed-bed column. It is usually expressed in terms of adsorbed fluoride concentration (C_{ad}), inlet fluoride concentration (C_o), outlet fluoride concentration (C_t), or normalized concentration (C_t/C_o). Normalized concentration is defined as the ratio of outlet fluoride concentration to inlet fluoride concentration (C_t/C_o), as a function of time or volume of effluent for a given bed height [11]. Effluent volume (V_{eff}) can be calculated as shown in Eq. (1).

$$V_{eff} = Qt_{total} \tag{1}$$

where t_{total} and Q are the total flow time (min) and volumetric flow rate (mL/min), respectively. The area under the breakthrough curve obtained by integrating the adsorbed concentration (C_{ad}; mg/L) vs. time (t; min) plot can be used to find the total adsorbed fluoride quantity (maximum column capacity). Total adsorbed fluoride quantity q_{total} (mg) in the column for a given feed concentration and flow rate is calculated as shown in Eq. (2) [12]:

$$q_{total} = \frac{Q}{1,000}\int_{t=0}^{t=t_{total}} C_{ad}dt \tag{2}$$

Equilibrium uptake or maximum capacity (q_{eq}; mg/g) of the column is defined by Eq. (3) as the total amount of adsorbed (q_{total}) per gram of adsorbent (w) at the end of total flow time [12]:

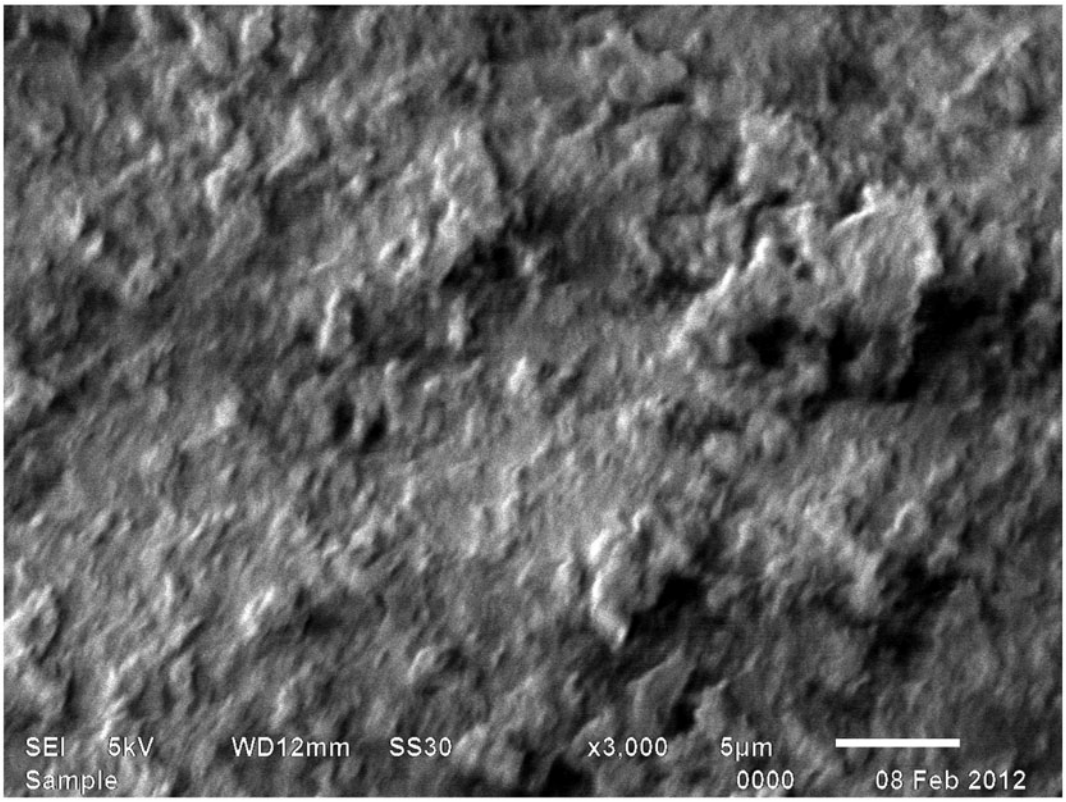

Fig. 1. SEM micrograph of Bio-F sorbent (3,000 ×).

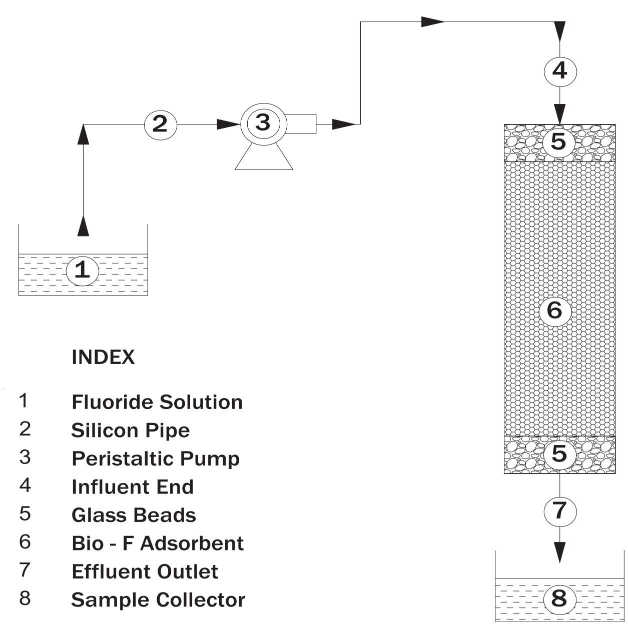

Fig. 2. Schematic diagram of experimental setup for column study.

$$q_{\text{eq}} = \frac{q_{\text{total}}}{w} \tag{3}$$

3. Result and discussion

3.1. Effect of initial fluoride concentration

The effect of variation of the inlet fluoride concentration from 10 to 30 mg/L used with the same adsorbent bed height (10 cm) and solution flow rate (20 mL/min) is shown by breakthrough curve in Fig. 3. As shown in Fig. 3, at the interval of 150 min, the value of C_t/C_o attained 0.90, 0.95, and 0.99 with inlet fluoride concentration of 10, 20, and 30 mg/L, respectively. It is illustrated from the breakthrough curve that the breakthrough time slightly decreases with increasing inlet fluoride concentrations. At lower inlet fluoride concentrations, breakthrough curves were dispersed and breakthrough occurred slower. Sharper breakthrough curves were obtained with increased inlet fluoride concentration. The breakthrough time decreases with increase in the inlet fluoride concentration, as the binding sites became more quickly saturated in the column. This can be explained

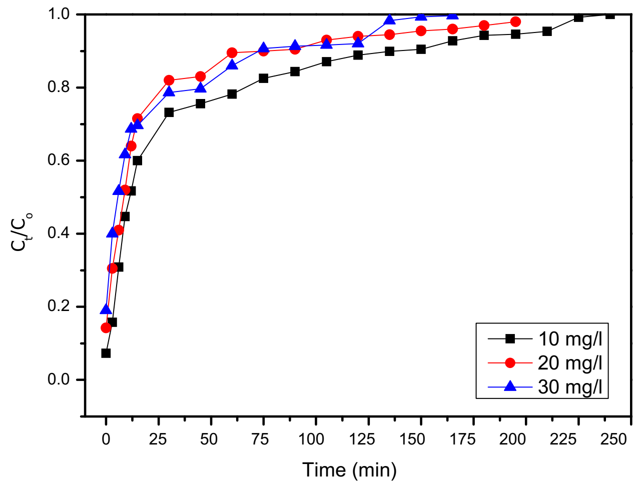

Fig. 3. Breakthrough curves for fluoride adsorption on Bio-F at different inlet fluoride concentration (bed height = 10 cm, flow rate = 20 mL/min).

by the fact that a lower concentration gradient caused a slower transport due to decrease in diffusion coefficient or mass transfer coefficient [13]. Larger the inlet fluoride concentration, steeper the slope of breakthrough curve, and smaller the breakthrough time. These results demonstrate the change in concentration gradient which affects the saturation rate and breakthrough time. In other words, it can be explained that the diffusion process is concentration dependent. The driving force for adsorption is the concentration difference between fluoride on the adsorbent and fluoride in the solution. Thus, high driving force due to high fluoride concentration resulted in better column performance [14]. These results were in agreement with those referred to the literatures [14–16].

The highest bed capacity of 9.86 mg/g was obtained using 30 mg/L inlet fluoride concentration, 10 cm bed height, and 20 mL/min flow rate. This can be attributed to higher influent fluoride concentration, which provides enhancement to the driving force to overcome the mass transfer barrier. All the adsorption capacities obtained are listed in Table 1.

3.2. Effect of the solution flow rate

The effect of the solution flow rate on the adsorption of fluoride using the Bio-F was investigated by varying the flow rate (10, 20, and 30 mL/min) with a constant adsorbent bed height of 10 cm and the inlet fluoride concentration of 20 mg/L (as shown by the breakthrough curve in Fig. 4). It was observed from the breakthrough curve that breakthrough generally occurred faster with higher flow rate. Breakthrough time attains significant increase in saturation with decrease in the flow rate. With provided low flow rate of inlet fluoride results in more time to make contact with Bio-F in higher removal of fluoride ions in column [17]. The variation in the slope of the breakthrough curve and adsorption capacity may be explained based on mass transfer fundamentals. The reason is that at higher flow rate the rate of mass transfer of fluoride adsorbed onto unit bed height (mass transfer zone) get increased with increase in flow rate leading to faster saturation at higher flow rate. At a higher flow rate, the adsorption capacity was found high due to high volume of the fluoride ion passing through the column and diffusion of the solute into the pores of the adsorbent.

3.3. Effect of Bio-F bed height

Fig. 5 illustrates the breakthrough curves for the adsorption of fluoride at different column bed heights of 10, 15, and 20 at a constant flow rate of 20 mL/min and influent fluoride concentration of 20 mg/L. The adsorption column data were evaluated and presented in Table 1. The breakthrough curves at different bed heights are shown in Fig. 5. It is observed from Fig. 5 that as bed height increases, fluoride had more time to contact with Bio-F, which results in higher removal efficiency of fluoride ion in column. Therefore, higher bed column resulted in a decreased effluent concentration at the same service time. The slope of the breakthrough curve decreases with increase in bed height, which resulted in a broadened mass transfer zone [18]. High uptake of fluoride was observed at the highest bed height i.e. 7.93 mg/g. This was due to an increase in the surface area of adsorbent which provided more binding sites for adsorption [11].

The mass transfer zone in a column moves from the entrance of the bed and proceed towards the exit at the bottom of the column. Therefore, an increase in bed height would broaden the mass transfer zone and provide a longer distance to reach the exit resulting in an extended breakthrough time [8]. Nevertheless, at lower bed height, axial dispersion is the governing mechanism for mass transfer. In other words, the time is insufficient for the fluoride ions to diffuse throughout the whole Bio-F bed causes even shorter breakthrough time. These results were in agreement with those referred to the literature [19].

3.4. Estimation of breakthrough curves and determination of kinetic constants

The dynamic behavior of the fluoride column was predicted with the Adam's–Bohart, Thomas, and Yoon–Nelson models. The breakthrough curves

Table 1
Column data parameters obtained at different inlet fluoride concentrations, bed heights, and flow rates (T = 28 ± 1°C)

Initial concentration (mg/L)	Flow rate (mL/min)	Bed height (cm)	q_{total} (mg)	q_{eq} (mg/g)
10	20	10	48	4.8
20	20	10	76.44	7.644
30	20	10	98.67	9.867
20	10	10	59.1	5.91
20	30	10	82.32	8.232
20	20	15	82.32	7.788
20	20	20	158.76	7.938

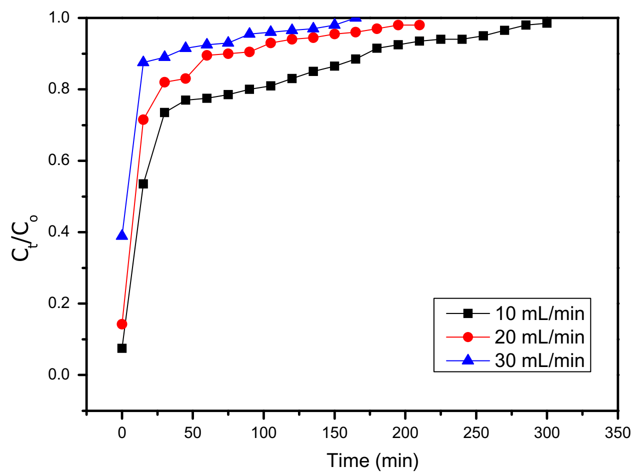

Fig. 4. Breakthrough curves for fluoride adsorption on Bio-F at different inlet flow rates (bed height = 10 cm, inlet Fluoride concentration = 20 mg/L).

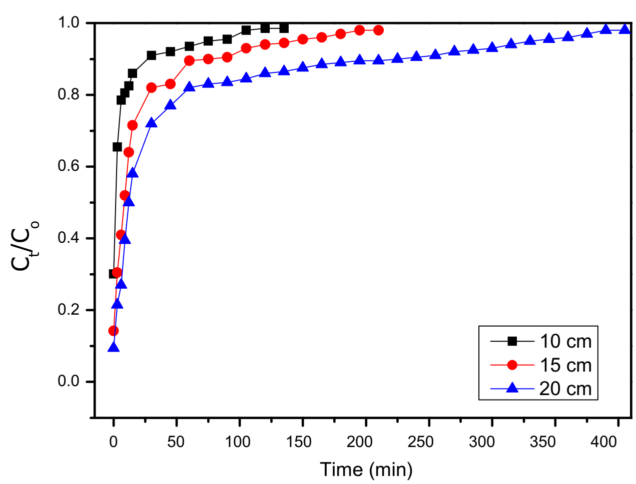

Fig. 5. Breakthrough curves for fluoride adsorption on Bio-F at different bed heights (inlet Fluoride concentration = 20 mg/L, inlet flow rate = 20 mL/min).

showed the superposition of experimental results (points) and the theoretical calculated points (lines). Sum of square error coefficients (SSE) showed the fit between experimental data and non-linear forms of Adam's–Bohart, Thomas and Yoon–Nelson equations. The calculated expressions of SSE functions are as following [20]:

$$\mathrm{SSE} = \sum_{i=1}^{n} (y_c - y_e)_i^2 \tag{4}$$

where n is the number of experimental data points, y_c is the predicted (calculated) data with the Adam's–Bohart, Thomas, and Yoon–Nelson models and y_e is the experimental data. In Eqs. (5–7), y represents the ratio of Ct/Co. The experimental data are fitted with all the three models as described above to determine the model kinetic parameters using non-linear regression analysis in SPSS 17.0 statistical software.

3.4.1. The Adam's–Bohart model

The Adam's–Bohart model [12] established the fundamental equations describing the relationship between C_t/C_o and t in a continuous system. The Adam's–Bohart model is used for the description of the initial part of the breakthrough curve [21]. The expression is the following:

$$\frac{C_t}{C_o} = \exp\left(k_{AB} C_o t - k_{AB} N_o \frac{Z}{F}\right) \tag{5}$$

where C_o and C_t (mg/L) are the inlet and effluent fluoride concentration. k_{AB} (L/mgmin) is the kinetic constant, F (cm/min) is the linear velocity calculated by dividing the flow rate by the column section area, Z (cm) is the bed depth of column and N_o (mg/L) is the saturation concentration. The values of k_{AB} and N_o were determined from a plot of C_t/C_o against t using non-linear regression analysis.

The Adam's–Bohart adsorption model was applied to experimental data for the description of the initial part of the breakthrough curve. For all breakthrough curves, respective values of N_o, and k_{AB} were calculated and presented in Table 2 together with the residual sum of squares. From Table 2, it is seen that the values of N_o is increased with increase in initial fluoride concentration and flow rate while k_{AB} increases with increase in initial fluoride concentration and decreases with increase in flow rate. This showed that the overall system kinetics is dominated by external mass transfer in the initial part of sorption in the column [19].

3.4.2. Thomas model

Thomas model [22] is used to fulfill the purpose of getting adsorption capacity of an adsorbent which is needed in column design. It also assumes plug flow behavior in the bed, and uses Langmuir kinetics of sorption–desorption and no axial dispersion is derived with the sorption that the rate driving force obeys second-order reversible reaction kinetics [8]. This model is suitable for adsorption processes where the external and internal diffusion limitations are absent. The Thomas model can be expressed as follows:

$$\frac{C_t}{C_o} = \frac{1}{1 + \exp(k_{TH} q_o{}^{w}/Q - k_{\mathrm{TH}} C_o t)} \tag{6}$$

where k_{TH} (mL/min-mg) is the Thomas rate constant; q_o (mg/g) is the equilibrium fluoride uptake per g of the adsorbent; C_o (mg/L) is the inlet fluoride concentration; C_t (mg/L) is the outlet concentration at time t; w (g) the mass of adsorbent, Q (mL/min) the flow rate, and t total (min) stands for flow time. The value of C_t/C_o is the ratio of outlet and inlet fluoride concentrations. The values of k_{TH} and q_o were determined from the plot of C_t/C_o against t using non-linear regression analysis.

The column data were fitted to the Thomas model to determine the Thomas rate constant (k_{TH}) and maximum solid-phase concentration (q_o). The determined coefficients and relative constants were obtained using non-linear regression analysis according to Eq. (6) and the results are listed in Table 3. From Table 3, it is seen that values of SSE range from 2.769 to 7.778 which shows that the Thomas model does not agree very well with the experimental data with high SSE value. A comparison of values of q_o obtained from calculation and experiment showed that they differ from given experimental conditions.

3.4.3. The Yoon–Nelson model

Yoon and Nelson [23] model is extremely concise in form, which is based on the assumption that the rate of decrease in the probability of adsorption of adsorbate molecule is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent. The Yoon–Nelson model for a single-component system is expressed as:

$$\frac{C_t}{C_o - C_t} = \exp(k_{\mathrm{YN}} t - \tau k_{\mathrm{YN}}) \tag{7}$$

where k_{YN} (1/min) is the rate velocity constant, τ (min) is the time required for 50% adsorbate breakthrough. The values of k_{YN} and τ were determined by plotting C_t/C_o against t using non-linear regression analysis. The values of k_{YN} and τ are listed in Table 4. As shown in Table 4, the 50% breakthrough time (τ) increased and the rate constant (k_{YN}) decreased with increase in bed height, decrease in flow rate, and decrease in initial fluoride concentration. The time required for 50% sorbate breakthrough with the Yoon–Nelson model agreed very well with the experimental data. Also, the model predicted the breakthrough curves very well, with low SSE.

Table 2
Adam's–Bohart parameters at different conditions using non-linear regression analysis

Inlet concentration (mg/L)	Bio-F bed height (cm)	Flow rate (mL/min)	$k_{\mathrm{AB}} \times 10^{-3}$ (L/mg min)	N_o (mg/L)	SSE
10	10	20	0.331	502.43	0.594
20	10	20	0.170	809.73	0.497
30	10	20	0.131	1,035.30	0.291
20	10	10	0.092	655.29	0.376
20	10	30	0.104	1,027.43	0.175
20	15	20	0.154	574.00	0.524
20	20	20	0.111	675.00	0.705

Table 3
Thomas model parameters at different conditions using non-linear regression analysis

Inlet concentration (mg/L)	Bio-F bed height (cm)	Flow rate (mL/min)	k_{TH} (mL/min mg)	q_o (mg/g)	SSE
10	10	20	0.046	8.56	7.737
20	10	20	0.030	9.01	5.806
30	10	20	0.023	10.10	5.006
20	10	10	0.007	7.89	4.761
20	10	30	0.008	9.92	2.769
20	15	20	0.025	9.95	6.176
20	20	20	0.023	11.01	7.778

Table 4
Yoon–Nelson parameters at different conditions using non-linear regression analysis

Inlet concentration (mg/L)	Bio-F bed height (cm)	Flow rate (mL/min)	k_{YN} (1/min)	τ (min)	SSE
10	10	20	0.0029	410.80	0.594
20	10	20	0.0031	365.96	0.497
30	10	20	0.0039	314.84	0.291
20	10	10	0.0032	386.39	0.294
20	10	30	0.0027	469.93	0.175
20	15	20	0.0032	396.90	0.524
20	20	20	0.0038	454.29	0.605

3.4.4. Comparison of Adam's–Bohart, Thomas, and Yoon–Nelson models

Among the Adam's–Bohart, Thomas, and Yoon–Nelson models, the value of SSE for Adam's–Bohart and Yoon-Nelson was lowest for a given experimental condition, while it was the highest for Thomas model. Thus, it may be concluded that the Adam's–Bohart and Yoon–Nelson models were better in describing the process of fluoride adsorption in a Bio-F column. In comparison with SSE values for predicted curves and experimental data, both the Adam's–Bohart and Yoon–Nelson models may be used to describe the behavior of the adsorption process, but the Thomas model did not give better results.

4. Conclusion

This investigation showed that the Bio-F was a promising adsorbent for removing fluoride from aqueous solutions using fixed-bed adsorption column. The fixed-bed adsorption system was found to perform better with high inlet concentration, high feed flow rate, and high Bio-F bed height. The Adam's–Bohart, Thomas, and Yoon–Nelson models were used to analyze the column experimental data. For fluoride adsorption, the column data were fitted well to the Adam's–Bohart and Yoon–Nelson models.

Acknowledgment

The authors are grateful to Dr A. B. Gupta and Sukanta Mondal for their valuable suggestion and support throughout this experiment.

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