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Adsorption of F on Bio-Filter sorbent: kinetics, equilibrium, and thermodynamic study

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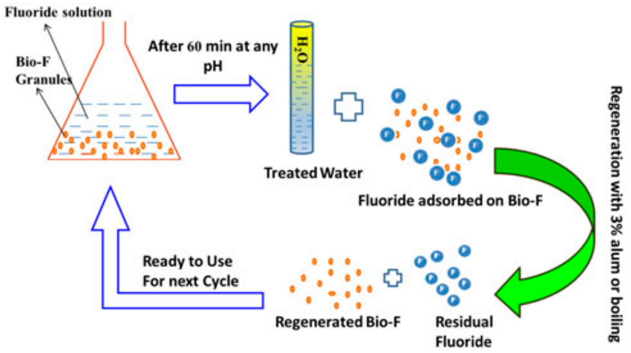

ABSTRACT

The aim of this research work is to investigate the potential of a commercially available Bio-Filter (Bio-F) sorbent for defluoridation of drinking water. Batch equilibrium experiments were conducted with respect to change in pH of solution, initial concentration of F, contact time, and competitive anions to evaluate the fluoride adsorption behavior of Bio-F. Sorption of F onto Bio-F was found to be independent of pH. Scanning electron microscopy, sieve method, and porosity test were used to characterize the physical attributes of Bio-F. More than 97% removal of fluoride (28 mg/L) was achieved within 60 min of contact time at neutral pH. Results demonstrated that among the kinetic models tested, pseudo-second-order model fitted the kinetic data well with a correlation coefficient greater than 0.99, suggesting the chemisorption mechanism. Different adsorption isotherm models like Langmuir, Freundlich, Redlich–Peterson, Sips, and Toth were used to analyze the experimental data and the model parameters were evaluated. Experimental data revealed that three-parameter Redlich–Peterson Isotherm model gives best fit for F removal. The maximum adsorption capacity of Bio-F for F deduced from Langmuir model was ~5.530 mg/g. The calculation of thermodynamic parameters at different temperatures showed that adsorption was

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spontaneous and endothermic. All studied competitive anions (SO_4^{2-}, NO_3^-, Cl^-) have negligible effect on F sorption by Bio-F. Regeneration studies were performed by alum solution (3% aqueous solution) and boiling means. This study showed that the removal of F by Bio-F is a promising technique.

Keywords: Defluoridation; Drinking water; Equilibrium isotherms; Adsorption kinetics; Error function; Thermodynamics

1. Introduction

Fluoride (F) is an essential trace element which is beneficial for human growth at low concentrations (0.4–1.0 mg/L) in drinking water [1–3]. Disproportionate amount of fluoride in water is an issue of serious health concern and elevated concentration of F in drinking water has been suspected being responsible for number of health problems such as dental fluorosis [1,3–6], bone fluorosis [7], abrasion of the thyroid [8], endocrine glands, Alzheimer's disease [3], and nervous system failure [9]. Moreover, excess levels of fluoride in water bodies may increase the risk of toxic effects to aquatic species [6].

F is a naturally occurring element in minerals such as fluorite and fluorapatite, geochemical deposits, natural water systems and can be leached out by either natural weathering or rainwater and causes F contamination of drinking water [3,10,11]. Despite the natural sources, many industrial activities such as pharmacy, fluorspar mining, semiconductor process, aluminum electrolysis, electroplating, generating electricity, and fertilizer production release fluoride into environment [12–14].

Excessive concentration of F is reported in Central Europe [15], Syria, Jordan, Egypt, Libya, Algeria, Sudan, Kenya, Turkey [16], Iraq, Iran [12], Afghanistan, India [6,17], northern Thailand [18], and China. Similar belts are also found in the America and Japan. It was estimated that more than 200 million people including about 70 million in India and 45 million in China were affected by fluorosis [13,19]. The maximal F concentration of 1.5 mg/L has been recommended in drinking water by World Health Organization [20] as the concentration above which dental fluorosis is likely [3], while Bureau of Indian Standard (BIS) recommended a desirable limit of 1.0 mg/L of F in drinking water, which can be extended up to 1.5 mg/L as permissible limit, if no alternative source of water is available [21].

Many methods such as adsorption [22,23], coagulation/precipitation [24], electrocoagulation [25], ion exchange [24], Donnan dialysis, electrodialysis, reverse osmosis, nano-filtration, and ultrafiltration [26] have been thoroughly investigated for defluoridation of drinking water. Of these adsorption and coagulation/precipitation are generally practiced for defluoridation [3]. The latter produce significant amounts of sludge which have to be treated to obtain a final safe product [12].

The coagulation/precipitation method has the drawback of not being efficient in waters having low F concentrations, and the process produces toxic AlF complexes in the treated water as well as large volumes of waste. While, adsorption processes are considered more appropriate because of its effectiveness, convenience, ease of operation, simplicity of design, and for economic and environmental reasons [3]. Several conventional and nonconventional adsorbents such as activated charcoal, leaf biomass, bio-char, algal biomass, activated alumina [27,28], bone char [29], laterite [30], granular ceramic [14], layered double hydroxides, bauxite, aluminum hydroxide coated rice husk, charcoals containing dispersed aluminum oxide, lanthanum hydroxide, iron-impregnated granular ceramics [31], and fly ash [32] have been used for F removal. Intensive reviews are also available regarding adsorbents and their defluoridation potentials [3,31]. These adsorbents have shown a certain degree of F adsorption capacity but most of them could not be used for wide range of pH and some of them are very expensive for field application. Furthermore, most of them are fine particulates or in powdered form which would be not suitable for column design and hence, there will be a problem of adequate separation. Therefore, it is necessary to explore efficient and low cost adsorbents for full-scale applications and which could be easily regenerated for reuse over several operational cycles without significant loss of adsorptive capacity [3].

Among the various adsorption techniques, biosorption is an emerging technique for water treatment utilizing abundantly available biomaterials [10]. Limited work is available on application of bioadsorbents such as chitosan derivatives, algal and fungal biomass, leaf biomass, bio-char, and agricultural waste such as coconut shell. It has been reported that the presence of chemical functional groups such as hydroxyl, carbonyl, carboxyl, sulfhydryl, theioether, sulfonate, amine amide, imidazole, phosphonate, and phosphodiester on the bio-sorbent surface contribute to bio-sorption but a detailed investigation is required to explore the potential of bioadsorbents [3,6,10].

With this in perspective, defluoridation feasibility of a commercially available biological adsorbent (Bio-Filter [Bio-F]) was studied using batch experiments. The present work reports the results of series of experiments. The main objectives were: (i) to reveal the F adsorption kinetics, (ii) to assess the impact of initial F concentration, temperature, pH, and competitive anions on F removal, (iii) to describe role of some important thermodynamic parameters, and (iv) to investigate regeneration ability of sorbent.

2. Materials and methods

2.1. Materials

All reagent grade chemicals obtained from Merck Co. and de-ionized water were used in this study. 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. For anion study, sulfate, chloride, and nitrate solutions were prepared using their respective salts. For batch adsorption studies, Bio-F adsorbent manufactured by HES Water Engineers (I) Pvt. Ltd. (a joint venture company of water engineers, Australia) was used for the removal of F from aqueous solution.

2.2. Characterization of adsorbent

To estimate the particle size distribution of Bio-F, sieve test was conducted. Density of the sorbent was calculated by pycnometer. Porosity was estimated as $V_b = V_g + V_p$, where the sum of the grain and pore volumes is equal to the bulk volume. Measurement of any two of the three volumes allows for the calculation of the third and subsequent determination of porosity. The surface morphology of the Bio-F was also examined by scanning electron microscopy (SEM).

2.3. Batch sorption experiments

Batch equilibrium adsorption experiments were conducted to determine the adsorption behavior of Bio-F at constant dose (10 g/L) and varying F concentrations. All adsorption experiments except thermodynamic studies were carried out at an ambient temperature (30 ± 1˚C). All the experiments were carried out in 250 mL conical flasks with working volume of 100 mL. These flasks, along with test solution and adsorbent, were shaken at 90 rpm in an orbital shaker with thermostatic control (Remi, India), to study the various parameters. At the end of desired contact time (when equilibrium was achieved), the conical flasks were removed from the shaker, and allowed to stand for 5 min for the adsorbent to settle. During kinetic studies sample was taken out at regular intervals (5, 10, 15, 20, 30, 40, and 60 min) and once the sorption equilibrium was reached (60 min), samples were filtered through Whatman filter paper No. 42 and stored in HDPE bottles for the analysis of the residual F using an Ion meter (Thermo Scientific Orion 5 Star Ion Meter). Calibrations were done using F standards of 0.1, 1, 10 mg/L and the electrode slope was kept at 54–64 mv/decade at room temperature. For decomplexation of aluminum complexes and avoiding interference with the electrode performance, an ionic strength fixer and buffer TISAB-II solution was added in 1:1 proportion to 10 mL sample.

Fluoride removal percentage was then computed based on the following equation [14]:

$$\% \text{ Fluoride removal} = (C_i - C_f/C_i) \times 100$$

where C_i and C_f are initial and final fluoride concentration (mg/L).

The adsorption data were used to determine best fit isotherm model, kinetic model, and their constants.

2.4. pH study

The pH studies were carried out to examine the removal of F from aqueous solution at different pH. A broad pH range of 2–10 was selected to optimize the system in terms of pH. Standard F solution of 5, 10, and 15 mg/L concentration were prepared from the stock solution of F. The pH of the prepared solutions was adjusted with the help of 0.01 N HCl and 0.01 N NaOH solutions using a pH meter (Eltronics India Deluxe 101 pH meter).

2.5. Thermodynamic study

Adsorption experiments were conducted at 10, 20, 30, and 40˚C with initial F concentration of 5, 10, 15, and 20, respectively. The liquid sample were withdrawn after 60 min, filtered, and analyzed for the residual F concentration.

2.6. Effect of competitive anions

The interference effect of different anions usually present in real ground water sample on F sorption by

Bio-F was also studied. All anions (Cl^-, NO_3^-, and SO_4^{2-}) at a concentration of 100, 500, and 1,000 mg/L were spiked with 10 mg/L of F solution.

2.7. Regeneration experiments

To test the regeneration ability of the adsorbent, regeneration of exhausted media was carried out with various concentrations of alum (1, 3, 5, and 7%) and by boiling. For this purpose, initially adsorption was conducted using 10 g/L Bio-F and 5 mg/L of F solution. The sorbent was then separated by means of filtration and washed with distilled water to remove liquid containing F. The adsorbent was then poured with various concentrations of alum for 4–5 h and then it was again filtered and dried for the subsequent use. The boiling was carried out for 1 h and then again it was dried out before its reutilization. F removal efficiencies were examined again at successive cycles after regeneration.

3. Results and discussion

3.1. Sorbent characterization

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.

3.2. Effect of solution pH on F removal potential of Bio-F

Among the several defluoridation affecting factors, pH is generally considered to be the most important factor [3]. Besides this, in most of the solid/liquid sorption processes, the solution pH has great importance in deciding the sorption potential of the sorbent. Effect of solution pH on F removal potential of Bio-F was studied in the pH range of 2–10 and results are illustrated in Fig. 2. The effect of pH on F adsorption was examined at different initial F concentrations (5, 10, and 15 mg/L) and at fixed adsorbent dose (10 g/L). It is clear from the Fig. 2 that at F concentration of 5 mg/L, removal was more than 98% at all pH, whereas a slight decrease in F removal was observed at higher pH (>8) for initial F concentration of 10 and 15 mg/L but it was insignificant as compared to overall removal. On the other side, for most of the adsorbents, pH at which maximum removal occurs lies between 4 and 8. Generally, defluoridation increases from acidic to near neutral pH and then decreases with increase in pH [3]. Therefore prior pH adjustment is not required for effective removal of F by Bio-F at full scale.

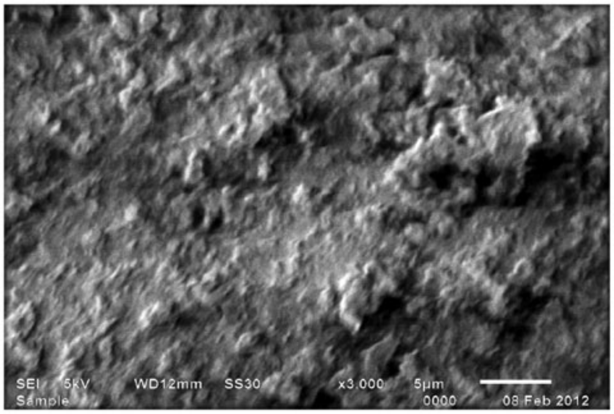

Fig. 1. SEM micrograph of Bio-F sorbent (3,000×).

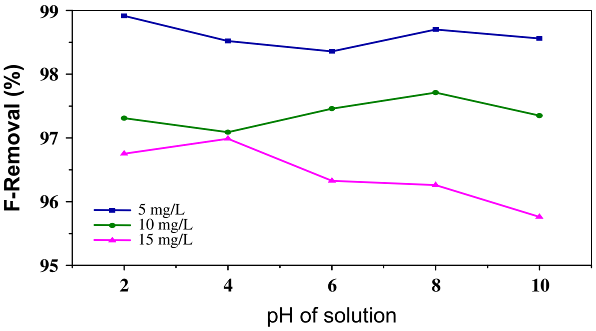

Fig. 2. Effect of solution pH on F removal by Bio-F.

3.3. Effect of initial F concentration and contact time

The initial concentration of adsorbate provides the driving force to overcome all mass transfer resistances between the aqueous and solid phases. That is why a higher initial concentration of F is favorable and it will increase the overall adsorption [31]. With this perspective, effect of initial concentration and contact time on the removal of fluoride has been studied. The effect of contact time on F sorption was investigated by adding a 10 g/L of Bio-F into 100 mL F-spiked solution at various F concentrations (7, 14, 21, and 28 mg/L).

Fig. 3 illustrates the percentage removal of fluoride by Bio-F at neutral pH with increasing contact time.

For all the F concentrations studied, most of the F removal took place within first 15 min and the system reached to equilibrium state gradually in next 45 min. No appreciable removal was noticed beyond 60 min of sorption study. This indicates that initial concentration

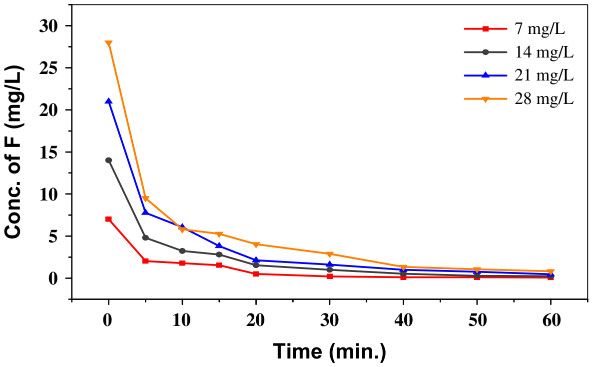

Fig. 3. Effect of contact time on F removal by Bio-F at various initial F concentrations.

of F has least effect on equilibrium time. From the shape of the kinetic curves (Fig. 3), it is also evident that the F sorption onto Bio-F is a two-step process, i.e. initial rapid adsorption during the first 15 min and slow rate of sorption until the equilibrium is reached. For an initial concentration of 28 mg/L of F, ~82% of the removal took place in first 15 min and later it reached up to a total of 97% in next 45 min.

3.4. *Adsorption kinetic studies*

The kinetics of sorption is an important parameter for designing sorption system and is required for selecting optimum operating conditions before applying it at full-scale process. The kinetic adsorption data can be processed to understand the dynamics of the adsorption in terms of reaction order and rate constants. Moreover, it is very helpful in prediction of adsorption rate, which gives important information for designing and modeling the processes [33].

Batch experiments were conducted to explore the rate of F adsorption on Bio-F at neutral pH and different initial F concentrations (7, 14, 21, and 28 mg/L) using fixed adsorbent dose (10 g/L).

As reported in earlier literatures, the process of F removal from aqueous phase by adsorbents has been represented by pseudo-first-order [34,35], pseudo-second-order [36], and intraparticle diffusion [33] kinetic models. The conformity between experimental data and the model predicted values which were expressed by the correlation coefficients (R^2, values close or equal to 1). The model showing relatively higher value is more applicable to the kinetics of F adsorption.

3.4.1. *Pseudo-first-order kinetic model*

The mathematical representations of this model is as given below [34,35],

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

where q_e (mg/g) is the amount of F adsorbed on the adsorbent at equilibrium, q_t (mg/g) is the amount of F adsorbed on the adsorbent at time t, k_1 is the rate constant of the pseudo-first-order adsorption (min^{-1}), and t is time (min).

If the pseudo-first-order kinetics is applicable, a plot of $\log(q_e - q_t)$ vs. t should provide a linear relationship from which k_1 and predicted q_e can be determined from the slope and intercept of the plot, respectively (Fig. 4(a)). The variation in rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. It was observed from Fig. 4(a) that the pseudo-first-order Lagergren model does not fit the experimental data. On the other hand, the experimental q_e values do not agree with the calculated ones, obtained from the linear plots even when the correlation coefficient R^2 are relatively high. Table 1 presents the summary of parameters of kinetic data model fittings. This shows that the adsorption of F onto Bio-F is not appropriate to describe the entire process and not a first-order reaction.

3.4.2. *Pseudo-second-order kinetic model*

Adsorption kinetic was explained by the pseudo-second-order model as given below [36]:

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

where k_2 is the rate constant of the pseudo-second-order adsorption (g/mg/h).

The plot of t/q_t vs. t should show a linear relationship if the second-order kinetics is applicable. Values of k_2 and q_e were calculated from the intercept and slope of the plots of t/q_t vs. t (Fig. 4(b)). The linear plots of t/q_t vs. t show good agreement between experimental and calculated q_e values at different initial F and adsorbent concentrations (Table 1) with correlation coefficients $R^2 \geq 0.99$, which indicated that the pseudo-second-order kinetic model provided good correlation for the adsorption of F onto Bio-F for all studied initial F and adsorbent concentrations in contrast to the pseudo-first-order model.

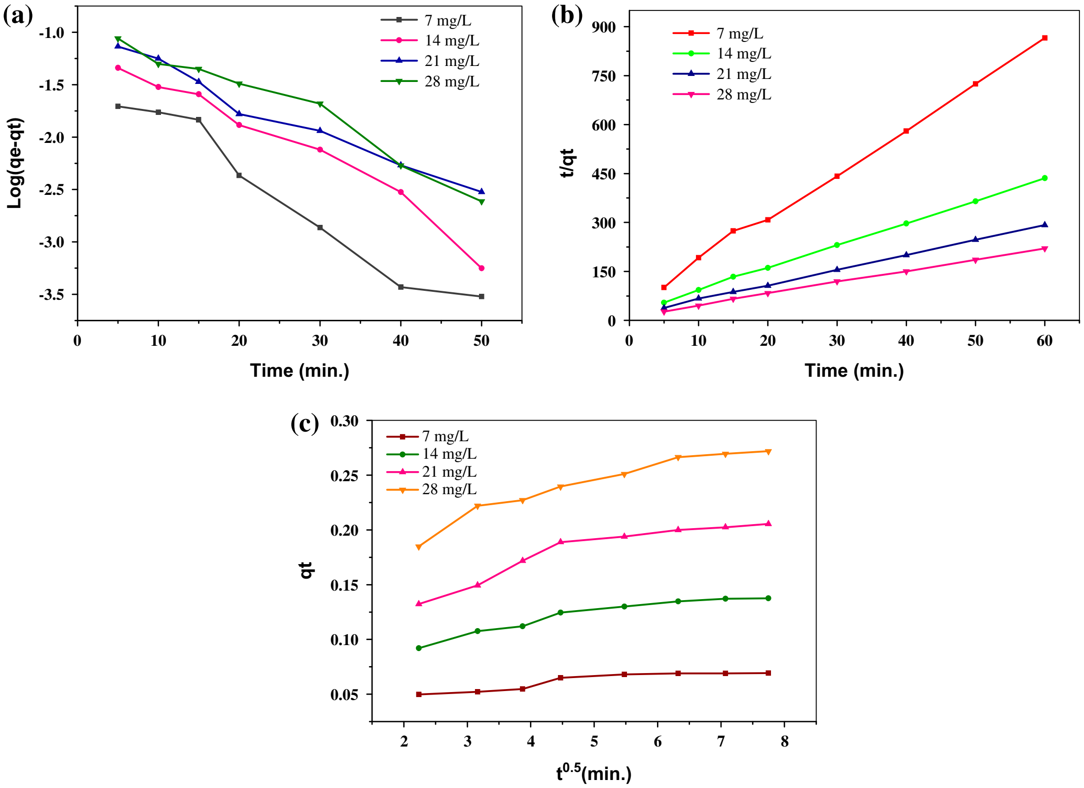

Fig. 4. Kinetics for adsorption of F onto Bio-F at 30°C: (a) pseudo-first-order; (b) pseudo-second-order; and (c) intraparticle diffusion model at various initial concentrations.

Table 1
Kinetic model used and their parameters at different initial F concentrations

	Pseudo-first-order equation			Pseudo-second-order equation			Intraparticle diffusion	
Conc.* of F$^-$ (mg/L)	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (min^{-1})	q_e (mg/g)	R^2	K_{dif} (min^{-1})	R^2
7	0.10732	0.254692	0.958	0.000117	0.073817	0.9976	0.004	0.8472
14	0.09235	0.346179	0.9664	0.000868	0.146199	0.9994	0.008	0.9097
21	0.071623	0.363637	0.9815	0.00276	0.218236	0.9994	0.013	0.8695
28	0.077381	0.420925	0.9689	0.006929	0.286517	0.9992	0.0147	0.9208

*Dose of adsorbent: 10 g/L; pH 6.5–7.

3.4.3. The intraparticle diffusion model

The adsorption process may follow a multi-step transport of solute (adsorbate) molecules from the aqueous phase to the surface of the solid particles followed by diffusion of the solute molecules into the interior of the pores, which is likely to be a slow process, and is therefore, a rate-determining step [33]. This type of adsorption behavior can be explored by applying intraparticle diffusion model by using the following equation [37].

$$q_t = K_{\text{dif}} t^{0.5} + C$$

where C is the intercept and K_{dif} (mg/g/min$^{-0.5}$) is the intraparticle diffusion rate constant. The values C provide information about the thickness of the boundary layer, since the resistance to the external mass transfer increases as the intercept increases.

The plot of q_t against $t^{0.5}$ may present a multi-linearity correlation, which indicates that two or more steps occur during adsorption process (Fig. 4(c)). The

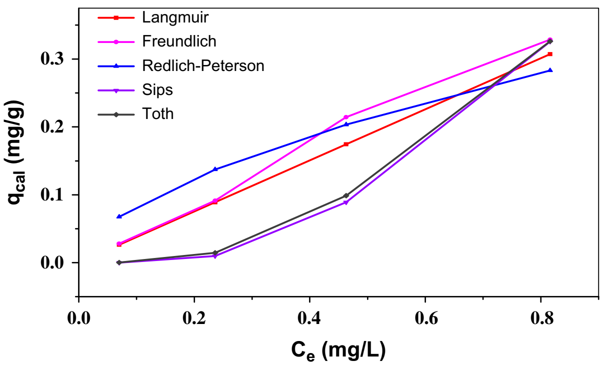

Fig. 5. Isotherm plots for various isotherm models.

rate constant K_{dif} directly evaluated from the slope of the regression line and the intercept is C and is reported in Table 1. The value of correlation coefficient R^2 (Table 1) is not supporting the model for the removal of F using Bio-F. The initial curve showed external mass transfer, while the straight line indicated intraparticle diffusion. It indicates that mechanisms of F removal by Bio-F were complex, and the intraparticle diffusion was not the only rate determining step.

3.5. Adsorption isotherms studies

Analysis of isotherm data is important for predicting the adsorption capacity of the sorbent, which is one of the main parameter required for the design of an adsorption system [38]. In general, an adsorption isotherm is an invaluable curve describing the fundamental information of adsorbent: adsorption capacity and equilibrium time at a constant temperature and pH. Adsorption equilibrium (the ratio between the adsorbed amounts with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time.

The adsorption isotherms of Bio-F were studied and the results are shown in Fig. 5. The experimental data obtained for the present system were analyzed by Langmuir, Freundlich, Redlich–Peterson, Sips, and Toth isotherm models as given in Table 2. The values of isotherm constants and parameters are given in Table 3. The results of Table 3 indicates that although both Langmuir and Freundlich models fitted the experimental data reasonably well but Redlich–Peterson model was best fit for F sorption onto Bio-F.

3.6. Error functions

Linear regression methods are commonly used for determining the best fit isotherm model. In recent

Table 2
Isotherm models, governing equations and their parameters

S. no.	Isotherm model	Equation	Model parameters
1	Langmuir	$q_e = \frac{Q_m K_L C_e}{1+K_L C_e}$	Q_m (mg/g), K_L (L/mg)
2	Freundlich	$q_e = K_F C_e^{1/n}$	K_F (L/g), $1/n$
3	Redlich–Peterson Isotherm	$q_e = \frac{K_R C_e}{1+a_R C_e^{\beta}}$	K_R (L/g), a_R (L/mg), β
4	Sips	$q_e = \frac{q_{m_s}(K_s C_e)^{m_s}}{(1+K_s C_e)^{m_s}}$	K_s (L/g), q_{ms} (mg/g), m_s
5	Toth	$q_e = \frac{q_{\text{mT}} C_e}{\left(A_T + C_e^T\right)^{1/T}}$	q_{MT} (mg/g), A_T (L/mg), T

Table 3
Isotherm model parameters and their values obtained by fitting equilibrium data

Isotherm model	Langmuir	Freundlich	Redlich–Peterson	Sips	Toth
Isotherm parameters	$Q_m = 5.530$ $K_L = 0.058$	$K_F = 1.324$ $n = 3.517$	$K_R = 142.776$ $a_R = 46.823$ $\beta = 0.418$	$q_{m_s} = 3.000$ $K_s = 3.033$ $m_s = 6.544$	$q_{\text{mT}} = 3.000$ $A_T = 2.095$ $T = 4.818$
R^2	0.969	0.972	0.998	0.803	0.825
SSE	0.006	0.005	0.000	0.038	0.034
RMSE	0.057	0.049	0.012	0.194	0.185

Table 4
Different error function used to find best fit in isotherm study

Error function	Abbreviation	Definition/expression
Coefficients of determination	R^2	$R^2 = \frac{\sum (q_m - \overline{q_e})^2}{\sum (q_m - \overline{q_e})^2 - \sum (q_m - q_e)^2}$
Sum squares errors	SSE	$\mathrm{SSE} = \sum_i^n \left(q_{e,\mathrm{cal}} - q_{e,\mathrm{exp}}\right)_i^2$
Root mean squared error	RMSE	$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{N} \left(q_{\mathrm{cali}} - q_{\mathrm{expi}}\right)^2}{n}}$

studies, contrary to the linearization methods, non-linear regression methods, have been one of the most viable tool defining the best-fitting relationship and it tells about the distribution of adsorbate at equilibrium, modeling of the adsorption systems, and verifies the consistency and theoretical assumptions of an isotherm model [39,40]. Nonlinear regression usually involves the minimization or maximization of error distribution (between the experimental data and the predicted isotherm) based on its convergence criteria. The optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the isotherm to the experimental equilibrium data in the single-component isotherm studies [41].

In present study, non-linear method was used to find the best-fitting model and isotherm parameters, which were found out by trial and error method by means of Microsoft's spreadsheet, Excel® software package using *solver* add-in option. In this study, coefficients of determination (R^2), sum squares errors (SSE), and root mean squared error (RMSE) were used to find out the best fit model. The expression used for these are shown in Table 4.

where q_{cal} and q_{exp} represent the predicted and measured value of solid phase F concentrations at equilibrium. q_m, equilibrium capacity obtained from isotherm model, q_e is experimental capacity obtained from the experiment, and $\overline{q_e}$ is the average of q_e.

Among the models listed in Table 2, Langmuir and Freundlich belong to the two constant models and the other belongs to the three constant models. The adsorption isotherm is plotted with C_e on the x-axis and q_e (cal) on the y-axis. MS Excel *Solver* is used to converge the q_e (cal) value to the experimental q_e value. The isotherm which generates maximum coefficients of determination (R^2) value with minimum SSE and RMSE value best represents the data. Redlich–Peterson Isotherm represents the equilibrium data appropriately, which is evident from the high R^2 value and low SSE and RMSE value (Table 3). The parameter values obtained from the models are presented in Table 3, from where we can see that the value of β is very close to 1, which infers that model follows Redlich–Peterson Isotherm. Freundlich and Langmuir Isotherm are followed after by Redlich–Peterson model. Freundlich was empirical model and can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. The n values came greater than zero, which indicates a favorable adsorption process. The Q_m value obtained from Langmuir model is 5.530 mg/g. Among the other three parameter model tested, Sips and Toth model did not represent the equilibrium data well, which is evident from the low R^2 and high SSE and RMSE value. Toth model is a combination of Langmuir and Freundlich models having features of both Langmuir and Freundlich equations. Toth model is an improved version of Sips model, which is derived from potential theory and is applicable for heterogeneous equations.

The estimated F sorption capacity of Bio-F is found to be much higher than many adsorbents used for the removal of F. In recent years, many other sorbents have been investigated for the removal of F from water systems. While comparing the F sorption potential of most of the sorbents reported in the recent literatures [42], Bio-F is found to be highly competitive. The maximum uptake capacity obtained from the different models is estimated ~5.53 mg/g of adsorbent, which is significantly comparable with other reported works [31].

3.7. Thermodynamic study

It is necessary to evaluate the thermodynamic feasibility and to confirm the nature of the adsorption process based on the determination of thermodynamic parameters such as changes in Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). Thermodynamic parameters associated to the adsorption process were determined using the following equations [43,44]:

$$k_{\mathrm{ad}} = \frac{C_{\mathrm{Ae}}}{C_e}$$

$$\ln k_{\mathrm{ad}} = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

Table 5
Thermodynamic parameters of F adsorption onto Bio-F

Concentration of F^- (mg/L)	Temperature (°C)	ΔG° (kJ/mol)	ΔS° (kJ/(mol K))	ΔH° (kJ/mol)
5	10	−8.78448	0.13575	29.61614
	20	−9.97851		
	30	−12.0869		
	40	−12.5768		
10	10	−8.0728	0.091301	17.97256
	20	−8.4559		
	30	−9.75851		
	40	−10.7082		
15	10	−7.30428	0.087352	17.56265
	20	−7.86294		
	30	−8.8437		
	40	−9.91203		
20	10	−6.97439	0.090694	18.84059
	20	−7.48058		
	30	−8.75729		
	40	−9.58722		

$$\Delta G = -RT \ln K_{\mathrm{ad}}$$

where C_{Ae} is the concentration of F in solid phase at equilibrium and C_e is equilibrium concentration.

Thermodynamic parameters for the adsorption of F on Bio-F are listed in Table 5. The values of ΔG° calculated using the K_{ad} were negative, which indicates spontaneity and thermodynamic stability of the process. The decrease in the negative value of ΔG° with the increase in temperature at the fixed initial F concentration indicates that the adsorption process of F onto Bio-F is more favorable at higher temperature. An endothermic reaction can be explained as due to enlargement of pore sizes and/or activation of the adsorbent surface [3].

The value of enthalpy of a sorption process may be used to distinguish between chemical and physical sorption. The enthalpy change at different initial F concentration for the adsorption was found to be from 17.56 to 29.61 kJ/mol. Chemical sorption value ranges from 40 to 800 kJ/mol while physical sorption ranges from 5 to 40 kJ/mol [12]. On the basis of above results it can be concluded that F sorption on Bio-F is a physical process. The positive values of ΔH° denote that the process was endothermic. At all initial F ion concentration the ΔS° values for the adsorption process is positive. This indicates the prevalence of a high degree of disorderliness at the solid solution interface during the adsorption of F ion onto Bio-F. This may be due to the fact that adsorbed water molecules which are displaced by the adsorbate species gain more translational entropy than entropy lost by the adsorbate molecule. Thus, allowing prevalence of randomness in system [3].

3.8. Effect of presence of competitive anions on fluoride removal

In natural water, several anions including chloride, nitrate, and sulfate are simultaneously present with F at different concentrations which can compete with F for the active sorption sites [3]. Therefore, interference effect of different co-anions on defluoridation by Bio-F was also studied.

Various concentrations of anions (Cl^-, NO_3^-, and SO_4^{2-}) were spiked with 10 mg/L of F solution. The dose of adsorbent was kept constant at 10 g/L and concentrations of all anions varied from 100 to 1,000 mg/L. Fig. 6 shows the results of such observations. From Fig. 6, it is observed that at all tested anion concentrations (100, 500, and 1,000 mg/L) the removal percentage of fluoride by Bio-F lies above 98%. This indicates that adsorbent is F specific and defluoridation remains unaffected in presence of other anions.

3.9. Fluoride desorption and spent adsorbent regeneration

Besides high F adsorption capacity and cost-effectiveness, an adsorbent must be amenable to easy desorption of the adsorbed F and must be capable of

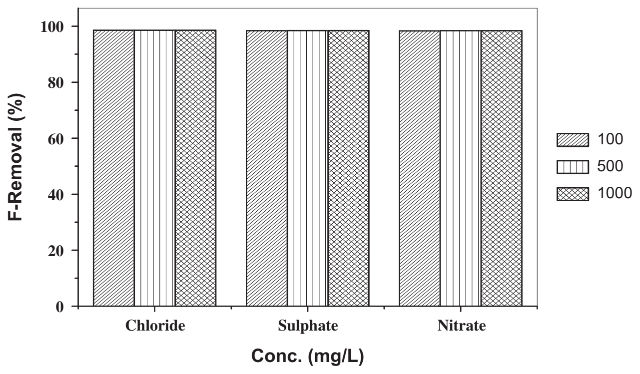

Fig. 6. Individual effect of different co-existing anions on F sorption by Bio-F (anions were added as their respective salts).

efficient regeneration for multiple reuse to improve the process economics. Therefore, in the present work the spent adsorbent was regenerated to assess its reusability. Desorption of F is generally carried out by acids, bases, and salts [3]. Earlier works [45] also reported the application of alum for regeneration of adsorbents. In present study, adsorbent was regenerated using alum treatment and boiling.

Adsorption studies were conducted by loading the adsorbent with fluoride solution (adsorbent dose: 10 g/L; conc. of F: 5 mg/L). Thereafter desorption experiments were carried out with various concentrations of alum (0.0–7%) as eluent and by boiling means. From Fig. 7(a) it was observed that 3% alum could elute nearly ~92% adsorbed F from Bio-F. Above 3% alum concentration, there was no effect of alum concentration on regeneration. Boiling was also exercised as regeneration method exhibiting an efficiency of 88%. In order to check the reusability of Bio-F, cyclic regeneration studies were conducted. The results of these studies (Fig. 7(b)) showed considerable reduction in adsorption efficiency in the subsequent second and third cycles when boiling was used for regeneration. When alum was used, there was no significant reduction in adsorption efficiency observed even after third cycle. Surprisingly, a slight increase in adsorption efficiency in second cycle was observed. The probable reason may be the complexation of F^- ions with dissolved aluminum which could have generated new site for F adsorption.

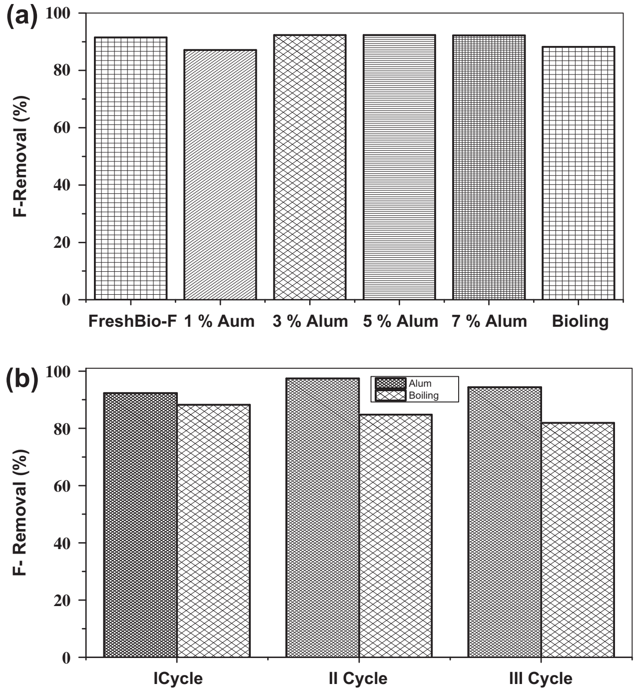

Fig. 7. Regeneration studies: (a) effect of Bio-F regeneration by alum (3%) and boiling on F removal efficiency and (b) removal efficiency at successive cycles.

4. Conclusions

In this study, Bio-F has been used as an adsorbent and examined for its potential in removing F from drinking water. This adsorbent has shown much higher and faster F removal. The main conclusions drawn from the present study are:

- Adsorption process was found to be independent of pH which allows the wide acceptability of sorbent for field applications.
- The F adsorption took place rapidly during the first 15 min and there after slowly reached to a pseudo-equilibrium state in next 45 min. Adsorption kinetics followed pseudo-second-order model. F uptake by Bio-F is a complex process and the intraparticle diffusion was not the only rate determining step.
- Three-parameter model Redlich–Peterson Isotherm could fit the equilibrium data reasonably, followed by two-parameter isotherm models (Freundlich and Langmuir) with high R^2 value and low SSE and RMSE value, whereas other three-parameter isotherm models such as Sips and Toth didn't represent equilibrium data well with low R^2 value and high SSE and RMSE value. The predicted F adsorption capacity of Bio-F by Langmuir model was found to be much higher than many other commonly used sorbents.
- Most of the common interfering anions (Nitrate, Sulfate, and Chloride) present in drinking water have shown negligible effect on F sorption by Bio-F. This shows the adsorbent's high F selectivity and suitability in practical situations.

- Thermodynamic study reveals that adsorption process is favorable at higher temperature. The values of enthalpy reveal that process is endothermic.
- The F bearing Bio-F could be effectively regenerated with 3% alum solution and by the boiling of sorbent with water.

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Nomenclature

C_e — equilibrium concentration of the adsorbate in the solution (mg/L)
q_e — amount of adsorbate removed from aqueous solution at equilibrium (mg/L)
$\overline{q_e}$ — average of q_e
q_t — amount of adsorbate sorbed onto adsorbent surface at any time t (mg/g)
q_{cal} — calculated solid phase F concentration at equilibrium (mg/g)
q_{exp} — experimentally measured solid phase F concentration at equilibrium (mg/g)
k_1 — first order rate constant of sorption (min^{-1})
k_2 — second order rate constant of sorption (g/mg/min)
K_{dif} — constant of intraparticle diffusion (g/mg/min$^{-1/2}$)
t — reaction time (min)
K_F — Freundlich isotherm constant (l/g)
K_R — Redlich–Peterson Isotherm constant (l/g)
K_S — Sips isotherm constant (l/g)
Q_m — monolayer capacity of Langmuir equation (mg/g)
q_{mS} — specific sorption capacity of Sips equation at saturation (mg/g)
q_{mT} — specific sorption capacity of Toth equation at saturation (mg/g)
n — Freundlich adsorption intensity
K_L — Langmuir isotherm constant (l/mg)
a_R — Redlich–Peterson Isotherm constant (l/mg)
A_T — Toth isotherm constant (l/mg)
β — Redlich–Peterson Isotherm model exponent
m_S — Sips isotherm model exponent
T — Toth isotherm model exponent
G° — Gibb's free energy (kJ/mol)
H° — enthalpy (kJ/mol)
S° — entropy (kJ/mol K)
T — temperature (°C)
K_{ad} — adsorption equilibrium constant of Langmuir
R — universal gas constant (J/mol/K)

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