Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina

Subhashini Ghorai, K.K. Pant*

Department of Chemical Engineering, Indian Institute of Technology, Delhi 110016, India

Received 9 April 2004; received in revised form 25 August 2004; accepted 1 September 2004

Abstract

Contamination of drinking water due to fluoride is a severe health hazard problem. Excess of fluoride (>1.5mg/l) in drinking water is harmful to the human health. Various treatment technologies for removing fluoride from groundwater have been investigated in the past. Present investigation aims to remove fluoride by activated alumina. Adsorption isotherm has been modeled by Langmuir equation and isotherm constants. The dependence of the adsorption of fluoride on the pH of the solution has been studied to achieve the optimum pH value and a better understanding of the adsorption mechanism. It was found that maximum adsorption takes place at pH value of 7. Breakthrough analysis revealed that early saturation and lower fluoride removal takes place at higher flow rate and at higher concentrations. Predicted simulation results of one-dimensional model for isothermal, axially dispersed fixed bed on the assumption of pore-diffusion rate-control conditions matches with the experimental data in the initial zone of the breakthrough curve, but deviated marginally in the final tailing zone. Bed depth service time (BDST) model was also applied successfully.

Keywords: Fluoride; Activated alumina; Adsorption; Regeneration; Breakthrough; Modeling

1. Introduction

Excess of fluoride (>1.5 mg/l) in drinking water is harmful to the human health. The amount of fluoride in groundwater is in excess in many regions. The physiological effects of fluoride upon human health have been studied since the early part of 20th century. Several reports and studies [1] established both the risks of high fluoride dosing and the benefits of minimal exposure. A low daily dose of fluoride was deemed responsible for inhibiting dental caries, while a higher daily dose was linked to permanent tooth and skeletal fluorosis [2]. Current treatment methods can be divided into two categories: precipitation and adsorption. Precipitation processes involve addition of chemicals and formation of fluoride precipitates or simultaneous co-precipitation of fluoride with a resulting precipitate. Among these are precipitation with calcium and aluminum salts [3,4]. Adsorption processes involve the passage of the water through a contact bed where fluoride is removed by ion exchange or surface chemical reaction while the solid bed matrix [5]. Adsorption on activated alumina, alum, charcoal, ash [6-11], ion-exchange [12-14] and membrane processes such as reverse osmosis, nanofiltration, electrodialysis and Donnan dialysis [15-18]. Among these technologies fluoride adsorption by an activated alumina appeared to be an interesting process. Activated alumina is an efficient fluoride remover from natural water and its fluoride removal efficiency is reported to be in the range of 1-9 g of fluoride per liter of the material. Most of the available materials for defluoridation are expensive and technically non-feasible for rural areas. Hence, the need to find locally available defluoridation media for safe and easy use at both household and small community levels is desirable. The objective of this research is to study the effect of various parameters such as pH, flow rate, initial fluoride concentration and bed height on the adsorption of fluoride onto activated alumina, experimentally as well as numerically. The service time and bed depth were correlated with the process parameters such as initial fluoride
Nomenclature

- \( b \) Langmuir isotherm constant
- \( C_e \) equilibrium concentration (mg/l)
- \( Q \) outlet fluoride concentration (mg/l)
- \( C_0 \) inlet fluoride ion concentration (mg/l)
- \( F_0 \) flow rate (ml/min)
- \( K_n \) Freundlich isotherm constants
- \( k_w \) adsorption rate constant (min\(^{-1}\))
- \( K_d \) intraparticle diffusion rate (mg\(\cdot\)g\(^{-1}\) h\(^{-1/2}\))
- \( m \) mass of adsorbent (g)
- \( M \) mass of adsorbent per unit volume of particle
- \( q \) amount of \( F^- \) adsorbed per gram of AA (mg/g AA)
- \( q_e \) equilibrium adsorption capacity (mg/g AA)
- \( q_i \) Langmuir constant related to the capacity and energy of adsorption (mg/g)
- \( r \) equilibrium parameter
- \( t \) flow time (s)
- \( V \) flow rate (m\(^3\)/s)
- \( x \) amount of fluoride adsorbed in solid phase (mg)

Greek letters

- \( \rho \) bed porosity
- \( \rho \) density (kg/m\(^3\))

Subscripts

- \( a \) ambient
- \( i \) component \( i \)
- \( l \) bulk fluid
- \( s \) solid (adsorbent) phase

Table 1

<table>
<thead>
<tr>
<th>S.no.</th>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Particle form</td>
<td>Spheres</td>
</tr>
<tr>
<td>2</td>
<td>Particle size (mm)</td>
<td>2-5</td>
</tr>
<tr>
<td>3</td>
<td>Water adsorption capacity at 30 °C by weight</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>Surface area (m(^2)/g) (minimum)</td>
<td>250</td>
</tr>
<tr>
<td>5</td>
<td>Pore volume (cm(^3)/g)</td>
<td>0.42</td>
</tr>
<tr>
<td>6</td>
<td>Bulk density (g/cm(^3))</td>
<td>0.90</td>
</tr>
<tr>
<td>7</td>
<td>Bed crushing strength (wt.%) (minimum)</td>
<td>92</td>
</tr>
<tr>
<td>8</td>
<td>Loss on attrition (wt.%) (maximum)</td>
<td>0.3</td>
</tr>
<tr>
<td>9</td>
<td>Loss on ignition (250-1000 °C)</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Chemical analysis

| 10    | Al2O3 (by difference) (minimum)        | 92.0  |
| 11    | Fe2O3 (maximum)                        | 0.05  |
| 12    | SiO2 (maximum)                         | 0.20  |
| 13    | Na2O (maximum)                         | 0.30  |

2. Experimental

2.1. Batch studies

Granulated activated alumina used in this study was procured from Oxide India Ltd., Durgapur, India. Synthetic fluoride solution was prepared by adding appropriate quantity of sodium fluoride (Merck, Germany) to distilled water. Batch experiments were carried out in different sets by taking activated alumina in the range of 4-40 g/l of synthetic fluoride sample of desired initial concentration (2.5-14 mg/l) in a series of reagent flasks at a varying pH (4-10) and at constant 80 ± 1 rpm in a mechanical shaker. pH was adjusted using either dilute NaOH or HCl. Samples were collected at different time intervals and analyzed using SPANDS photometric method for fluoride concentration. Exhausted activated alumina was regenerated with NaOH and H2SO4 either separately or in combination. Exhausted activated alumina was dipped in 0.1N NaOH and then left for 12 h. These pellets were washed repeatedly and then activated with 0.4N H2SO4 for 12 h. Subsequent water washing was carried to raise the pH to 7 followed by drying in oven for 5 h. This makes activated alumina ready for the next delustration cycle. The procedure was used for the regeneration of exhausted activated alumina after each cycle and continued up to 3-5 cycles in order to study the effect of various parameters on fluoride uptake capacity. Similar experiments were conducted for different regeneration cycles of activated alumina. Equilibrium data were collected by taking the synthetic solution of fluoride of known concentration in a series of reagent flasks. The properties of activated alumina are given in Table 1.

Table 1 Properties of activated alumina, Grade OX-25 (Oxide India Ltd.)

2.2. Column studies

The adsorption isotherms do not give accurate scale-up data in fixed bed systems therefore the practical applicability of activated alumina was ascertained in the column operations. A Perspex column of length 550 mm and internal diameter 50.8 mm was used to which the flow was controlled from a feed reservoir of 20 L capacity at the top using a flow controller. The effluent was collected at the bottom through a 2 mm diameter orifice. The column experiments were aimed at studying the effect of process parameters such as inlet flow rate, initial fluoride concentration and bed height at various throughput volumes. Samples of the outlet bulk solution were collected at definite intervals of time and examined for fluoride concentration. Exhausted activated alumina bed was regenerated in situ in column using acid/alkali treatment method as done for batch studies.
3. Results and discussion

3.1. Effect of pH

The pH controls the adsorption at the water-adsorbent interfaces. Hence, optimization of pH for adsorption of fluoride was done by studying the uptake of fluoride over activated alumina as a function of pH. It is evident from Fig. 1 that the removal of fluoride is maximum (69.5%) at a pH of 7 and was independent of sorbent dose and initial fluoride concentration. Therefore, all the experiments were conducted at pH 7. The probable reason for low adsorption at pH > 7 is that silicates and hydroxyl ions appeared to compete more strongly with F⁻ ions for alumina exchange sites. At pH < 7, the soluble alumino-fluoro complexes are formed resulting in the presence of aluminium ions in the treated water. Hence, it is preferable to carryout defluoridation at normal water pH to avoid aluminium dissolution and moreover no acid/alkali treatment is required after treatment.

3.2. Equilibrium studies and adsorption isotherms

Equilibrium studies were carried out to determine the conditions for maximum fluoride removal on activated alumina. It was observed that adsorption capacity reaches an equilibrium value beyond which there was negligible change in the residual fluoride concentration. The distribution of fluoride between the liquid phase and the solid phase is a measure of the position of equilibrium in the adsorption process and can be expressed by the Freundlich and Langmuir equations. These two models are widely used, the former being purely empirical and the latter assumes that maximum adsorption occurs when the surface is covered by the adsorbate.

The Freundlich model, which is an indicative of surface heterogeneity of the sorbent, is given by the following linearized equation:

\[ \log \left( \frac{X}{q_e} \right) = \log k + \frac{1}{n} \log C_e \]  

where \( k \) and \( \frac{1}{n} \) are Freundlich constants related to adsorption capacity and adsorption intensity respectively. The value of \( k \) is 1.78 mg/g and \( \frac{1}{n} \) is 0.32 for Freundlich isotherm. Since the value of the constant, \( \frac{1}{n} \) (adsorption intensity) is less than unity, it indicates a favorable adsorption.

The Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number of identical sites, is given by

\[ \frac{1}{q_e} = \frac{1}{q_o b} + \frac{1}{q_o} \frac{1}{C_e} \]  

where \( q_o \) is the maximum amount of the fluoride ion per unit weight of activated alumina to form a complete monolayer on the surface bound at high \( C_e \) and \( b \) is a constant related to the affinity of the binding sites. \( q_o \) represents a particle limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, particularly in case where the sorbent did not reach its full saturation in experiments. The linear plot of \( \frac{1}{C_e} \) versus \( \frac{1}{q_e} \) (Fig. 2) indicates the applicability of Langmuir adsorption isotherm. The values of Langmuir parameters, \( q_o \) and \( b \) are 2.41 mg/g and 0.31l/mg, respectively.

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter was determined by using the following equation [19]:

\[ r = \frac{1}{1 + bC_0} \]  

where \( Q \) is the initial concentration. Values of \( r < 1 \) represent favorable adsorption. The \( r \)-value for the initial concentration of 5 mg/l was found to be 0.392. The value obtained shows that our system is favorable.

![Fig. 1. Effect of pH on the adsorption of fluoride [Co (mg/l): 13.8, AA (g/l): 4].](image)

![Fig. 2. Langmuir plot for the adsorption of fluoride.](image)
3.3. Kinetics study

It was obtained that the uptake of fluoride increases with the lapse of time. However, the adsorption of fluoride was rapid in the first 6 h after which the rate slowed down as the equilibrium approached. The results obtained from the experiments were used to study the rate-limiting step. The adsorption rate constant \((K_a d)\) for adsorption was determined from the following first order rate expression:

\[
\log(q_e - q) = \frac{2.303}{4} t + \log(q_e) - \frac{2.303}{K_a d} \tag{4}
\]

where \(q_e\) and \(q\) (both in mg/g) are the amount of fluoride adsorbed per unit mass of activated alumina at equilibrium and time \(t\), respectively, and \(K_a d\) is the rate constant (min\(^{-1}\)).

The value of \(K_a d\) was calculated from the slope of the linear plot of \(\log (q_e - q)\) versus time (Fig. 3). The adsorption rate constants were found to be 0.56, 0.59, 0.51, and 0.48 min\(^{-1}\) for initial fluoride concentration of 2.7, 3.5, 5.0, and 7.5 mg/l, respectively. The variation in rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and the rate of adsorption will not be linear when pore diffusion limits the adsorption process. The possibility was tested in terms of a graphical relationship between amount of fluoride adsorbed and square root of time (Fig. 4).

In order to show the existence of intraparticle diffusion in the adsorption process, the amount of fluoride sorbed per unit mass of adsorbents, \(q\) at any time \(t\), was plotted as a function of square root of time, \(t^{1/2}\). The rate constant for intraparticle diffusion was obtained using the equation:

\[
q = K_d t^{1/2} \tag{5}
\]

where \(K_d\) (mg g\(^{-1}\) h\(^{-1/2}\)) is the intraparticle diffusion rate constant. The plot for intraparticle diffusion shows that initially curved portion reflects film or boundary layer diffusion and the subsequent linear portion attribute to the intraparticle diffusion effect. Fig. 4 depicts that intraparticle diffusion is slow and the slope of the linear portion of the curve at each solute concentration gives the value of \(K_d\). The \(K_d\) values were found to be 0.11, 0.16, 0.21, and 0.23 mg g\(^{-1}\) h\(^{-1/2}\) at initial fluoride concentration of 2.7, 3.5, 5.0, and 7.5 mg/l, respectively. This suggests that the adsorption is governed by diffusion within the pores of the adsorbent. The linear portions of the curves do not pass through the origin (Fig. 4) indicating that mechanism of fluoride removal on activated alumina is complex and both the surface adsorption as well as intraparticle diffusion contribute to the rate determining step.

3.4. Mass transfer coefficient

Mass transfer analysis for the removal of fluoride was carried out using the following equation [20]:

\[
\ln \left( \frac{C_t}{C_0} \right) = \ln \left( \frac{1}{1 + MK} \right) - \left( \frac{1}{MK} \right) \beta S \varepsilon \tag{6}
\]

where \(K\) is the constant obtained by multiplying \(q_c\) and \(b (l/g)\), \(M\) is the mass of the adsorbent per unit volume of particle free adsorbate solution (g/l), \(S\) is the outer surface of adsorbent per unit volume of particle free slurry (l/cm), \(\beta\) is the mass transfer coefficient (cm/min). \(\ln (C_t/C_0) - \left( \frac{1}{1 + MK} \right)\) versus \(t\) for the initial concentration of 2.7 and 3.5 mg/l gives the straight line of slope \((1 + MK)/MK\)\(\beta S\) and the value of mass transfer coefficient \(\beta\) was calculated from the slope of the plots and was found to be 0.0083 and 0.009 cm/s, respectively (Fig. 5). The \(\beta\) obtained in this study is comparable to the values reported for benzaldehyde-carbon (9 x 10\(^{-3}\) cm/s), phenol-carbon (3.9 x 10\(^{-3}\) cm/s) and p-bromophenol-carbon (3.9 x 10\(^{-3}\) cm/s).
3.5. Breakthrough analysis

The general position of the breakthrough curve along the volume axis depends on the capacity of the column with respect to the feed concentration, flow rate and bed height. Adsorption involves interface accumulation or concentration of an adsorbate species at an adsorbent surface or interface. In a fixed bed adsorption system, the adsorbent located closest to raw water saturates first where maximum adsorption takes place initially. This adsorption zone moves further as time passes and then approaches the exit of the bed. When the adsorption zone has moved through the column, the concentration of the adsorbate at the exit becomes equal to the feed concentration. A plot of exit concentration as a function of lapse time or volume throughput reacted is known as breakthrough curve. The characteristic shape of the breakthrough curve depends on the inlet flow rates, concentration and other properties such as column diameter and bed height. The area under the breakthrough curve gives the total quantity of fluoride sorbed for a given feed concentration. Removal of fluoride ion with flow volume can also be found from the ratio of adsorbed quantities to the amount of fluoride ion sent to the column. The design of a fixed bed adsorber and prediction of the length of the adsorption cycle between regeneration require knowledge of the approach to saturation at the breakthrough point. In the present study, the shape of the breakthrough curve (Fig. 6) shows that adsorption is mainly mass transfer controlling. A mathematical study of breakthrough analysis was done using one-dimensional model for isothermal, non-equilibrium and non-adiabatic, axially dispersed single component fixed bed adsorption. The details of the model are given elsewhere [21]. The simulated breakthrough curves for fluoride removal were optimized for different values of mass transfer coefficient to match experimental data. The values of mass transfer coefficient and axial dispersion coefficient were $5.6 \times 10^{-5}$ m/s and $5.9 \times 10^{-2}$ m$^2$/s, respectively.

Bohart and Adams [22] proposed a relationship between bed depth and time taken for breakthrough to occur. The service time was related to process conditions and operating parameters as

$$\ln \left( \frac{C(t)}{C_0} \right) = -k_a C_0 t$$

where $N_o$ is adsorption capacity (mg solute/g adsorbent), $k_a$ is rate constant in bed depth service time (BDST) model ($l/(mg h)$) and $Z$ is bed depth of column (m).

Thus, if $\ln \left( \frac{C(t)}{C_0} \right) - 1$ is plotted against $t$, then the slope given by $k_a C_0$ can be used to calculate $k_a$.

The breakthrough profile can then be evaluated from the original equation recasted in form:

$$\frac{C(t)}{C_0} = e^{k_a C_0 t}$$

where $W$ is the bed capacity (total weight of sorbate adsorbed). The profile can be constructed from knowledge of two experimentally determined values: $k_a$ and $W$. $W$ is the capacity under dynamic conditions and becomes equal to the static capacity when capacity becomes invariant with bed depth.

The effects of varying $k_a$ at fixed capacity for a given sorbate/sorbent combination is shown in Fig. 7. The lower the value of $k_a$, the greater the likelihood of an early breakthrough.

Hutchins [23] proposed a linear relationship between bed depth and service time given by Eq. (9):

$$t = \frac{N_o Z}{C_0^0} - \frac{1}{k_a C_0} \ln \frac{r_{t_1}}{r_{t_2}} - \frac{1}{k_a C_0}$$

Eq. (9) enables the service time, $t$, of an adsorption bed to be determined for a specified bed depth, $Z$, of adsorbent.
The service time and bed depth are correlated with the process parameter such as initial pollutant concentration, solution and flow rate and adsorption capacity. It can be expressed in the form of a straight line:

\[ t = \frac{m_x}{Z_c} - C \_c \]  

(10)

where \( m_x \) is the slope of the BDST line and the intercept of this equation represents \( C_c = \frac{1}{C_0} \).

BDST plot for fluoride adsorption onto activated alumina has been shown in Fig. 8 with \( R^2 \) value >0.99. The slope of the BDST line represents the time required for the adsorption zone to travel a unit length through the adsorbent under the selected experimental conditions at a given concentration and in the present study it was found to be 10 h for \( Q = 5 \) mg/l. This is used to predict the performance of the bed, if there is a change in the initial solute concentration, \( C_0 \) to a new value of solute concentration.

The critical bed depth, \( Z_c \), is obtained for \( t=0 \) and for fixed outlet concentration \( C_t = C_b \) where \( C_b \) is the concentration at the breakthrough defined as a limit concentration or a fixed percent of initial concentration

\[ Z_c = \frac{V}{k_a N} \ln \left( \frac{C_0}{C_b} \right) \]  

(11)

The critical bed depth for fluoride obtained from BDST plot is 5.6 cm. The critical bed depth represents \( Z_c \) the theoretical depth of adsorbent, which is necessary to prevent the sorbate concentration to exceed the limit concentration \( C_b \).

### 3.6. Effect of Flow Rate

The effect of flow rate was studied at 20 and 30 ml/min while the inlet fluoride concentration was kept constant at 5 mg/l for both the experiments. Initially the adsorption was very rapid at lower flow rate probably associated with the availability of reaction sites able to capture metal ions around or inside the cells. In the next stage of the process due to the gradual occupancy of these sites, the uptake becomes less effective. The column is capable of accumulating fluoride even after breakthrough occurs although at a progressively lower efficiency.

The breakthrough curve becomes steeper when the flow rate is increased with which the break point time and adsorbed ion concentration decreases. The probable reason behind this is that when the residence time of the solute in the column is not long enough for adsorption equilibrium to be reached at that flow rate, the fluoride solution leaves the column before equilibrium occurs. Thus, the contact time of fluoride ions with activated alumina is very short at higher flow rate, causing a reduction in removal efficiency. Breakthrough curves, \( Q/Q \) against volume throughput is shown in Fig. 9 for two different flow rates, 20 and 30 ml/min. The maximum percentage fluoride removals for these two flow rates were found to be 92 and 86%, respectively. Adsorption rate also increased with the increase in the dose of the adsorbent. The maximum removal percentage was exhibited at a dosage of 200 g activated alumina (96%). Regeneration/reactivation of exhausted activated alumina bed were carried out for repeated cycles and a loss of 2% in the uptake capacity of
from early breakthrough points using the plots values of bed capacity under dynamic conditions, which may not be fluoride concentration. A suitable module for the removal tentatively describe effluent profiles, e.g. the rate constant of Freundlich isotherms. Data revealed that fluoride removal on process follows a first order kinetics and the regression results. This part has been left for future considerations. curves were obtained with activated alumina at higher inlet/Ct) - 1] against t. Much sharper breakthrough of ln [C] adsorption rate and can explain the dependence of the shape of fluoride from dilute solutions using activated alumina determining step. The breakthrough curves for adsorption as well as intraparticle diffusion contribute to the rate analysis of the equilibrium data fitted the Langmuir and aqueous solutions strongly depends on the contact time, pH of the solution and adsorbent concentration. The adsorption process follows a first order kinetics and the regression determination step. The breakthrough curves for adsorption of fluoride from dilute solutions using activated alumina show the mutual effects of the adsorption capacities and diffusion dialysis, Desalination 89 (1993) 325-341.

References