Fixed bed column performance of *Tinospora cordifolia* for deflouridation of water

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**ABSTRACT**

A continuous adsorption study in a fixed-bed column was carried out by using *Tinospora cordifolia* as an adsorbent for the removal of fluoride from aqueous solution. The effect of flow rate, influent fluoride concentration and bed depth on the adsorption characteristics of adsorbent was investigated at pH 7. The dependencies of breakthrough curves on these parameters were confirmed from the data obtained. Modeling of data was done. Thomas, Yoon–Nelson and Adams–Bohart models were applied to experimental data to predict the breakthrough curves. These kinetic models were helpful to determine the characteristic parameters of column designing for deflouridation on a large scale. Thomas and Yoon-Nelson models were found to be more suitable for the description of the breakthrough curve than the Adams–Bohant model in the present study. It was concluded that the *Tinospora cordifolia*-packed column can be used for effective deflouridation of water.

**Key words** | adsorption, fluoride, kinetic studies, mathematical models, Menispermaceae

**HIGHLIGHTS**

- Large scale removal of fluoride from waste water.
- Low cost removal method of removing fluoride from water.
- Environment-friendly deflouridation method.
- Removal at neutral pH.
- Effective regeneration of adsorbent.
INTRODUCTION

Fluoride, part of numerous minerals and rocks, has become a significant pollutant for groundwater assets everywhere in the present reality. Little convergence of fluoride (up to 0.5 mg/l) is a basic need for dental enamel and bones; yet, when an individual is exposed to high accumulation of fluoride (more than 1.5 mg/l) for an extensive stretch of time, it causes fluorosis. Water is the principal wellspring of fluoride consumption in the human body. Water is polluted with fluoride because of land and anthropogenic reasons, out of which the significant commitment is of topographical assets (Nath & Dutta 2010). On the off chance that a zone has bedrocks with high amounts of fluoride minerals such as apatite, fluorite and topaz, at that point these minerals break down in groundwater and build fluoride fixation there (Handa 1975; Farooqi et al. 2007; Singh & Garg 2012).

As groundwater is the lone wellspring of savoring water in numerous parts of India, just as in different nations of the world, individuals have no other alternative than to drink fluoride-contaminated water. Because of this, a great many individuals from various parts of the world are experiencing fluorosis. The issue is serious in India and China, which are profoundly populated nations on the planet (Rao & Devadas 2003; Xiang et al. 2003). In India, Andhra Pradesh, Rajasthan, Gujarat, Uttar Pradesh and Tamil Nadu are seriously influenced by the issue (Vardhan & Karthikeyan 2011). To battle the issue of fluorosis, defluoridation has become basic.

Different strategies are available for removal of fluoride from water; for example, switch assimilation, synthetic treatment, particle trade, layer division, electrolytic defluoridation and electrodialysis (Dieye et al. 1998; Singh et al. 1999; Reardon & Wang 2000; Mameri et al. 2001) and so on; however, every single technique has its own impediment: some require enormous amounts of energy and synthetics; some influence the climate (Murugan & Viswanathan 2006). Adsorption is one of the critical means of defluoridation. Removal of fluoride through a fixed bed section with appropriate adsorbent is a powerful methodology and has more extensive appropriateness (Gupta et al. 2009). Various adsorbents, for example, actuated alumina (Ghorai & Pant 2004), titanium-rich bauxite (Das et al. 2005), manufactured saps (Meenakshi & Viswanathan 2006), manganese oxide-covered alumina (Maliyekkal et al. 2006), carbon nanotubes (Li et al. 2005), fish bone charcoal (Killedar & Bhargava 1995), rice husk carbon (Prabavathi et al. 2003) are utilized for defluoridation with various levels of accomplishment. This paper is an endeavor to investigate the possibility of using a bioadsorbent, *Tinospora cordifolia* to eliminate fluoride from an aqueous solution through a fixed-bed segment for huge scope. The impact of bed depth, influent focus and stream rate on adsorption of fluoride by a segment filled with *Tinospora cordifolia* was contemplated. The Thomas, Yoon-Nelson and Adams-Bohart models were utilized to anticipate the exhibition of picked bioadsorbent.
METHODS

Preparation of adsorbent

*Tinospora cordifolia* is the member of Menispermaceae family. It is easily available in various locations of Durg district in Chhattisgarh. The bioadsorbent was first washed with distilled water to remove impurities. Then it is dried in the sun; after that, it was further dried in a hot air oven at 60 °C till dryness. It was then powdered with the help of a grinder and used for removal of fluoride.

Equipment and chemicals

A known amount of sodium fluoride of analytical grade was dissolved in distilled water to prepare fluoride stock solution. Then the required concentrations of fluoride solutions were obtained by dilution of the stock solution. Solutions were kept in plastic flasks at 29 °C. Fluoride analysis was carried out using a fluoride ion selective electrode (Orion Model 720 Aplus) equipped with combination pH/ISE meter (Orion Model, 720 Aplus).

Column studies

A fixed-bed column study for fluoride removal from water by bioadsorbent was performed using a column of 4.5 cm diameter and 59 cm length. The column was packed with bioadsorbent between two supporting layers of glass beads. The bulk density of adsorbent packed in the column was 0.078 gm/cm³. The study was conducted at a temperature of 29 ± 2 °C and the pH of the fluoride solution was 7.0. The column was treated with fluoride solutions of different concentrations under different experimental conditions to study the effect of flow rate (15, 21 ml/min), initial concentration of influent (3, 5, 7 mg/l) and bed depth (30, 36, 40 cm) on column adsorption.

Modeling of column adsorption

The behavior of the adsorption column was described by a breakthrough curve, which is a typical plot of the ratio of outlet solute concentration to inlet solute concentration in the fluid as a function of time from the start of flow or volume of effluent at a particular bed depth.

Data collected during practical work in the laboratory can be used to design full-scale adsorption columns. Successful design of a column adsorption process requires prediction of the concentration-time profile or breakthrough curve for the effluent. In order to describe the fixed-bed column behaviour and to scale up it for industrial applications, many mathematical models have been developed. In the present research work Thomas, Yoon–Nelson and Adams–Bohart models were used to obtain the kinetic behaviour of the column (Table 1).

Error analysis

In the linear regressive analysis, different formulas were used to calculate the value of correlation coefficient R², but this may affect the accuracy of results significantly. Therefore nonlinear regressive analysis can be chosen as a better way to minimise such errors of calculation (Ho et al. 2005; Han et al. 2007). So the nonlinear analysis with the least square of errors was used to calculate the parameters of different kinetic models. The relative

| Model         | Mathematical equation | Linear dependence | Model parameter | Breakthrough curve          |
|---------------|-----------------------|-------------------|----------------|-----------------------------|
| Thomas        | \( \ln \left( \frac{C_0}{C} - 1 \right) = K_T \left( \frac{q_m}{Q} - C_0 t \right) \) | \( \ln(C_0/C - 1) vs t \) | \( K_T, q \) | \( \frac{C}{C_0} = \frac{1}{1 + \exp\left[\frac{q_m}{Q} - C_0 t \right]} \) |
| Yoon–Nelson   | \( \ln \left( \frac{C}{C_0 - C} \right) = K_{YN}(t - \tau) \) | \( \ln(C/(C_0 - C)) vs t \) | \( K_{YN}, \tau \) | \( \frac{C}{C_0} = \frac{1}{1 + \exp[K_{YN}(t - \tau)]} \) |
| Adams–Bohart  | \( \ln \left( \frac{C}{C_0} \right) = k_{AB}C_0t - k_{AB}N_aZ/U_0 \) | \( \ln(C/C_0) vs t \) | \( N_a, k_{AB} \) | \( \frac{C}{C_0} = \exp\left[ k_{AB}C_0 t - \frac{k_{AB}N_aZ}{U_0} \right] \) |
mathematical formula of SS is:

\[
SS = \frac{\sum \left[ \left( \frac{C}{C_0} \right) - \left( \frac{C}{C_0} \right)_e \right]^2}{N}
\]

where \((C/C_0)_e\) and \((C/C_0)_c\) are the ratio of effluent and influent fluoride concentrations obtained from models, and from experiment, respectively; \(N\) is the number of the experimental point. In order to verify the best fit model for the adsorption, it is necessary to analyze the data using SS, combined with the values of the determined coefficient (R²).

**RESULT AND DISCUSSION**

**Column study**

The most important parameters for the study of the breakthrough curve are flow rate, bed depth and initial inlet concentration. The effects of these parameters on the shape of the breakthrough curve and column performance were investigated at pH 7.

**Effect of flow rate on breakthrough curves**

The breakthrough curves at various flow rates (13 and 21 ml/min) at constant adsorbent dose of 45 g and initial concentration of fluoride of 5 mg/l at pH 7 are shown in Figure 1. It is clear from the figure that as flow rate increases, breakthrough point is obtained quickly and breakthrough time decreases because the residence time of fluoride in packed column was not sufficient to achieve adsorption equilibrium at higher flow rate.

**Effect of bed depth on breakthrough curves**

The breakthrough curves at different bed depths (30, 36, 40 cm) at constant flow rate of 13 ml/min and initial fluoride concentration of 5 mg/l at pH 7 are shown in Figure 2. As we increase the adsorbent mass in the column, bed height increases, thus the surface area of the adsorbent increases and fluoride had more binding sites for adsorption (Zulfadhly et al. 2001). Thus adsorption capacity of the column \(q_{\text{exp}}\) increases with increase in bed height (Table 2).

Ratio of bed depth and column diameter is an important parameter for column study. This ratio is related to the residence time (empty bed contact time, EBCT) of adsorbate on adsorbent. More the residence time in the column, more...
time will be available for the adsorbate to be adsorbed on the adsorbant.

EBCT is the relation between the bed length ($Z$) and the feed solution velocity ($Qv$) (Abusafa & Yucel 2002) as given by:

$$EBCT = \frac{Z}{Qv} = \frac{Z}{(Q/A)}$$

where $A$ denotes the column cross sectional area ($A = \pi r^2$ where $r$ is the radius of the column).

The values of EBCT obtained from different experimental conditions are shown in Table 2.

From the above table, it is clear that the maximum uptake ($Q_{exp} = 3.40$ mg/g) is obtained for higher bed depth ($Z = 40$ cm) for the same influent concentration ($C_0 = 5$ mg/L) and the same flow rate ($Q = 13$ mL/min) because at higher bed depth, large surface area and more active sites of adsorbent is available for adsorption. It is also evident from the table that increase in influent concentration increases the uptake capacity due to increase in mobility of fluoride ions and increase in flow rate decreases the uptake capacity as higher flow rate of influent decreases the residence time of adsorbate on adsorbent.

**Effect of influent fluoride concentration on breakthrough curves**

The breakthrough curves were obtained at different concentrations ($3, 5, 7$ mg/l) at a constant bed depth of 36 cm and flow rate 13 ml/min. As the influent fluoride concentration increases, breakthrough time decreases (Figure 3). This may be due to relatively slower transport because of a decrease in the diffusion coefficient and decreased mass transfer coefficient at low concentrations of fluoride (Goel et al. 2005; Gupta & Babu 2009). However, the value of column adsorption capacity $q_{exp}$ increases with the increase of the inlet fluoride concentration (Table 3). This may be due to a higher concentration of influent solution causing fast transport of the fluoride on the adsorbent (Han et al. 2008).

**Breakthrough curve models**

**Thomas model.** The column data were fitted to the Thomas model. The Thomas rate constant $k_T$ and maximum adsorption capacity $q$ were determined for different experimental conditions (Table 3). It is clear from Table 3 that the value of $q$ increased but the value of $k_T$ decreased with increase in the initial concentration of fluoride ($C_0$) in the column, because at higher $C_0$, the difference in fluoride concentration between solution and adsorbent increases, which provides more driving force for better adsorption (Zulfadhly et al. 2001; Aksu & Gonen 2004; Ho et al. 2005; Han et al. 2009). Furthermore, the value of $q$ increased and the value of $k_T$ decreased at slow flow rate and higher bed depth as the fluoride solution remained in contact with the adsorbent for sufficient time under these conditions. A comparison of experimental adsorption capacity $q_{exp}$ with adsorption capacity obtained from the model showed that they were close enough under the given experimental conditions (Table 3).

**Yoon-Nelson model.** Column data were fitted to the Yoon Nelson model and the values of rate constant $K_{YN}$ and time required for 50% breakthrough $\tau$ were determined (Table 4). It is clear from the table that the value of $\tau$ increases at slow
flow rate of influent and at higher initial concentration and higher bed height of column. The experimental values and breakthrough curves were in good agreement with the \( \tau \) values obtained from the model (Table 4 and Figures 1–3).

**Adams-Bohart model.** The Adams–Bohart adsorption model was applied to experimental data. The adsorption capacity (\( N_a \)) and kinetic constant (\( k_{AB} \)) were calculated from the model (Table 5), which shows that the adsorption capacity of the column increases with increase in bed depth and initial concentration of the fluoride solution. Figures 1–3 show the comparison of the experimental curve and the predicted curve according to the Adams–Bohart model. The experimental breakthrough curves are not close to those predicted by this model. Hence, the Adams–Bohart model cannot be used to predict the experimental data in the range of conditions used in this study.

**Comparison of Thomas, Yoon–Nelson and Adams–Bohart models**

In order to find out the fitness of Thomas, Yoon–Nelson and Adams–Bohart models with experimental data, values of correlation coefficients \( R^2 \) and value of error \( SS \) of these model were compared. For Thomas model, the values of \( R^2 \) range from 0.95 to 0.99 (Table 3) for the Yoon–Nelson model, \( R^2 \) ranges from 0.93 to 0.99 (Table 4), which is an indication of good agreement between experimental data with the data obtained from these models. The value of \( R^2 \) was found to be in the range of 0.80 to 0.95 (Table 5) for the Adams–Bohart model, which was slightly lower than that of the Thomas and Yoon–Nelson models under the same experimental conditions.

Comparing the values of \( SS \) from the Thomas, Yoon–Nelson and Adams–Bohart models (Tables 3–5), the values of \( SS \) from the Thomas and Yoon–Nelson model were lower at almost all the experimental conditions than that obtained from the Adams–Bohart model. Lower values of \( SS \) ensure the good fitting of curves with experimental data for the Thomas model and Yoon–Nelson model compared to that of the Adams–Bohart model for fluoride adsorption on *Tinospora cordifolia*.

**Regeneration of the adsorbent**

Regeneration of adsorbent is very important from the economical and environmental point of view. In the present study, it was done by repeating the adsorption-desorption cycle three times. Regeneration was done using 0.1 M NaOH solution. The reagent was passed through the column and effluent concentration was noted at certain time intervals. In the first cycle, 98% removal was achieved and in the third cycle, a removal efficiency of 82% was achieved (Figure 4).

![Figure 4](http://iwaponline.com/ws/article-pdf/21/5/2324/919770/ws021052324.pdf)

**Table 4 | Parameters of Yoon-Nelson model**

| \( C_0 \) Ppm | \( Z \) cm | \( Q \) ml/min | \( K_{YN} \) | \( \tau \) (hrs) | \( R^2 \) | \( \tau_{exp} \) (hrs) | \( SS \) |
|---|---|---|---|---|---|---|---|
| 5 | 30 | 13 | 0.12 | 10.0 | 0.99 | 9.0 | 0.03 |
| 5 | 36 | 13 | 0.116 | 21.6 | 0.93 | 22.0 | 0.42 |
| 5 | 40 | 13 | 0.097 | 31.09 | 0.96 | 31.0 | 0.02 |
| 3 | 36 | 13 | 0.2 | 21.2 | 0.98 | 24.0 | 0.02 |
| 7 | 36 | 13 | 0.08 | 22.1 | 0.96 | 18.0 | 0.02 |
| 5 | 36 | 21 | 0.1 | 12.8 | 0.95 | 17.0 | 0.02 |

**Table 5 | Parameters of Adams-Bohart model**

| \( C_0 \) Ppm | \( Z \) cm | \( Q \) ml/min | \( k_{AB} \) | \( N_a \) mg/l | \( R^2 \) | \( SS \) |
|---|---|---|---|---|---|---|
| 5 | 30 | 13 | 0.0094 | 143.21 | 0.83 | 0.04 |
| 5 | 36 | 13 | 0.01 | 190.53 | 0.85 | 0.34 |
| 5 | 40 | 13 | 0.0082 | 251.04 | 0.80 | 0.02 |
| 3 | 36 | 13 | 0.029 | 101.94 | 0.85 | 0.04 |
| 7 | 36 | 13 | 0.008 | 251.26 | 0.95 | 0.06 |
| 5 | 36 | 21 | 0.01 | 219.4 | 0.94 | 0.14 |
After regeneration, some of the adsorption sites are not free from fluoride. Therefore the number of adsorption sites decreases after regeneration, which causes a decrease in adsorption capacity.

After the third cycle of regeneration, the removal capacity of adsorbant decreases continuously. Therefore, only three cycles of regeneration were considered.

Comparison of uptake capacity of *Tinospora cordifolia* with other adsorbents

Referring to the maximum uptake capacity, we note that the value found in this study is comparable with the values determined for different adsorbents used for removal of fluoride from water by other researchers (Table 6), which shows that the adsorbent chosen can be used efficiently for defluoridation purposes.

**Tinospora cordifolia** as adsorbent

Some researchers have used *Tinospora cordifolia* as an adsorbent for removal of other harmful pollutants from water. *Tinospora cordifolia* can be used as adsorbent for removal of Ni (II) and Mn (II) ions from water (Sao et al. 2014, 2016) and the present study shows that it can also be used for removal of fluoride from water. Therefore *Tinospora cordifolia* as an adsorbent is very useful for removal of pollutants from water.

The FTIR analysis of fluoride-loaded biomass was done in our laboratory by Pandey et al. (2012) and it was found that major changes were obtained in the region of 500–1,600 cm⁻¹. This range is assigned to amino group in bioadsorbent. Change in the frequency range of fresh and loaded biomass indicates that binding of fluoride in biomass occurs due to substitution of the amino group by fluoride.

Effectiveness of bioadsorbent used

The bioadsorbent *Tinospora cordifolia* used for removal of fluoride from water in the present study is easily available plant material. It is widely spread in Durg district in Chhattisgarh. Moreover, the plant possesses medicinal properties. Bioadsorbent can be used for defluoridation at neutral pH. Residue of this adsorbent after defluoridation process can be easily disposed of without changing the pH of the disposed field. Therefore, economically, its use is beneficial for removal of fluoride from water at large scale (Table 7).

| S. no. | Adsorbent | Cost (Rs/ kg) | Reference | Remarks |
|-------|-----------|---------------|-----------|---------|
| 1     | Bauxite   | 12            | www.indiamart.com | Effluent disposed contains precipitate of aluminium hydroxide, which increases the pH of the effluent discharged |
| 2     | Activated alumina | 120         | www.indiamart.com | Costly |
| 3     | Activated carbon | 52          | www.indiamart.com | Costly |
| 4     | Bottom ash | 0.5           | www.indiamart.com | Low uptake capacity |
| 5     | Kanuma mud | –             | Chen et al. (2011) | Low uptake capacity |
| 6     | *Tinospora cordifolia* | 23          | Present study | Low cost & good removal efficiency at pH 7, residue can be disposed of without changing the pH of the disposed field |

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**Table 6** | Comparative study of uptake capacity of *Tinospora cordifolia* with other adsorbents

| S. no. | Adsorbent | Uptake Capacity (mg/g) | pH | Reference |
|--------|-----------|------------------------|----|-----------|
| 1      | High alumina content bauxite | 3.125 7.0 ± 0.1 | Lavecchia et al. (2012) |
| 2      | Activated alumina | 1.45 7.0 | Ghorai & Pant (2004) |
| 3      | Activated carbon and aligned carbon nanotubes | 3.0 7.0 | Li et al. (2003) |
| 4      | Bottom ash | 0.3714 6.0 | Ramesh et al. (2012) |
| 5      | Kanuma mud | 1.558 7.0 | Chen et al. (2011) |
| 6      | *Tinospora cordifolia* | 3.88 7.0 | Present study |

**Table 7** | Cost analysis of *Tinospora cordifolia* as bioadsorbent

| S. no. | Adsorbent | Cost (Rs/ kg) | Reference | Remarks |
|--------|-----------|---------------|-----------|---------|
| 1      | Bauxite   | 12            | www.indiamart.com | Effluent disposed contains precipitate of aluminium hydroxide, which increases the pH of the effluent discharged |
| 2      | Activated alumina | 120         | www.indiamart.com | Costly |
| 3      | Activated carbon | 52          | www.indiamart.com | Costly |
| 4      | Bottom ash | 0.5           | www.indiamart.com | Low uptake capacity |
| 5      | Kanuma mud | –             | Chen et al. (2011) | Low uptake capacity |
| 6      | *Tinospora cordifolia* | 23          | Present study | Low cost & good removal efficiency at pH 7, residue can be disposed of without changing the pH of the disposed field |
CONCLUSION

Experiments were conducted to investigate the potential of *Tinospora cordifolia* for defluoridation of water and it was found that the adsorption was dependent on flow rate, initial concentration of fluoride and bed depth of adsorbent in column. The Thomas and Yoon-Nelson models can be used to describe the behavior of the breakthrough curve. Adsorbent can be regenerated and reused with minimal loss of efficiency up to three adsorption–desorption cycles. Hence, the packed bed column of *Tinospora cordifolia* with continuous flow method was found to be very effective and economic in the desorptive removal of fluoride from aqueous media.

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DATA AVAILABILITY STATEMENT

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

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