Activated tamarind seed coat: a green biosorbent to remove fluoride from aqueous solutions
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ABSTRACT
A novel, inexpensive, easily available and eco-friendly biosorbent, *Tamarindus indica* activated seed coat, has been evaluated for its capability to remove fluoride from water. Batch experiments were carried out to study the effect of various parameters affecting the biosorption such as pH (2–10), biosorbent dose (0.05 g/L to 0.35 g/L), contact time (10–80 min) and initial fluoride concentration (0.001–0.006 g/L) for the biosorption of fluoride at room temperature. The maximum removal of fluoride was found at pH 6, biosorbent dose 0.3 g and contact time 60 min. Physicochemical characterization studies revealed the suitable morphology and chemical functional groups present on the biosorbent. Isothermal data agreed well with the Langmuir isotherm adsorption model with $R^2$ value 0.976 and $K_L$ 0.1. The biosorption interface of fluoride onto *Tamarindus indica* activated seed coat obeyed the pseudo-second-order rate equation with $R^2$ 0.976. The present study demonstrates that *Tamarindus indica* activated seed coat can effectively remediate fluoride-contaminated water.

Key words | biosorption, fluoride, isotherms, kinetics, *Tamarindus indica* activated seed coat

HIGHLIGHTS
- Activated tamarind seed coat powder used as biosorbent for the removal of fluoride.
- Physicochemical studies of biosorbent revealed favourable features for F removal.
- Desorption studies obtained 90% recovery within three cycles.
- Developed sorbent applied to real field water samples and succeeded.
- This biosorbent can be considered a potential, cost-effective and eco-friendly biosorbent.
INTRODUCTION

The majority of developed and developing countries along with India are trapped in the fangs of fluoride contaminated groundwater (Sankararamakrishnan et al. 2008). As per the World Health Organization (WHO) guidelines and Bureau of Indian standards, the concentration of fluoride in drinking water is not supposed to increase beyond 1.5 mg/L (Gómez-Hortigüela et al. 2016). As per the aforementioned report, traces of fluoride in daily intake are beneficial in the form of mineralization of bones and tooth enamel and help to prevent tooth decay. An excess concentration of fluoride causes dental and skeletal fluorosis (Nabbou et al. 2019).

At present, activated carbons prepared from different raw materials reveal good fluoride uptake capacity. These techniques experience one or other drawback, and economically feasible, simple and eco-friendly methods still suggest research. But the main disadvantages are the high treatment cost and difficult regeneration, increasing the cost of water treatment in large-scale applications. A successful adsorption process depends not only on the adsorption performance of the sorbents, but also on the constant supply of the raw materials for the process (Suneetha et al. 2015).

From a literature review, it is learnt that Tamarind seed is a household material and is left as waste after removing Tamarind pulp for food preparation. Since this material is familiar to all kinds of people, an attempt has been made in the present study to use activated seed coat biomass for the removal of fluoride. Using both laboratory aqueous solution and groundwater field samples, the study aims to devise a simple, cheap and viable defluoridation method that could be adopted easily by village communities and urban dwellers.

MATERIALS USED AND METHODOLOGY

Fluoride stock preparation

A stock of 2.21 g anhydrous sodium fluoride was weighed and immediately dissolved in 100 mL of distilled water. Then the volume was made up to 1,000 mL to make the final fluoride stock solution. Various concentrations from 0.05 to 0.3 g/L fluoride solutions were prepared freshly from the stock whenever required.

Preparation of biosorbent

The tamarind seed used in this study was collected from the kitchen as a waste material. It was soaked in tap water for an
hour to remove the adhering pulp, washed well with the same tap water and then with double distilled water until reaching pH 7, dried in an air oven at 150 °C for six hours, its coat was manually separated and it was crushed with pestle and mortar and then sieved with a 100-micron-size mesh to get uniform size (as shown in Figure 1) particles. The obtained fine powder was stored for further experiments in an airtight container to protect it from humidity (Tang & Zhang 2016).

Analytical instruments

To adjust the pH of buffers, prior to starting the experiment the pH meter was calibrated with standard pH buffer solutions (Hanna Instruments) and adjusted.

For the measurement of fluoride ion concentration, a sophisticated fluoride meter (Extech FL700, USA) was used. Before proceeding to the preparation of different fluoride concentration solutions, we ensured the machine was calibrated with Total Ionic Strength Adjustment Buffer (TISAB) (Tang & Zhang 2016). The potentiometer method was employed to measure the fluoride ion concentration in different solutions.

Batch biosorption experiment

Bisorption experiments were carried out by varying pH, initial concentrations (mg/L), biosorbent dose (g/0.1 L), contact time (minute) and initial fluoride concentration. All experiments were carried out at room temperature of 21–25 °C. The influence of pH (2.0–10.0), biosorbent dose (0.05–0.35 g/50 mL), contact time (10–60 min) and initial fluoride concentration (0.001–0.006) was evaluated during the present study in a 100 mL Erlenmeyer flask, and 50 mL of fluoride solution of known concentration was added. The contents (biosorbent/50 mL solution) were kept in constant shaking for a fixed time in an orbital shaker, and then the solids were separated through filtration using Whatman 42 filter paper and the volume was finally adjusted to 25 mL. Then solutions were collected for analysis, and residual fluoride concentration was determined using the fluoride ion selective meter (Extech FL700, USA). Each experiment was conducted three times, and average values are reported. Control experiments, performed without addition of adsorbent, confirmed that the sorption of fluoride on the walls of the Erlenmeyer flasks was negligible. The percentage removal of fluoride was obtained using the equation:

\[ Q_e = \frac{(C_i - C_e)}{m} \times V \tag{1} \]

where,

- \( Q_e \) = fluoride ion concentration sorbed at equilibrium
- \( C_i \) = fluoride initial concentrations in g/L
- \( C_e \) = fluoride final concentrations in g/L
- \( m \) = sorbent mass in mg
- \( V \) = solution volume in mL

Percentage fluoride ion removal (%) was considered by using the following equation:

\[ \text{Fluoride ion removal efficiency (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \tag{2} \]
where,

\[ C_i = \text{fluoride initial concentrations in g/L} \]
\[ C_e = \text{fluoride final concentrations in g/L}. \]

**Biosorption isotherm models**

Biosorption describes a quantitative equilibrium link between the concentrations of sorbate in solution, i.e. mass/volume, and its concentration, i.e. mass sorbate/mass biosorbent. The biosorption isotherm relates the concentration of solute on the surface of the biosorbent to the concentration of the solute in the fluid with the biosorbent in contact. All the experimental values are determined. In turn, to explain the equilibrium isotherm of the biosorption process, Langmuir and Freundlich adsorption models are discussed in the present research.

**Langmuir isotherm model**

The Langmuir isotherm model follows the hypothesis below:

- each energetic site always interacts with only one adsorbate,
- all the sorbate molecules are adsorbed on to specific restricted sites,
- none of the adsorbed molecules will interact with neighboring ones, and
- surface adsorption sites are always equally active.

The Langmuir isotherm equation:

\[ Q_e = \frac{K_L Q_{\text{max}} C_e}{1 + K_L C_e} \quad (3) \]

where,

\[ Q_e = \text{biosorbent equilibrium fluoride ion concentration (mg/g)} \]
\[ C_e = \text{equilibrium fluoride ion concentration in the solution (mg/g)} \]
\[ Q_{\text{max}} = \text{biosorbent maximum adsorption capacity (mg/g)} \]
\[ K_L = \text{biosorption Langmuir constant}. \]

A linear form of Equation (3) is given below:

\[ \frac{C_e}{Q_e} = \frac{1}{K_L q_{\text{max}}} + \frac{C_e}{q_{\text{max}}} \quad (4) \]

The Langmuir constant values, \( q_{\text{max}} \) and \( K_L \), were calculated from the slope and intercept of the linear plot of \( C_e/Q_e \) versus \( C_e \). Important features of the Langmuir isotherm model were expressed by the equilibrium parameter separation factor, i.e. \( R_L \), represented by the equation given below:

\[ R_L = \frac{1}{1 + K_L C_i} \quad (5) \]

The resultant values of the \( R_L \) equation signify the biosorption isotherm type: if the \( R_L \) value is equal to 1 then the biosorption isotherm is considered as linear, if 0 is less than \( R_L \) and \( R_L \) is less than 1 this indicates biosorption is a favourable condition, if \( R_L \) is greater than 1 then the biosorption isotherm is in an unfavourable condition and if \( R_L \) is equal to 0 then the biosorption isotherm indicates an irreversible reaction.

**Freundlich isotherm model**

This model is a derivative form of the Gibbs adsorption of surface free energy combined with mathematical expression. An equation was proposed called the empirical isotherm equation with an assumption of biosorption heterogeneous surface and active sites along with its diverse energy.

The Freundlich isotherm is a derivative of the Langmuir isotherm with an assumption that there exists a distribution of sites on the biosorbent with different affinities for each specific biosorbent and every site behaves as per the Langmuir isotherm. Here, \( K_f \) indicates the ability of the biosorbent and \( n \) indicates the measurement of how attraction for the adsorbate changes with changes in biosorption density. When \( n \) gives rise to 1, the Freundlich isotherm shows a linear isotherm and specifies that all the biosorbent sites have an equal affinity. If the value of \( n \) is greater than 1, this means the affinities decrease with an increase in density of biosorption. The Freundlich isotherm linear form equation is as below:

\[ \log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (6) \]

The Freundlich isotherm constants \( 1/n \) and \( K_f \) are considered from the intercepts and slopes of the linear plot of \( \log Q_e \) versus \( \log C_e \).
Biosorbent characterization

Fourier transform infrared (FT-IR) spectrum

The surface functional groups on the activated carbon of the biosorbent were examined using FTIR. The Fourier transform infrared (FT-IR) spectrum was recorded on a Thermo-Nicolet Nexus 670 FT-IR spectrophotometer (ThermoFisher Scientific Inc., Madison, WI, USA) using KBr pellets containing 1% finely ground EPS and the spectrum was collected at a resolution of 4 cm⁻¹ in the wavenumber region of 400–4,000 cm⁻¹.

Scanning electron microscope (SEM)

The SEM is one of the most versatile instruments available for the examination and analysis of microstructure morphology and chemical composition characterizations. The surface morphology analysis of the biosorbent was performed using a scanning electron microscope (SEM). The experimental solution was added to aluminium stubs and air dried. The sample was gold sputtered using an SC7620 Sputter Coater device and analyzed by scanning electronic microscopy.

Brunauer–Emmett–Teller (BET) analysis

The surface area of the biosorbent was determined by using a Brunauer–Emmett–Teller (BET) analyzer. The BET surface area was determined at 77 K by nitrogen adsorption using a Micromeritics ASAP 2020 V3.04 H surface area analyzer.

Groundwater quality studies

Groundwater samples were collected from different rural habitats of Mahabubnagar district of Telangana State, India, in prewashed polyethylene bottles, and labeled with a description of the sampling such as habitat and date. Then, the samples were transported to the research laboratory, Department of Microbiology, Palamuru University, Mahabubnagar, and stored in a dark place at room temperature before the analysis was carried out (Dasaiah et al. 2020). Physicochemical parameters were analyzed as per the APHA standard methods with special reference to the concentrations of fluoride determined using the fluoride meter (Extech FL700, USA).

RESULTS AND DISCUSSION

Characterization of biosorbent

Scanning electron microscopy

To understand the biomass surface morphology, scanning electron microscopy with coupled energy dispersive spectroscopy (EDS) was used. It was observed from the SEM image of the control sample that the Tamarindus indica activated seed coat biomass appeared dull and to have a nonadhesive nature (Figure 2(a)). Each biomass particle boundary appeared sharp and had a distinctive irregular structure. Microporous particles of the powder were visible and permeable with clear gaps between each molecule that provide suitable binding sites for fluoride ions. SEM visibility of porosity and gaps between the particles of activated seed coat biomass indicates that the isolated biosorbent morphology has an ability to adsorb fluoride ions (George & Tembhurkar 2019).

In the SEM image of the experimental sample, i.e. after biosorption, the adhesion of fluoride ion particles appeared (Figure 2(b)). The EDX analysis of the Tamarindus indica activated seed coat showed the dominance of O, C, Ca and Mg ions in untreated (Figure 2(c)) and F⁻ treated samples (Figure 2(d)). From the analysis, it was obvious that the F⁻ ion was observed as a new element in the treated samples and was absent on the untreated (as pure) samples. It can undoubtedly be stated that the elemental oxygen concentration was reduced (as O peak intensity decreased in the EDX spectra of fluorideloaded biomass) after biosorption, and the new fluoride ion as F⁻ introduced on the biosorbent (Figure 2(d)) suggesting that the F⁻ ion may replace the oxygen-atom-(OH⁻)-containing ion on the surface of the adsorbent.

Fourier transform infrared spectroscopic (FTIR) analysis

The FTIR spectrum of Tamarindus indica activated seed coat biomass after biosorption (shown in Figure 3) was
analyzed to understand the nature of the functional groups. The number of peaks displayed from 4,000 to 500 cm\(^{-1}\) in the FTIR spectra represents the complex nature of the biosorbent. The first peak was found in the range of the wavelength 3,300–3,600 cm\(^{-1}\), i.e., 3,417.88 cm\(^{-1}\), which indicates the presence of the hydroxyl functional group which could be associated with the organic acid, alcohol, or phenol functional group. The second group was 1,620.36 cm\(^{-1}\) found in the range of the 1,500–1,600 cm\(^{-1}\) wavelength attributed to carbonyl (\(-\text{C} = \text{O}\)) stretching (Ji \textit{et al.} 2007). Carbonyl functional groups are known to be pronounced in oxidized carbon materials rather than the original parent carbon material (Budinova \textit{et al.} 2006). In addition, there were stretching vibration bands of surface and hydrogen bonded \(-\text{O} - \text{H}\) groups of alcohols, phenols, and chemisorbed water. These two broad and long peaks observed on the surface of the adsorbent were probably associated with the chemical activation process of the adsorbent. This particular surface modification might be attributed to the hydrogen ion released from sulfuric acid and could result in the development of the hydroxide functional group on the surface of the adsorbent.

The surface area of \textit{Tamarindus indica} activated seed coat biomass was determined by using the Brunauer–Emmett–Teller (BET) analyzer and was found to be 286.94 m\(^2\) g\(^{-1}\). The BET surface area was determined at 77 K by nitrogen adsorption using a Micromeritics ASAP 2020 V3.04 H surface area analyzer. It was found that the surface area of \textit{Tamarindus indica} activated seed coat adsorbent before adsorption was 286.94 m\(^2\) g\(^{-1}\) and after the biosorption of fluoride it was reduced to 93.38 m\(^2\) g\(^{-1}\). This reduction in surface area might be

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\textbf{Figure 2} | Scanning electron microscopy (SEM) images of \textit{Tamarindus indica} activated seed coat biomass: (a) pure, (b) fluoride-loaded; and EDX images: (c) pure and (d) fluoride-loaded.
due to the biosorption of fluoride onto the biosorbent surface.

**Batch experiment results**

**Effect of pH**

The pH of an aqueous solution is a significant monitoring parameter in a fluoride solution, as it affects the surface charge of the adsorbent material (Mahdavi *et al.* 2015). Thus, the hydrogen ion concentration was estimated at different concentrations of pH ranging from 2 to 10. The acidic pH was adjusted with 0.5 N HCl and alkaline pH was adjusted with 0.1 M NaOH solution. To identify the effect of different concentrations of pH (2–10) on fluoride removal, two concentrations of biosorbents were chosen for this study. The results observed that the pH played a vital role in fluoride uptake and the highest percentage

![FTIR spectrum of Tamarindus indica activated seed coat biomass before and after fluoride biosorption.](http://iwaponline.com/ws/article-pdf/21/4/1594/903064/ws021041594.pdf)
(94%) biosorption of fluoride ions was found at pH = 6.0. A very similar result was reported by Bhaumik & Mondal (2014) for their earlier paper where they recorded that Ca-pretreated coconut fiber dust (CFD) can remove a high level of fluoride at pH 6. They also suggested that fluoride ions are more attached to the surface of CFD-3 due to being chemically treated with Ca²⁺ solution (extracted from eggshell) (Bhaumik & Mondal 2014, 2015). At acidic pH, due to the protonated effect of surface functionalities including amino, carboxyl, thiol, etc, positive charges impart on the surface and hence increase the biosorption of negatively charged fluoride ions at lower pH. At higher pH, the adsorption of fluoride is gradually decreased due to higher accumulation of hydroxyl ions on the surface of the adsorbent (Bhaumik & Mondal 2015). However, in the present study, fluoride sorption effectiveness was 85%, which was seen at pH 7.0 (Figure 4(a)).

**Effect of biosorbent dose (g/L)**

An important parameter of identifying the amount of biosorbent required for the removal of fluoride ions per unit weight of biomass from drinking water is essential and assessed in the present study. The rate of adsorption is a function of the initial concentration of the adsorbate, which makes it an important factor to be considered for effective adsorption (Bhaumik & Mondal 2015). Adsorption basically depends on the particle size: the smaller the particle size, the greater the surface area and the greater the adsorption capacity per unit mass of adsorbent (Bhaumik & Mondal 2015). Different concentrations from

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**Figure 4** | Batch experiment various conditions: (a) effect of pH on biosorption, (b) effect of biosorbent dose, (c) effect of contact time, (d) effect of initial fluoride concentration.
0.05 g/L to 0.35 g/L were analyzed and the yielded results showed a dose-dependent increase in the biosorption capacity. Similarly, another study also found a dose-dependent adsorption capacity of the biosorbent material (Tang & Zhang 2016). In the present investigation, the highest biosorption capacity (92%) of *Tamarindus indica* activated seed coat biomass was observed at 0.3 g/L (Figure 4(b)). Beyond 0.3 g/L did not show any significant increase in the biosorption capacity. The changes in the extent of removal might be due to the fact that initially all adsorbent sites were vacant and the solid concentration gradient was high. Later, the fluoride uptake by adsorbent decreased with the number of adsorption sites possibly due to the aggregation of available binding sites (Tembhurkar 2006).

**Effect of contact time (min)**

The time required for *Tamarindus indica* activated seed coat biomass to equilibrate upon the adsorption of the fluoride ions was recorded at various time intervals. It was observed that the contact time required for adsorption was directly proportional to fluoride removal. As shown in Figure 4(c), a gradual increase was observed from ten minutes to 60 minutes and then a fall was seen in the peak after 60 minutes. This indicates that the adsorption capacity of the activated seed coat was rapid and active in less than 60 minutes. Another study proposed that the rapid nature of the activated biocarbon helps in quick adsorption of fluoride on to its surface. A fall in the biosorption after a certain time period could be due to limited surface area or previously occupied ions (Dong & Wang 2016).

**Effect of initial fluoride ion concentration**

At a constant pH of 6.0 and 60 minutes of contact time, an attempt was made to identify the initial fluoride ion concentration effect (0.001–0.006 g/L) on the biosorption rate. It was observed there was a fall in the concentration of fluoride ions at the higher initial fluoride ion concentration. A little uptake at higher fluoride concentration was seen because of the enhanced ratio of the initial number of moles of fluoride to the available vacant sites. A decrease in the fluoride removal was observed based on the given dose of biosorbent fixed with the number of vacant sites. Thus, the adsorption of fluoride ions was almost equal to the fixed vacancies and resulted in decreased fluoride removal, which was a subsequent action to the increase in initial fluoride concentration as shown in Figure 4(d). The present results indicate that the fluoride biosorption was totally dependent on the initial fluoride ion concentration.

Batch adsorption experiments using activated carbon prepared from *Moringa indica* bark were conducted to remove fluoride from aqueous solution. A minimum contact time of 25 min was required for optimum fluoride removal (Karthikeyan & Siva 2007). When sandalwood leaves were used as biosorbent, the results showed that the amount of sorption ($q_t$) increased with time (min) up to 120 min and after this time interval, no more significant sorption was observed. It indicated that the time necessary for SLP–fluoride interaction to reach equilibrium was just over 120 min. Further, the equilibrium time of 120 min was found to be independent of initial concentrations and was maintained as the optimum time of contact during the other sets of experiments (Khound et al. 2018). Further Alagumuthu & Rajan (2010) reported 180 min as minimum contact time for the maximum defluoridation of the sorbent. The zirconium-impregnated cashew nut shell carbon recorded a maximum percentage of fluoride removal of 80.53%. Similarly a maximum fluoride removal was obtained at pH 7, initial concentration 5 mg/L, contact time 120 min using *Ficus benghalensis* leaf as biosorbent (George & Tembhurkar 2019). Comparison of the fluoride removal percentages of different biosorbents for the removal of fluoride is shown in Table 1.

The obtained results showed how carbon slurry is very competitive and its performance is better than the commercial product (4.86 mg/g versus 1.10 mg/g). Bibi *et al.* (2015) designed the measurement of selected industrial waste materials for simultaneous removal of arsenic and fluoride from drinking water in order to find cost-effective adsorbents. Commercially available hydrated cement, marble powder (waste) and brick powder (waste) were used. Removal percentages of the studied adsorbents followed the decreasing trend: hydrated cement > brick powder > marble powder. All the adsorbents (hydrated cement, brick powder and marble powder) showed removal percentages
90% for arsenic and 75% for fluoride from an aqueous solution of 1,000 mg/L of arsenic and 30 mg/L of fluoride at pH 7.0 and 8, with a contact period of 60 min and a dose of 30 g/L.

Further effects of hardness and chloride ion on defluoridation were studied in the present study. The research revealed that Samadi et al. (2014) investigated the effect of competing ions such as hardness, chloride, sulfate and nitrate to examine possible interactions. The results showed that hardness, nitrate and chloride slightly reduced the fluoride sorption efficiency, since their concentrations decreased to 253, 13 and 337 mg/L after 120 min, respectively (Samadi et al. 2014). Martínez-Miranda et al. (2011) found that chloride and bicarbonate ions competed for the sorption sites, and sulfate and nitrate ions were very little adsorbed by the corrosion products of iron from drinking water.

### Effect of temperature

Biosorption of fluoride onto activated carbon developed from Tamarindus indica seed coat was conducted in the range of 20–40 °C keeping previously obtained experimental conditions constant. It was observed that an increase in temperature decreases the percentage sorption. This may be due to the weakening of adsorptive forces between biosorbent and fluoride ion as reported by Murugan et al. (2006). These results obviously show that temperature is an unfavourable factor for fluoride sorption on the biosorbent.

### Biosorption isotherm models

The process of a biosorption isotherm expresses the biosorbent and sorbate equilibrium relationship and also expresses the adsorbed ion distribution within the liquid and solid phases in the equilibrium state. In addition to this, equilibrium modeling also gives the information to study the mechanism involved in the whole biosorption system. The Langmuir and Freundlich biosorption equilibrium isotherm models describe the biomass equilibrium and help in comparing various biomaterials in diverse working conditions. All the fluoride biosorption parameters along with the regression coefficient were analyzed with the Langmuir isotherm biosorption model, and this model found the best correlation with the present research data as shown in Figure 5: it yielded a high $R^2$ value (0.97), the maximum biosorption capacity ($Q_{max}$) was 1.79 for complete monolayer coverage, and $K_L = 0.1$, which indicates that the particle radius of the biosorbent was small towards biosorption. Overall, the Langmuir parameters revealed that fluoride sorption on the Tamarindus indica activated seed coat is encouraging as the value lies between 0 and 1 (Srinivasulu et al. 2019).

The Freundlich isotherm parameters revealed multilayer sorption on the heterogeneous surface and linking adsorbate ion interaction. The capacity of biosorption and the rest of the parameters were calculated by using the Freundlich equation. In the formula, $K_F$ is the Freundlich constant that represents biosorption capacity on heterogeneous sites with non-uniform distribution of energy level, and $n$ is calculated for the strength between sorbate and biosorbent. Hence, the present Tamarindus indica activated seed coat $n$ value (1.49) was between 0 and 10, which indicates a good biosorption capacity.

### Biosorption kinetics

The kinetics explains the sorption mechanism of the activated carbon and biosorption rate of fluoride ions that maintain the sorbate residence time between the solid and liquid interface. In the present, Tamarindus indica activated carbon powder linearized kinetics and the regression coefficient explained the best correlation with the pseudo-second-order kinetics. However, the yielded...
results also correlated with the pseudo-first-order models. The kinetics of the sorbate and biosorbent interface depends on many factors such as the characteristic features of sorbate and biosorbent, pH of the aqueous medium, temperature of the biosorption reaction, typical time of contact between sorbate and biosorbent and mass-transport course of action (Achak et al. 2019). Pseudo-first-order and pseudo-second-order kinetic model plots are shown in Figure 5(c) and 5(d).

Thermodynamic parameters

In order to study the feasibility of the process using Tamarindus indica activated seed coat for fluoride removal, thermodynamic parameters, such as the changes of Gibbs free energy, \( \Delta G \), enthalpy, \( \Delta H \) and entropy, \( \Delta S \) for the adsorption of fluoride on adsorbent, are calculated by the following equations:

Gibbs free energy, \( \Delta G = -2.303RT \log_{10} K_L \)

Enthalpy, \( \Delta H = \log_{10} K_L(T2) - \log_{10} K_L(T1) \)

Entropy, \( \Delta S = (\Delta H - \Delta G)/T \)

where,

\( R \) is the ideal/universal gas constant (i.e. 8.314 J mol\(^{-1}\) K\(^{-1}\)),

\( T \) is the absolute temperature (K), and

\( K_L \) is the Langmuir equilibrium constant.

The Gibbs free energy change values (kJ mol\(^{-1}\)) calculated using the Langmuir equilibrium constant (\( K_L \)) obtained by linear analysis are 1.65, 1.20, and 0.51 at 323, 313 and 303 K, respectively. These Gibbs free energy (\( \Delta G \)) change values obtained for the biosorption of fluoride ions on the biosorbent indicated that the biosorption process is
spontaneous in nature, and the spontaneity of the biosorption reaction increases with temperature. The negative value of $\Delta G$ decreased with increasing temperature from 313 to 343 K, suggesting the adsorption process is unfavourable and non-spontaneous at higher temperature. The negative values of $\Delta H$ and $\Delta S$ for *Tamarindus indica* activated seed coat indicate no structural changes and support physical sorption on the biosorbent surface after fluoride adsorption.

**Real-time application of the developed biosorbent**

The isolated *Tamarindus indica* activated carbonated seed coat was applied to the fluoride-affected water collected from the different areas of Mahabubnagar district. The collected water samples were tested for the fluoride concentration and the results crossed the fluoride ion concentration prescribed in WHO guidelines. To the one litre of groundwater samples (of previously measured fluoride concentration) 0.3 g of *Tamarindus indica* activated seed coat biomass was added and kept in a mini-orbital shaker at 150 rpm for 60 minutes. The removal efficiency of fluoride from the five real field water samples varied (it was 53% to 67%) and these values were lower than the removal efficiency observed in aqueous solutions in the pilot-scale study (94%). The presence of high concentrations of interfering anions like CO$_3^{2-}$, HCO$_3^-$, SO$_4^{2-}$, nitrate and Cl$^-$ in the contaminated groundwater might be the reason (as shown in Table 2) for this variation in removal efficiencies. Thus, anions like CO$_3^{2-}$, HCO$_3^-$, SO$_4^{2-}$, nitrate and Cl$^-$ could impart a competition with fluoride ions at the surface of the biosorbent for active sites. These anions might have interfered with fluoride biosorption and consequent removal of the contaminant by this biosorbent. Then, the fluoride removal efficiency of biosorbent estimates was tabulated in Table 5.

**Desorption studies**

It is necessary to regenerate and reuse biosorbent to maintain the cost-effectiveness of the product and maximize its efficiency. Also, it is noteworthy that during desorption of the biosorbent it should not undergo any stressful damage that affects its biosorption capacity. In the present study, we regenerated the activated *Tamarindus indica* seed coat biomass with 10% sodium hydroxide (NaOH) solution and recovery efficiency was tested for up to three cycles of biosorption and desorption. The elution efficiency was increased to 90% with 10% NaOH in all three cycles. This high regeneration capacity of the biosorbent indicates that the overall biosorption system is efficient enough to remove fluoride from fluoride-contaminated water.

**CONCLUSION**

In the present study, preparation of activated carbon from tamarind seeds, characterization and fluoride removal

**Table 2** Characterization of groundwater quality with special reference to fluoride

| Village          | pH   | EC (electrical conductivity) | TDS in mg/L | T.Alk in mg/L | TH (in mg/L as CaCO$_3$) | Cl in mg/L | F in mg/L | NO$_3$ in mg/L | Fe in mg/L |
|------------------|------|------------------------------|-------------|---------------|--------------------------|------------|-----------|----------------|------------|
| Zamisthapur      | 7.30 | 773                          | 572         | 224           | 236                       | 110        | 1.91      | 10             | 0.3        |
| RR Gudem         | 8.16 | 1,267                        | 937         | 536           | 200                       | 136        | 1.65      | 15             | 0.3        |
| Obilaipally      | 7.94 | 1,157                        | 874         | 340           | 296                       | 133        | 1.63      | 7              | 0.3        |
| Narsapur         | 8.08 | 902                          | 667         | 459           | 260                       | 62         | 1.81      | 0.5            | 0.5        |
| Obilaipally Thanda | 8.11 | 1,737                        | 1,287       | 653           | 312                       | 218        | 1.70      | 0.5            | 0.3        |

**Table 3** Application of developed biosorbent in real field water samples

| Sampling station | Fluoride present (mg/L) | Adsorbed (mg/L) | Removal efficiency (%) |
|------------------|-------------------------|-----------------|------------------------|
| Zamisthapur      | 1.91                    | 1.28            | 67.01                  |
| RR Gudem         | 1.65                    | 0.94            | 56.96                  |
| Obilaipally      | 1.63                    | 1.05            | 64.41                  |
| Narsapur         | 1.81                    | 0.96            | 53.03                  |
| Obilaipally Thanda | 1.7                  | 1.01            | 59.41                  |
from aqueous solutions was investigated. *Tamarindus indica* activated seed coat biomass played a significant role in the removal of fluoride from fluoride-contaminated water. The SEM and FTIR data revealed that the suitable surface and the presence of amide, –OH, carbonyl and amine functional groups on the surface of the biosorbent helped the better adsorption of the fluoride. The results concluded that the optimum pH was 6, and the best possible time was 60 minutes with a 0.3 g concentration. The Langmuir isotherm model with good $R^2$ value (0.976) indicated monolayer sorption on the biosorbent surface. Biosorption kinetics was studied by using pseudo-first-order and pseudo-second-order kinetic models. The data fitted well ($R^2 = 0.976$) to pseudo-second-order kinetics, which indicated that the fluoride removal by *Tamarindus indica* seed coat biosorption was by chemisorption. These results contributed to successful fluoride removal from the samples. The biosorption isotherm model and biosorption equilibrium capacity analytics were better correlated to the Langmuir and Freundlich isotherms in quantitative fluoride removal. The kinetics of the activated carbon interrelated with first- and second-order chemical reactions. Precisely the selected *Tamarindus indica* activated seed coat is a reliable, cost-effective, efficient, reusable and green biosorbent for the removal of fluoride from contaminated water.

**CONFLICT OF INTEREST**

The authors declare no conflict of interest.

**ETHICAL APPROVAL**

Not applicable since no human or animals were used for the study.

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

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