Defluoridation and empirical models in column studies using fishbone charcoal

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Column bed adsorption studies have been carried out to study the fluoride removal on fishbone charcoal, and to determine the effects of the various operating variables. The useful (or effective) treated effluent volume (corresponding to the desired breakthrough concentration of 1.0 mg/L of fluoride) is found to be a function of the effluent flow rate, initial solute concentration and column bed depth. The useful treated effluent volume decreased with an increase in the flow rate and initial fluoride concentration, but it increased with the column bed depth. Empirical relationships have been developed to predict the stated useful treated effluent volume for the known values of flow rate, column bed depth and initial fluoride concentration for the observed test conditions. The relationships evolved manifest high correlation coefficients. The studies are useful in small installations.

A comprehensive account of fluoride implications and permissible concentration in drinking water along with a summary of fluoride removal methods, materials, interferences, mechanisms, etc. is readily available elsewhere. The authors have presented the numerous aspects of fluoride removal through adsorption on fishbone charcoal in a batch system as well as in a moving media system of adsorption reactor operations. The aspects of such an adsorption process using a fixed-bed column operation involving a continuous effluent flow which is more practical in real life situations, are not readily available in all its variations and analysis. This paper is intended to bridge such a gap.

In a continuous flow, fixed-bed column operation, the efficiency and system cost depend on the removal capacity of the media, i.e., the amount of solute adsorbed per gram of the adsorbent. This capacity is a function of several factors such as flow rate, column bed depth, initial solute concentration, pH temperature, regenerant used, and desired quality of the treated water. In this study, the effect of some of these parameters, viz., the flow rate (Q), the initial solute concentration (C₀), and the column bed depth (D), on fluoride removal by fishbone charcoal in a fixed bed with continuous flow operation have been investigated. An attempt has also been made to evolve possible inter relationships among these parameters.

Experimental Procedure

A description for preparing the fishbone charcoal has been described previously and the characteristics of the prepared charcoal would depend on the kind of bone, its processing, carbonisation (temperature and time) and cooling scheme. Bhargava and Kiledar presented a comprehensive economic analysis to show that the fishbone charcoal costs very little, and can be regarded as an economical (Rs. 11.00 per kg)
adsorbent material in India. To simulate field conditions, the test fluoride solutions were prepared using the tap water. The interference of the competing ions (such as sulphates and chlorides) present in tap water and also the presence of calcium in tap water was found to be negligible through a trial batch run. The test runs were conducted at a temperature of 20±2°C. The test condition details for batch studies have been stated elsewhere for studying the effects of variation 16,21

Fixed bed column studies were conducted with 2.5 cm diameter glass column filled with fishbone charcoal. Four sets of column studies were performed. In each set, for a given initial fluoride concentration (Co = 2.5, 5.0, 10.0, or 20.0 mg/L) the downward flow rates were varied and maintained at 15 mL/min (3.06 mL/min/cm²), 30 mL/min (6.12 mL/min/cm²), 50 mL/min (10.2 mL/min/cm²), and 75 mL/min (15.3 mL/min/cm²) corresponding to each of the various Co and column bed depth (D) values. Additional runs were also conducted with fishbone charcoal filled to a column bed depth (D) of 15 cm with (i) the initial fluoride concentration of the test solution kept constant at 5 mg/L and the flow rate maintained at either 15, 25, 50 or 75 mL/min; (ii) a constant flow of 15 mL/min maintained and the initial fluoride concentration of the test solution kept at 2.5, 6.0, 10.0, and 20.0 mg/L; and (iii) the initial solute concentration and the flow rate kept constant at 10 mg/L of F⁻ and 15 mL/min, respectively, while the depth of the media bed varied from 15 cm to 30 cm to 50 cm.

The fishbone charcoal was filled in glass columns to the required depths in such a way that the bulk density of the filled absorbent material was 0.61 g/cm³ for example, a 15 cm column bed depth of fishbone charcoal weighed 45 g such that

\[ \frac{45}{(\pi/4) \times 2.5^2 \times 15} = 0.61 \text{ g/cm}^3 \]

The top of the column connected to a constant head maintaining tank which was charged by an overhead tank containing the feed solution.

In each of these tests, the effluent concentration was monitored at different times and samples were analysed for fluoride concentration by the above stated Ion Analyser. The various runs were terminated when the effluent fluoride concentration at the bottom of the column beds exceeded 1 mg/L (the permissible concentration, designated as the breakthrough concentration). The volume of the effluent treated prior to the breakthrough concentration, was designated as the 'useful (or effective) treated effluent volume'.

Results and Discussion

Variation of breakthrough with influent flow rate (Q)—Based on the observed data, the breakthrough curves for the initial fluoride concentration (Co) of 5.00 mg/L corresponding to the different influent flow rate (Q = 15, 25, 50 and 75 mL/min) are depicted in Fig. 2. The adsorbent material weight (Ws = 45 g) and bed depth (D = 15 cm) in the column were kept constant for all the runs. The bulk density of the adsorbent material is 0.61 g/cm³. The retention time or hydraulic residence time corresponding to the flow rates (Q) of 15, 25, 50 and 75 mL/min are 4.92, 2.95, 1.47 and 0.98 min, respectively.

The volume of treated effluent at the different flow rates at the chosen effluent fluoride concentration at breakpoint, Ce of 1.0 mg/L was evaluated from the breakthrough curves as 9.45,
between the solute and the media. This is causing a required for completing the sorption reaction rates of 15, 25, 50 and 75 mLimin, respectively. The volume of treated effluent decreases with an increase in flow rate per gram of the adsorbent. This variation may be occurring because at higher flow rates, the available retention time (or hydraulic residence time) of solution in the column height decreases and might be inadequate as compared to the optimum time of retention time required for completing the sorption reaction between the solute and the media. This is causing a shorter breakthrough (at \( C_e = 1.0 \) mg/L) for the higher flow rates and thus less quantity of effluent volume is treated.

Mass balance calculations were done to determine the amount of fluoride removed at different flow rates (Fig. 2) till the breakthrough concentration point (\( C_e = 1.0 \) mg/L). The effluent concentration up to the breakthrough point varied from 0 to 1.0 mg/L as seen in Fig. 2. During the breakthrough time, an average breakthrough effluent fluoride concentration (\( C_{e-w} \)) of 0.5 mg/L was assumed for the time interval in which \( C_e \) varied from 0 to 1.0 mg/L instead of using the procedure of integration of breakthrough curve or considering small time intervals. To illustrate, for a flow rate (\( Q \)) of 15 mL/min and breakthrough time (\( t_b \)) of 10.5 h (\( C_e \) assumed 0 up to 7 h), the amount of fluoride removed equals \([((15/1000) \times (7 \times 60) \times 5 + (15/1000) \times (10.5 - 7) \times 60 \times (5 - 0.5)] = 31.5 + 14.175 = 45.7\ mg\). Similarly, the amount of fluoride removed for flow rates of 25, 50 and 75 mL/min worked out to be 38.6, 17.1 and 11.0 mg, respectively. The lesser fluoride removal at higher flow rates may be due to shorter available retention or contact time (or hydraulic residence time).

The plot presented in Fig. 3 follows a relationship of the type shown in Eq. (1).

\[
V = a_1 + b_1(1/Q_w)
\]

(1)

In Eq. (1), \( V \) represents the useful volume of the treated effluent, in litre at a flow rate of \( Q_w \), in mL/min per gram of the adsorbent which yields an effluent concentration of fluoride, \( C_e \) of 1.0 mg/L, and \( a_1 \) and \( b_1 \) are coefficients.

The values of the coefficients \( a_1 \) and \( b_1 \) were determined as 1.748 and 2.80, respectively manifesting a coefficient of correlation of 0.931, through the regression of data shown in Fig. 3. Thus, Eq. (1) is rewritten as Eq. (2)

\[
V = 1.748 + 2.80 \left(1/Q_w\right)
\]

(2)

Eq. (2) can be used to determine the total weight of absorbent required for treating a known influent volume at a given flow rate at an initial fluoride concentration of 5.0 mg/L under the observed test conditions.

**Variation of breakthrough with initial fluoride concentration (\( C_0 \))**—Based on the observed data, breakthrough curves at the different initial fluoride concentrations (\( C_0 \)) are shown in Fig. 4. These curves are obtained corresponding to a constant flow rate of 15 mL/min. At the chosen breakpoint concentration of \( C_e = 1.0 \) mg/L, the useful volume of the treated effluent decreases with an increase in \( C_0 \) value. This is due to the fact that for a given flow rate and quantity of the adsorbent, the adsorption or exchange sites of the adsorbent are exhausted earlier when a higher initial fluoride concentration influent is encountered. Therefore, the time to the breakthrough point is less. Mass balance calculations were carried out, as before to determine the amount of fluoride removal at different initial fluoride concentrations (Fig. 4). The amount of fluoride removed at \( C_0 \) of 2.5, 6.0, 10.0 and 20.0 mg/L was 28.2, 44.6, 51.3 and 63.18 mg, respectively. The breakthrough times are shorter for higher initial fluoride concentrations, but the amount of fluoride removed increases with \( C_0 \). This is probably due to higher concentration gradients at higher \( C_0 \) values.

From Fig. 4, the values of the useful volume of the treated effluents corresponding to \( C_e = 1.00 \) mg/L were calculated as 18.8, 8.1, 5.4 and 3.24 L corresponding to \( C_0 \) values of 2.5, 6.0, 10.0 and 20.0

![Fig. 4—Breakthrough curves (C vs t) corresponding to the different initial fluoride concentrations (\( C_0 \)).](image)
mg/L, respectively. The variation of volume of the treated effluent versus the initial fluoride concentration \( (C_0) \) is shown in Fig. 5. The curve in Fig. 5 follows the relationship of the type shown in Eq. (3).

\[
V = a_2 + b_2 \left( \frac{1}{C_0} \right)
\]

In Eq. (3), \( V \) represent the useful volume of the treated effluent in litre at an initial fluoride concentration, \( C_0 \) corresponding to \( C_e = 1.00 \) mg/L, \( a_2 \) and \( b_2 \) are coefficients. The values of the coefficients \( a_2 \) and \( b_2 \) were determined as 0.897 and 44.58, respectively, manifesting a coefficient of correlation of 0.999 through the regression of the data shown in Fig. 5. Thus, Eq. (3) can be rewritten as Eq. (4).

\[
V = 0.897 + 44.58 \left( \frac{1}{C_0} \right)
\]

Eq. (4) can predict the useful volume of the treated effluent (corresponding to \( C_e = 1.0 \) mg/L) at any initial fluoride concentration (in the range of 2.5-20.0 mg/L) for the observed test conditions.

The coefficients \( a_1 \) and \( b_1 \) (Eq. (1)) and \( a_2 \) and \( b_2 \) (Eq. (3)) are appropriate for a pH of 8.0. As previously presented, the fluoride removal increases with a decrease in the pH. Therefore, the useful treated effluent volume will increase with decreasing pH at a given flow rate or initial fluoride concentration. Thus, the variation curves corresponding to pH values lower than 8 would be placed above the curve shown in Figs 3 and 5. It is therefore, easily inferred that the coefficients \( a_1, b_1, a_2, \) and \( b_2 \) would increase with decreasing pH.

**Figure 6**—Sample variation plot of useful treated effluent volume \( (V) \) with influent flow rate per unit column bed area \( (Q_a) \) corresponding to the different column bed depths \( (D) \), for \( C_0 = 2.5 \) mg/L.

**Figure 7**—Sample variation plot of useful treated effluent volume \( (V) \) with influent flow rates per unit column bed area \( (Q_a) \) corresponding to the different initial fluoride concentrations \( (C_e) \) for \( D = 65 \) cm.
and 6.12 mL/min/cm²). The decrease in the useful treated effluent volume with increasing flow rates may be occurring because at higher flow rates (Q= 10.2 and 15.3 mL/min/cm²), the shorter contact time in the column bed might be insufficient for a significant fluoride removal and thus the breakthrough occurs early. At lower flow rates the contact time is increased, resulting in greater fluoride removal. The overall effect is an increase in the useful treated effluent volume V. For higher flow rates (Q = 10.2 and 15.3 mL/min/cm²), this decreasing trend more or less stabilizes and the variation curves appear to become asymptotic to the flow rate axis. Such a stabilization in the V values occurs beyond a high flow rate of 15.3 mg/min/cm² for most of the cases reported in this study. At higher flow rates, V remains more or less same probably because the fresh adsorbent takes up that much material instantly even in the shorter contact time (thus early breakthrough) at the still higher flow rates. This indicates that operating the column bed at flow rates greater than 15.3 mL/min/cm² does not significantly change the useful treated effluent volume, V.

For a given Co and Q values, the useful treated effluent volume increases with an increase in bed depth (Fig.6). This is obviously expected because the increase of the column bed material depth provides more grain surfaces, more sorption sites, and greater contact opportunities to enable an increased useful volume of the treated effluent. A plot between V and D is depicted in Fig.8 for the various Q values. The various straight line plots pass through the origin as expected. The slopes of such straight lines indicate the V value per unit depth and is determined as 1.68, 1.05, 0.92 and 0.83 L/cm depth for 15, 30, 50 and 75 mL/min flow rates, respectively. The close scatter of the observed points to the straight line plots indicate observational reliability. These figures indicate slightly more V value per unit depth for low flow rates, as seen earlier.

Fig. 9 depicts a sample plot (based on observed data) of the useful treated effluent volume versus the initial fluoride concentration for one value of flow rate (Q = 10.2 mL/min/cm²) and column bed depth (D= 42 cm). The same trend is observed for other test Q and D values. The useful treated effluent volume V, decreases very significantly for higher initial fluoride concentration values. The useful (or effective) volume of treated effluent has decreased by about 60% when the initial fluoride concentration has increased from 2.5 to 5.0 mg/L while it has decreased by about 75% when initial fluoride concentration was increased from 10.0 to 20.0 mg/L. This indicates a marked role of the initial fluoride concentration on the amount of the useful treated effluent volume. The decrease in the useful treated effluent volume with an increase in initial influent fluoride concentration is due to the fact that for a given flow rate and bed depth, the adsorption
sites are exhausted earlier. This results in a shorter breakthrough time and hence, a smaller useful volume of the effluent is yielded.

Predictive empirical models—The observed data were analysed to determine possible correlations between the useful treated effluent volume and variables such as the flow rate, bed depth, and initial solute concentration. Each plot \((V\text{ vs } Q_a)\) of the type shown in Figs 6 and 7 follows a relationship of the type shown in Eq. (5).

\[
\log V = V - K Q_a \quad \ldots (5)
\]

In Eq. (5), \(V\) is the useful treated effluent volume in litre, \(Q_a\) is the flow rate in \(\text{mL/min/cm}^2\), and \(V_x\) and \(K\) are the regression coefficients which represent the intercept and slope, respectively. Through a regression analysis of the observed data, the values of \(V_x\) and \(K\) were determined and are tabulated in Table 1 along with their coefficients of correlation \((r)\).

The values of \(V_x\) (Table 1) increase with increasing \(D\), while the values of \(K\) decrease with increasing \(D\) values for all \(C_0\) values. Trial plots of the values of \(V_x\) and \(K\) versus \(D\) were prepared for each set of \(C_0\) and \(Q_a\) values, for a possible correlation. Two sample plots, one relating the values of \(V_x\) and \(D\) and the other relating the \(K\) and \(D\) values are shown in Fig.10 for \(C_0 = 5.0 \text{ mg/L}\) and \(Q_a = 10.2 \text{ mL/min/cm}^2\). The plots presented in Fig.10 follow the relationship of the type shown in Eqs. (6) and (7), respectively.

\[
V_x = e + f(D) \quad \ldots (6)
\]
\[
\ln K = -g - h(D) \quad \ldots (7)
\]

In Eqs (6) and (7), \(e, f, g,\) and \(h\) are coefficients. Their values were determined through the regression analysis of the data given in Table 1 and are presented in Table 2 along with their coefficients of correlation \((r)\). The values of coefficients \(e, g,\) and \(h\) are varying with \(C_0\) values. The value of coefficient \(f\) does not vary with \(C_0\), to any significance. Therefore, an average value of \(f\) is computed for further use \((f_{\text{average}} = 0.0112)\).

Plots were prepared between the coefficients \(e, g,\) and \(h\) versus \(C_0\) for a possible correlation. The plots showing the variation of coefficients \(e, g\) and \(h\) versus \(C_0\) are presented in Figs. 11 and 12, respectively, and are seen to follow the relationships respectively for \(e, g,\) and \(h\) shown in Eqs. (8), (9) and (10).

\[
e = \frac{1}{i + j C_0} \quad \ldots (8)
\]
\[
g = m - n C_0 \quad \ldots (9)
\]
\[
h = p + q C_0 \quad \ldots (10)
\]

<table>
<thead>
<tr>
<th>Initial Fluoride concentration (C_0)</th>
<th>Column bed depth (D)</th>
<th>Coefficients for Eq. (5)</th>
<th>Coefficient of correlation (r)</th>
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<tr>
<td>(C_0 = 2.5)</td>
<td>(D=20)</td>
<td>1.530</td>
<td>0.0223</td>
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<tr>
<td>(C_0 = 2.5)</td>
<td>(D=42)</td>
<td>1.837</td>
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<td>(C_0 = 5.0)</td>
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</table>
In Eqs. (8) - (10), i, j, m, n, p, and q are coefficients. Their values are 0.640, 0.062, 1.836, 0.0535, $4.013 \times 10^{-4}$, and $5.647 \times 10^{-4}$, respectively. The coefficients of correlation vary between 0.967 to 0.989.

Substitution of Eqs. (6) - (10) in Eq. (5) yields a relationship presented in Eq. (11).

$$
\log V = \left[ \left( \frac{1}{0.640 + 0.062 C_0} \right) + 0.0112 D \right]
- \left[ \exp \left\{ -1.836 + 0.0533 C_0 \right\} \right]
- \left(4.013 \times 10^{-4} + 5.647 \times 10^{-4} C_0 D\right) Q_a
$$

In Eq. (11), $V$ is the useful volume of treated effluent at breakthrough concentration of 1.0 mg/L of fluoride (F) in liter, $C_0$ is the initial fluoride concentration in mg/L, $D$ is the column bed depth in cm, and $Q_a$ is the flow rate in mL/min cm$^2$.

*Alternate model*—As an alternative, the polynomial based fitting concept was used to develop another empirical relationship (Eq. (12)) between the useful treated effluent volume and the variables, flow rate, column bed depth and initial fluoride concentration.

$$
V = [Y_1 + Y_2 \log Q_a + Y_3 D + Y_4 \log C_0]^3
$$

Using the data presented in Table 1 and multilinear regression analysis, the values of coefficients $Y_1$, $Y_2$, $Y_3$, and $Y_4$ in Eq. (12) are 3.8227, -0.8869, 0.0263, and -1.949, respectively. With these values of coefficients, the coefficient of correlation for Eq. (12) worked out as 0.970.

The relationships obtained in Eq. (11) and Eq. (12) can be exploited to estimate the amount of useful volume of treated effluent for the desired $C_0$, $Q_a$, and $D$ values under the observed test conditions. The high coefficients of correlation ranging from 0.950 to 0.995 for Eq. (11) and 0.958 to 0.998 for Eq. (12) for various test conditions manifest the justification of the relationships presented in Eqs (11) and (12). This is also reinforced in Fig. 13 which compares sample observed data with the predicted values [through the use of Eqs (11) and (12)]. Similar empirical relationships can be obtained for the different adsorbate-adsorbent systems for any other chosen conditions, and also for effluent fluoride concentrations other than 1.0 mg/L.

*Practical applications*—Fishbones can be considered to be a comparatively cheaper and
effective material for the preparation of bone charcoal. De fluoridation of drinking water with fishbone charcoal is feasible for isolated communities of small sizes as well as at domestic level in the form of home filters.

The empirical relationships\textsuperscript{1,6,23,24} obtained in this study can be used to predict the fraction of fluoride remaining in solution at any pH and time. The empirical relationships developed in this study can be exploited to estimate the quantity of the useful treated effluent volume corresponding to the stated breakthrough concentration (1.0 mg/L of fluoride in this study) for the known values of flow rate, column bed depth, and initial fluoride concentration as per the stated test conditions. Such relationships can be of practical help in the design of small installations.

The operating cost of a fixed bed column reactor mainly depends upon the service time (the time at which the desired breakthrough concentration occurs). Such studies can be useful in determining the economical service time to be provided for a given set of variables to minimise the operating cost of the reactor.

Conclusions

The treated effluent volume corresponding to the effluent concentration of 1.0 mg/L of fluoride decreased with an increase in flow rate per gram of adsorbent and also with an increase in initial fluoride concentration of solution. The volume of treated effluent increases with an increasing column bed depth. A relationship is developed to predict (i) the total weight of adsorbent required for treating a known influent volume at a given rate at an initial fluoride concentration of 5.0 mg/L and (ii) the treated effluent volume at any initial fluoride concentration for a flow rate of 15 mL/min.

The useful treated effluent volume decreased with an increase in flow rate per unit area for a given initial fluoride concentration and column bed depth. An empirical relationship was developed to predict the useful effluent (treated) volume for any given values of initial fluoride concentration (in the range of 2.5-20.0 mg/L), flow rate (in the range of 3.06-15.3 mL/min/cm\textsuperscript{2}) and column bed depth (in the range of 20-65 cm). The relationship manifested high coefficients of correlation when projected against the observed values.

References