Adsorption Isotherms on Fluoride Removal: Batch Techniques

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ABSTRACT

The ability of cynodon dactylon based thermally activated carbon to remove fluoride from aqueous solution has been investigated. The batch adsorption studies were carried out at neutral pH as the functions of contact time, adsorbent dose, adsorbate concentration, temperature and effect of co-anions, which are commonly present in water. The rate of adsorption was rapid during initial 105 minutes and attained equilibrium. Adsorption isotherms have been modeled by Langmuir, Freundlich, Temkin and Redlich–Peterson isotherms. The data indicate that prepared adsorbent surface sites are heterogeneous in nature and that fits into a heterogeneous site binding model. The present system followed the Redlich–Peterson isotherm as well as Langmuir adsorption isotherm model. The enthalpy change ($\Delta H^\circ$) and entropy change ($\Delta S^\circ$) for the adsorption reaction are calculated as +8.725 kJ/mol and +0.033 J/mol K respectively. The adsorption is endothermic in nature. Instrumental analysis XRD, FT-IR and SEM gives the conformation about the fluoride binding ability of adsorbent. Field studies were carried out with the fluoride containing water sample collected from a fluoride-endemic area in order to test the suitability of the sorbent at field conditions and obtained good success rate.

Key words: Fluoride, cynodon dactylon, adsorption, isotherms, kinetic models.

INTRODUCTION

High fluoride levels in drinking water has become a critical health hazard of this century as it induces intense impact on human health including skeletal and dental fluorosis [1]. Though fluoride is an essential constituent for both humans and animals, it can be either beneficial or detrimental to human health depending on the level of fluoride in drinking water [2]. In India, the problem is common in places such as Andhra Pradesh, Tamilnadu, Karnataka, Kerala, Rajasthan, Gujarat, Uttar Pradesh, Punjab, Orissa and Jammu and Kashmir [3]. Free fluoride level in drinking water was identified at 3.02 mg/L in Kadayam block of Tamilnadu [4]. Fluoride survey in Nilakottai block of Tamilnadu showed a positive correlation between prevalence of dental fluorosis in children and levels of fluoride in portable water is 3.24 mg/L [5].
Adsorption is one of the significant techniques in which fluoride adsorbed onto a membrane, or a fixed bed packed with resin or other mineral particles. Many natural and low cost materials such as red mud [6,7], zirconium impregnated coconut shell carbon [8], cashew nut shell carbon [9], ground nut shell carbon [10] and clays [11] have been used as adsorbents for fluoride removal from drinking water. Recently, amorphous alumina supported on carbon nanotubes [12], aligned carbon nanotubes [13], ion exchange polymeric fiber [14], and an ion exchanger based on a double hydrous oxide of Al and Fe (Fe$_2$O$_3$Al$_2$O$_3$·xH$_2$O) [15] have been assayed for removing fluoride from drinking water as well as industrial wastewater.

Thus, it is important to develop or find cheaper adsorbents for fluoride removal from water that have greater fluoride adsorption capacities like the above said adsorbents. This paper concentrates on investigate low cost material for fluoride sorption which can effectively remove fluoride from aqueous solutions at a relatively low level. The novel adsorbent obtained by burning, carbonization and thermal activation of the *cynodon dactylon*, possess appreciable defluoridation efficiency. The thermally activated carbon should have high surface area and strong sorption capacity towards various sorbates [16]. This adsorbent is abundantly available in all dry and wet lands in huge amount. We report here the results of defluoridation studies using *cynodon dactylon*. This study leads to the assumption that fluoride deposition occurs by the forces of adsorption over the surface of the activated carbon and this was characterized by the surface morphological studies of the adsorbent material. In addition, the dynamics and kinetics of the adsorption process are discussed.

**MATERIALS AND METHODS**

*Adsorbent preparation*

In the present study, the derived activated carbons from *cynodon dactylon*, common name, Bermuda grass, was utilized for the removal of fluoride from its aqueous solution. The *cynodon dactylon* was cut into small pieces and they were washed several times with water to remove the dirt and other materials attached to its surface. Final washings were done with double distilled water and the pieces were dried in shade. Then the material was dried at 105-110°C for 24 hours and then the carbonized material was powdered and washed well with doubly distilled water to remove the free acid and dried at the same temperature for 3 hours. Later the dried adsorbent was thermally activated in Muffle furnace at 800°C (here we avoid acid treatment for charring). The resulting product was cooled to room temperature and sieved to the desired particle sizes, namely, <53, 53 - 106, 106-150, 150 - 225 and 225-305 mesh. Finally, the product was stored in vacuum desiccators until required.

*Sorption experiments*

The sorption isotherm and kinetics experiments were performed by batch adsorption experiments and were carried out by mixing 1.25 g (obtained by the study effect of adsorbent dose) of sorbent with 100 mL of sodium fluoride containing 3 mg/L as initial fluoride concentration. The mixture was agitated in a thermostatic shaker at a speed of 250 rpm at room temperature. The defluoridation studies were conducted for the optimization of various experimental conditions like contact time, initial fluoride concentration, adsorbent dose, particle size and influence of co-ions with fixed dosage. The reagents used in this present study are of analytical grade. A fluoride ion stock solution (100 mg/L) was prepared and other fluoride test solutions were prepared by subsequent dilution of the stock solution. All the experiments were carried out at room temperature. Fluoride ion concentration was measured with a specific ion selective electrode by use of total ionic strength adjustment buffer II (TISAB II) solution to maintain pH 5–5.5 and to
eliminate the interference effect of complexing ions [9]. The pH of the samples was also measured by Orion ion selective equipment. All other water quality parameters were analysed by using standard methods [17]. Kinetic studies of sorbent were carried out in a temperature controlled mechanical shaker. The effect of different initial fluoride concentrations viz., 2, 4, 6, 8 and 10 mg/L at four different temperatures viz., 303, 313, 323 and 333K on sorption rate were studied by keeping the mass of sorbent as 1.25 g and volume of solution as 100 ml in neutral pH.

The fluoride concentration retained in the adsorbent phase, \( q_e \) (mg/g), was calculated according to [18],

\[
q_e = \frac{(C_o - C_e)}{W}
\]

where \( q_e \) is the amount of fluoride adsorbed (mg/g); \( C_o \) and \( C_e \) are the initial and residual concentration at equilibrium (mg/L), respectively, of fluoride in solution; and \( W \) is the weight (g) of the adsorbent.

**Characterization of sorbents**

The X-ray diffraction (XRD) pattern of adsorbent was obtained using a Bruker AXS D8 Advance, Inst ID: OCPL/ARD/26-002 X-ray diffractometer. Fourier transform infrared spectra were recorded using Nicolet 6700, Thermo Electronic Corporation, USA made spectrophotometer. The scanning electron microscopy (SEM) analysis performed using a Philips XL-20 electron microscope. Computations were made using Microcal Origin (Version 6.0) software. The accuracy of fit are discussed using regression correlation coefficient (r) and chi-square analysis (SSE). The chi-square statistic test is basically the sum of the square of the difference between the experimental data and data obtained by calculating from the models, with each squared difference divided by the corresponding data obtained by calculating from the models. The equivalent mathematical statement [19] is:

\[
\chi^2 = \sum \frac{(q_e - q_e,m)^2}{q_e,m}
\]

where \( q_e,m \) is equilibrium capacity obtained by calculating from the model (mg/g) and \( q_e \) is experimental data of the equilibrium capacity (mg/g).

**Theory of Isotherm models**

The abilities of four widely used isotherms, the theoretical Langmuir, empirical Freundlich, Temkin and Redlich–Peterson isotherms, to model the adsorption equilibrium data were examined. To express the mechanism of fluoride adsorption onto the surface of adsorbent, the kinetic models pseudo first order, pseudo second order, intra particle diffusion and Elovich models are used to analyze the present adsorption data to determine the related kinetic parameters.

*Langmuir adsorption isotherm* [20] is perhaps the best known of all isotherms, which is often applied in solid/liquid system to describe the saturated monolayer adsorption. It can be represented as:

\[
q_e = \frac{q_mK_aC_e}{1 + K_aC_e}
\]
where $C_e$ is the equilibrium concentration (mg/L); $q_e$ is the amount of ion adsorbed (mg/g); $q_m$ is $q_e$ for a complete monolayer (mg/g); $K_a$ is adsorption equilibrium constant (L/mg). To evaluate the adsorption capacity for a particular range of adsorbate concentration, the aforementioned equation (Eq. (3)) can be used as a linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$$  \hspace{1cm} (4)

The constants $q_m$ and $K_a$ can be determined from a linearised form of Eq. (4) by the slope of the linear plot of $C_e/q_e$ versus $C_e$.

**Freundlich adsorption isotherm** [21] based on adsorption on heterogeneous surface is the earliest known relationship describing the adsorption equilibrium and is given by:

$$q_e = K_F C_e^{1/n}$$  \hspace{1cm} (5)

where $q_e$ is the amount of ion adsorbed (mg/g); $C_e$ is the equilibrium concentration (mg/L); $K_F$ and $1/n$ are empirical constants, indicating the adsorption capacity and adsorption intensity, respectively. The Eq. (5) may be converted to a linear form [22] by taking logarithms:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  \hspace{1cm} (6)

The plot of $\log q_e$ versus $\log C_e$ of Eq. (6) should result in a straight line. From the slope and intercept of the plot, the values for $n$ and $K_F$ can be obtained.

**Temkin Isotherm** [23], the simple form of adsorption isotherm model, has been developed considering the chemisorption of an adsorbate onto the adsorbent, is represented as

$$q_e = a + b \log C_e$$  \hspace{1cm} (7)

where $q_e$ and $C_e$ have the same meaning as noted previously and the other parameters are called the Temkin constants. The plot of $q_e$ versus $\log C_e$ will generate a straight line. The Temkin constants $a$ and $b$ can be calculated from the slope and intercept of the linear plot.

**Redlich–Peterson isotherm** [24] contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. It can be described as follows:

$$q_e = \frac{A C_e}{1 + B C_e^g}$$  \hspace{1cm} (8)

Eq. (8) can be converted to a linear form by taking natural logarithms:

$$\ln \left( A \frac{C_e}{q_e} - 1 \right) = g \ln (C_e) + \ln (B)$$  \hspace{1cm} (9)

Three isotherm constants, $A$, $B$, and $g$ ($0 < g < 1$), can be evaluated from the linear plot represented by Eq. (9) using a trial and error optimization method [25].
RESULTS AND DISCUSSION

Effect of contact time and initial fluoride concentration
Contact time plays a very important role in adsorption dynamics. The effect of contact time on adsorption of fluoride onto *cynodon dactylon* is shown in Fig. 1. Batch adsorption studies using the concentrations 2.0, 3.0, 4.0, 6.0, 8.0 and 10.0 mg/L of fluoride solution and with 1.25 g of the adsorbent were carried out at 303K as a function of time to evaluate the defluoridation and adsorption rate constants. The adsorption of fluoride increases with time and gradually attains equilibrium after 105 minutes. From Fig. 1, the time to reach equilibrium conditions appears to be independent of initial fluoride concentrations. Therefore 105 minutes was fixed as minimum contact time for the maximum defluoridation of the sorbent. The adsorption of fluoride decreased from 84 to 51% by increasing fluoride concentration from 2.0 to 10.0 mg/L. Further, it was observed that the removal curves are smooth and continuous indicating the possibility of the formation of monolayer coverage of fluoride ion at the interface of adsorbent.

![Fig.1 Percentage of fluoride adsorbed on *cynodon dactylon* versus time for different initial fluoride concentration.](image)

Effect of particle size
The defluoridation experiments were conducted using *cynodon dactylon* with five different particle sizes viz. >53, 53–106, 106–150, 150–225 and 225–303µm. As the adsorption process is a surface phenomenon, the defluoridation efficiency of the sample with 53µm registered high defluoridation efficiency due to larger surface area. The percentages of fluoride removal by the sample with different particle sizes are studied. Hence, the material with particle size of 53µm has been chosen for further experiments. Higher percentage of adsorption by *cynodon dactylon* with smaller particle size is due to the availability of more specific surface area on the adsorbent surface.

Influence of Adsorbent dose
The influence of varying concentrations of adsorbent on the adsorption of fluoride at neutral pH is shown in Fig. 2. While increasing the adsorbent dose proportional removal observed for fluoride until some extent. After that, the curve lapse as flat indicating the higher fluoride adsorption occurs at 1.25 g and the followings remains constant. A distribution coefficient $K_D$
reflects the binding ability of the surface for an element. The $K_D$ values of a system mainly depends on pH and type of surface. The distribution coefficient $K_D$ values for fluoride and *cynodon dactylon* at neutral pH were calculated [26] with

$$K_D = \frac{C_s}{C_w}$$

(15)

where $C_s$ is the concentration of fluoride in the solid particles (mg/kg) and $C_w$ is the concentration in water (mg/L). It is seen that the distribution coefficient $K_D$ increases with an increase in adsorbent concentration, indicating the heterogeneous surface of the adsorbent. It is observed in Fig. 3 that $K_D$ increases with an increase in adsorbent concentration at constant pH. If the surface is homogeneous, the $K_D$ values at a given pH should not change with adsorbent concentration. All the forthcoming experiments were carried out using constant adsorbent dose 1.25 g.

Fig.2 Variation of fluoride removal for different adsorbent dosage at constant temperature.

Fig.3 The relationship between distribution coefficient $K_D$ with different adsorbent dosages.
Effect of Interfering co-ions
The effects of coexisting anions such as sulfate, nitrate, chloride, and bicarbonate on fluoride adsorption by the *cynodon dactylon* adsorbent were examined and the results are given in Fig. 4. Chloride and nitrate did not perceptibly interfere with fluoride removal even at a concentration of 500 mg/L, while sulfate began to show some adverse effects when the SO$_4^{2-}$ concentration increases. However, bicarbonate showed great competitive adsorption with fluoride. The fluoride adsorption amount decreased quickly from 83.7 to 51.5% with the increase of bicarbonate concentration 0–300 mg/L, and then decreased slightly with further increase of bicarbonate concentration. This may be attributed to the competition of bicarbonate ions with the fluoride ions at the active site, on the surface of the sorbents. The selective nature of the fluoride by the sorbent depends on size, charge, polarizability, electronegativity difference, etc. The order of interference for fluoride removal observed as in the following order, HCO$_3^-$ > SO$_4^{2-}$ > Cl$^-$$\geq$ NO$_3^-$ for the adsorbent *cynodon dactylon*. Similar trend was reported while studying zirconium impregnated cashew nut shell carbon as a sorbent for fluoride removal [9].

Fig.4 Interference of co-ions on defluoridation studies using *cynodon dactylon* adsorbent.

Adsorption isotherms
The equilibrium data isotherm analysis for fluoride adsorption onto the *cynodon dactylon* at pH 7.0(± 0.2) and a temperatures of 303, 313, 323 and 333K are shown in Fig. 5–8. Results indicate that the adsorbent has a high affinity for fluoride adsorption under these conditions. The equilibrium data has been analyzed by linear regression of isotherm model equations, viz. Langmuir (Fig. 5), Freundlich (Fig. 6), Temkin (Fig. 7), and Redlich-Peterson (Fig. 8). The related parameters obtained by calculation from the values of slopes and intercepts of the respective linear plots are shown in Table 1. The present data fit the Langmuir and Redlich-Peterson models (Fig. 5 and 8) well ($r^2$ > 0.99). The average monolayer adsorption capacity ($q_m$) obtained for *cynodon dactylon* is 4.702 mg/g. The value for the Redlich-Peterson constant $A$ that is obtained as high (72.9–102.1 L/g) for the maximum optimized value for $g$ (0.825–0.872), which indicates the high affinity of *cynodon dactylon* for fluoride. These high $g$-value of the Redlich-Peterson model required to describe the best fit of the present data indicated that the adsorption of fluoride is due to the Langmuir monolayer surface adsorption. However, the Freundlich isotherm model, based on multilayer adsorption, described the data fairly well ($r$ = 0.994–0.997). The Freundlich adsorption constants ($K_F$) obtained from the linear plot were fall
between 3.0 and 3.4. The Freundlich coefficient ($n$), which should have values ranging from 1 to 10, is high (5. –6.3), and that supports the favorable adsorption of fluoride onto the adsorbent. The linear plot for Temkin adsorption isotherm, which contains the features of chemisorption, relatively described the present isotherm adsorption data ($r = 0.996$–$0.998$). This indicated that the adsorption of fluoride onto the adsorbent might be happened by chemisorptions with physical forces. Hence, the order of isotherm equations obeyed by the present data is Redlich-Peterson > Langmuir > Freundlich > Temkin isotherm.

The effect of isotherm shape can be used to predict whether an adsorption system is ‘favorable’ or ‘unfavorable’. I.A.W. Tan et.al. used the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter $R_L$ which is defined by the following relationship [27]:

$$R_L = \frac{1}{1 + K_a C_0}$$  \hspace{1cm} (16)

where $R_L$ is a dimensionless separation factor, $C_0$ the initial fluoride concentration (mg/L) and $K_a$ the Langmuir constant (L/mg). The parameter $R_L$ indicates the isotherm shape accordingly:

<table>
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<tr>
<th>Value of $R_L$</th>
<th>Type of Isotherm</th>
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<tr>
<td>$R_L &gt; 1$</td>
<td>Unfavorable</td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td>Linear</td>
</tr>
<tr>
<td>$0 &lt; R_L &lt; 1$</td>
<td>Favorable</td>
</tr>
<tr>
<td>$R_L = 0$</td>
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</tbody>
</table>

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<td>Favorable</td>
</tr>
<tr>
<td>$R_L = 0$</td>
<td>Irreversible</td>
</tr>
</tbody>
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Fig.5 Langmuir isotherms obtained by using linear method for the adsorption of fluoride using activated adsorbent at various temperatures.
Fig. 6 Plot of the Freundlich isotherm for fluoride adsorption on *cynodon dactylon*.

Fig. 7 Adsorbent response to Temkin isotherm for fluoride removal at different temperatures.

Fig. 8 Redlich–Peterson isotherms for the sorption of fluoride ions by using *cynodon dactylon* at various temperatures.
A figure with a relationship between $R_L$ and $C_0$ was presented in Fig. 9 to show the essential features of the Langmuir isotherm. Table 2 showed the values of $R_L$ for *cynodon dactylon* at different experimental temperatures. In this work, the $R_L$ values calculated in the studied range of fluoride concentration are determined to be in the range of 0.044–0.24, which suggests the favorable adsorption of fluoride onto the studied adsorbent, under the conditions used for the experiments.

**Fig.9** Separation factor $R_L$ values verses initial fluoride concentration for various temperatures derived by Langmuir constants.

![Figure 9](image)

**Fig.10** Plot of Gibbs free energy change $\Delta G^\circ$, versus temperature $T$.

![Figure 10](image)
Fig. 11 Scanning Electron Microscope view of fluoride treated thermally activated cycnodon dactylon adsorbent

Fig. 12 XRD pattern of pure and fluoride treated adsorbent
Thermodynamic parameters
The effect of temperature has a major influence in the sorption process and hence the sorption of *cynodon dactylon* was monitored at four different temperatures 303, 313, 323 and 333K under the optimized condition and thermodynamic parameters viz., standard free energy change (ΔGº), standard enthalpy change (ΔHº) and standard entropy change (ΔSº) were calculated [28] and presented in Table 3 (Fig. 10). The negative values of ΔGº indicated the spontaneity of the
The positive values of $\Delta H^\circ$ indicated the endothermic nature of the sorption process. The positive value of $\Delta S^\circ$ showed the increasing randomness at the solid/liquid interface during sorption of fluoride. The results showed the increase in adsorption capacity of fluoride with increasing temperature, which is presumably due to control of the adsorption process by diffusion phenomenon. Thus, the result indicates the endothermic nature of the diffusion controlled adsorption process. It also indicates the increased disorder in the system with changes in the hydration of adsorbing fluoride ions [29].

**Instrumental Analysis**

The surface, morphology, and size distribution of the *cynodon dactylon* adsorbent particles were observed by means of a SEM, XRD and FTIR spectral analysis. The morphology of the fluoride treated adsorbent shown in SEM Fig.11 and it can be observed that the particles presented as surface texture, flock and different levels of porous surface. The forms and sizes of the particles are very irregular after fluoride treatment. The X-ray diffraction patterns of raw and fluoride treated material are given in Fig. 12. The XRD data of the fluoride treated adsorbent provided evidence of considerable modification over the crystal cleavages by indicating some peak appearance at 20 values of 29.38, 32.48 and 47.68 and intensity differences at 26.17 and 32.48. This shows the strong adsorption of fluoride on the surface of the adsorbent. The FTIR spectrum obtained (Fig. 13) for the adsorbent displayed the following major bands: 3448.8 cm$^{-1}$: O-H stretch; 2924.18 cm$^{-1}$: C-H stretch; 1106.25 cm$^{-1}$: C-O stretch; 619.17 cm$^{-1}$: C-OH twist. It is reflecting the complex nature of adsorbent and shows significant band shifting and intensity changes due to fluoride sorption (Fig. 13 and 14).

Table 1. Isotherm parameters obtained using the linear method for the adsorption of fluoride onto *cynodon dactylon* at different temperatures.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>Temperature (K)</th>
<th>303</th>
<th>313</th>
<th>323</th>
<th>333</th>
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<tbody>
<tr>
<td>Langmuir</td>
<td>$q_m$ (mg/g)</td>
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<td></td>
<td>$K_a$ (dm$^3$/mg)</td>
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<td>1.773</td>
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<td></td>
<td>$r$</td>
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<tr>
<td>Freundlich</td>
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<td></td>
<td>$1/n$</td>
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<td>$B$ (dm$^3$/mg)$^b$</td>
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<tr>
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<td>0.064</td>
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Field trial
The defluoridation efficiency of *cynodon dactylon* in the field level was experienced with the sample collected from a near by fluoride-endemic villages. About 1.0 g of sorbent was added to 100 mL of fluoride water sample and the contents were shaken with constant time at room temperature. These results are presented in Table 4. There is a significant reduction in the levels of other water quality parameters in addition to fluoride. It is evident from the result that the sorbent, *cynodon dactylon* based adsorbent can be effectively employed for removing the fluoride from water.

### Table 2. \( R_L \) values at different temperatures, which were calculated using Langmuir constants.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Fluoride Concentration (mg/L)</th>
<th>Temperature (K)</th>
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<td>1</td>
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<tr>
<td>2</td>
<td>4</td>
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</tr>
<tr>
<td>3</td>
<td>6</td>
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</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.073</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0.060</td>
</tr>
</tbody>
</table>

### Table 3. Thermodynamic parameters of fluoride sorption on *cynodon dactylon*.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Thermodynamic Parameters</th>
<th>Temperature (K)</th>
<th>Thermodynamic Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \Delta G^\circ ) (kJ/mol)</td>
<td>303</td>
<td>-1.153</td>
</tr>
<tr>
<td></td>
<td></td>
<td>313</td>
<td>-1.490</td>
</tr>
<tr>
<td></td>
<td></td>
<td>323</td>
<td>-1.866</td>
</tr>
<tr>
<td></td>
<td></td>
<td>333</td>
<td>-2.116</td>
</tr>
<tr>
<td>2</td>
<td>( \Delta H^\circ ) (kJ/mol)</td>
<td></td>
<td>8.725</td>
</tr>
<tr>
<td>3</td>
<td>( \Delta S^\circ ) (J/(mol K))</td>
<td></td>
<td>0.033</td>
</tr>
</tbody>
</table>

### Table 4. Physico-chemical parameters of defluoridated drinking water from field

<table>
<thead>
<tr>
<th>Water quality parameters</th>
<th>Before treatment</th>
<th>After treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride (mg/L)</td>
<td>3.14</td>
<td>1.03</td>
</tr>
<tr>
<td>pH</td>
<td>8.2</td>
<td>7.7</td>
</tr>
<tr>
<td>Electrical conductivity (µS/cm)</td>
<td>361</td>
<td>217</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>112</td>
<td>60</td>
</tr>
<tr>
<td>Total hardness (mg/L)</td>
<td>394</td>
<td>212</td>
</tr>
<tr>
<td>Total alkalinity (mg/L)</td>
<td>317</td>
<td>196</td>
</tr>
</tbody>
</table>

Regeneration study
Any adsorbent is economically viable if the adsorbent can be regenerated and reused in many cycles of operation. For checking the desorption capacity of the sorbent, the material was subjected to an adsorption at an initial fluoride concentration of 3 mg/L. The exhausted adsorbent was regenerated using 0–10% NaOH. At 2% NaOH concentration, *cynodon dactylon* based adsorbent had desorbed up to the level of 67.4% of fluoride. To test the adsorption

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potential of regenerated adsorbent, two more cycles of adsorption–desorption studies were carried out by maintaining the initial conditions of the same. In third cycle, the adsorbent capacity has shown 19%. From the observations this adsorbent having somewhat reuse potential for fluoride removal.

**CONCLUSION**

The defluoridation studies of the bioadsorbent *cynodon dactylon* have been carried out in batch mode. The most excellent defluoridation occurred at the optimum time 105 minutes to get the success rate as 83.77% while keeping 3.0 mg/L fluoride concentration and 1.25 g dosage of adsorbent at neutral pH. Thus, it shows superior adsorptive efficiency than previously studied defluoridation works using natural adsorbents [8–10]. However, the presence of bicarbonate ions interfere the effective removal of fluoride using this adsorbent. The sorption of fluoride using this adsorbent followed Redlich-Peterson isotherm as well as Langmuir isotherms. The sorption process was found to be spontaneous and endothermic in nature. Field studies indicated that *cynodon dactylon* could be used as an effective defluoridating agent. The used adsorbents could be regenerated by 67.4% using of 2% sodium hydroxide. Based on the above said description, *cynodon dactylon* bioadsorbent could be used to remove fluoride selectively from water.

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**REFERENCES**