CHAPTER 5
CRITICAL ANALYSIS OF MECHANISM OF DEFLUORIDATION OF GROUND WATERS USING DIFFERENT TYPES OF ALUMINA

5.0. Introduction

Systematic studies are carried out using F-1 activated alumina, and γ-alumina on the effect of controlling factors such as pH, the contact time, and the ratio of adsorbate to adsorbent. Rate of fluoride removal and adsorption kinetics in batch studies. Studies are also carried using typical adsorbents i.e., F-1 activated alumina, and γ-alumina to estimate fluoride removal capacity at different pH values. The regeneration capacity of F-1 activated alumina and γ-alumina are also carried out to find the number of times the column saturated by fluoride could be regenerated.

5.1. Materials and methods

The details of instruments, materials, and methods adapted for the defluoridation of fluoride water samples with F-1 activated alumina and γ-alumina are presented in this unit.

5.1.1. Activation of alumina

Thermal treatment of gibbsite, \( \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \), results in its partial dehydration. Depending on the treatment conditions, products having different properties can be obtained.

Various transition aluminas are obtained when gibbsite is heated at temperatures below that necessary to form α-aluminium oxide. These transition aluminas are frequently termed
'activated' or 'active' aluminas. Ulrich designated the aluminas obtained by dehydroxylation of aluminium trihydroxide as γ-aluminas, which contain in addition to Al₂O₃, small amounts of gibbsite, Al₂O₃·3H₂O. This term persisted and came to be used for all the aluminas obtained by calcination at temperatures below 1000°C. The generally agreed forms of transition aluminas are γ, δ, η, θ, χ, K and ρ. ρ-Alumina is amorphous but the other forms have reasonably well-defined X-ray diffraction patterns. The transition phases that occur on heating aluminium trihydroxide (gibbsite) in vacuum are ρ-alumina (100-400°C), η-alumina (270-500°C), θ-alumina (870-1150°C) and finally α-alumina. In air, two distinct routes may be followed: either via boehmite (180-300°C), γ-alumina (500-850°C), δ-alumina (850-1050°C) and θ-alumina to α-alumina; or via χ-alumina (200-500°C) and K-alumina (900-1000°C) to α-alumina. The route followed is determined by a number of factors, in particular the particle size of the gibbsite and the hydrothermal conditions in the vicinity of the particles; other factors that have an influence on the path include the heating rate, moisture level in the feed, pressure, bed depth and soda content. It has been found that a material with a higher surface area, 250-375 m²g⁻¹, could be made by heating aluminium trihydroxide to temperatures between 400 and 800°C to give predominantly amorphous ρ-alumina. Pelletisation of this material allows the making of spheres which can be rehydrated and activated to give the desired strength and pore volume. On rehydration, pseudoboehmite and bayerite are produced and these transform to η-alumina on dehydration. Higher initial dehydration temperatures lead to crystalline products with improved rehydration characteristics and final surface areas of 300-350 m²g⁻¹.

The adsorbents used for the study are F-1 activated alumina and γ-alumina. These were supplied by Sri Balaji Adsorbents. Uppal, Hyderabad, the properties of these aluminas are as
Given in Table 5.1. Prior to any adsorption experiment, the alumina is washed with deionized, distilled water dried in oven.

Table 5.1 Properties of F-1 activated alumina and γ-alumina

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Characteristics</th>
<th>F-1 activated alumina</th>
<th>γ-alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Particle form</td>
<td>Spheres</td>
<td>Spheres</td>
</tr>
<tr>
<td>2.</td>
<td>Particle size, mm</td>
<td>0.5-1</td>
<td>0.8-1.5</td>
</tr>
<tr>
<td>3.</td>
<td>Water adsorption capacity by wt.,</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>at 30°C, 60% R.H.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Surface area, m²/gm (min.)</td>
<td>300</td>
<td>130</td>
</tr>
<tr>
<td>5.</td>
<td>Bulk density, gm/cc</td>
<td>0.85</td>
<td>0.9</td>
</tr>
<tr>
<td>6.</td>
<td>Loss on ignition (250 – 1100°C)</td>
<td>6.5</td>
<td>8.5</td>
</tr>
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</table>

Chemical Analysis

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃ Min. %</th>
<th>92.0</th>
<th>92.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.</td>
<td>Fe₂O₃ Max. %</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>9.</td>
<td>SiO₂ Max. %</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>10.</td>
<td>Na₂O Max. %</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>
5.1.2. Equipment

1. NEOLAB rotary shaker, OS261-A.
2. Orion Ion Analyser EA 940 for measurement of Fluoride.

5.1.3. Procedure

5.1.3.1. Test procedure

It is the purpose of this research to study the effects of important adsorption controlling factors such as pH and the ratio of adsorbate (fluoride ion) to adsorbent on the rate of fluoride removal are systematically studied. The kinetic effects and adsorption equilibria using agitated non-flow systems and continuous flow system are also investigated. The Kinetic studies include investigations of rate at which removal process occur under varying conditions of adsorbate, adsorbent and systematic environment of adsorptive equilibria, and of the ultimate capacities of the F-1 activated alumina and γ-alumina for fluoride.

The analysis of pH, conductivity, chlorides, alkalinity, and total hardness is done following the methods published in Standard methods for examination of water and wastewater (Standard Methods, 1998).

Fluorides have been estimated by utilizing the Ion Selective Electrode Method.

5.1.3.1.1. Procedure for Batch operations

The batch experiments are run in 1000 ml plastic reagent bottles using a NEOLAB rotary shaker. Probe kinetics had shown that the rate of adsorption is independent of stirring rate
at rotations greater than 80 rpm hence 100 rpm was maintained (Bulusu & Nashakhe, 1988). Each bottle was filled with a measured volume of test water, pre-weighed quantities of F-1 activated alumina and γ-alumina in the range 0.5-8.0 g are added and shaking commenced. The pH of the test solution is adjusted by adding 0.1 N HCl or 0.1 N NaOH. The experimental set up is shown in Fig 5.1

The samples are drawn from each reactor prior to the start and after 1 minute, 5 minutes, 10 minutes, 30 minutes, 60 minutes, 120 minutes, and 180 minutes. 10.0 ml samples were withdrawn each time and 1.0 ml of TISAB (Total Ionic strength Adjustment Buffer) is added and the fluoride measurements made using Orion Ion Analyser, calibrated every three hours using appropriate standards from 0.1, 1.0, and 10.0 depending upon the anticipated fluoride ion concentration.

The effect of pH, adsorbent dose and adsorption isotherms was investigated using F-1 activated alumina and γ-alumina.
Fig 5.1. Experimental setup for batch experiments
5.1.3.1.2. Column studies

A glass column (i.d. 16 mm, length 180 mm) is used with a feed reservoir of 1 L capacity at the top of the column. For uniform distribution of the liquid, glass beads are placed at the top of the adsorbent packing. The schematic experimental set up for the column experiments is shown in Fig. 5.2.

20 g hydrous F-1 activated alumina or γ-alumina is mixed well with distilled water and the mixture is poured into the adsorption columns. Distilled water is run through the columns to permit adjustment of the flow to 180 ml/h. The distilled water is drained from the remainder of the system and the feed solution is then introduced. The samples are taken at appropriate intervals after displacement of initial volumes of distilled water remaining in the column at the beginning of the run. In addition to “instantaneous” sampling, samples of total effluent collected in a beaker are taken at appropriate intervals of time after initiation.

5.1.4. Adsorbate

The test water reservoirs are located at a height to facilitate gravity operation. The test water is prepared from the distilled water suitably supplementing fluoride each time. Alkalinity is adjusted with laboratory grade Sodium bicarbonate. Four test water alkalinites are studied, viz. 100, 200, 400, 600, and 800 mg/L as CaCO₃.
Fig 5.2. Experimental setup for column experiments
5.1.5. Operational flow rate and limitations

The operation is terminated when the residual fluoride in the effluent reached 2mgF/L to prevent over-exhaustion of the F-1 activated alumina and γ-alumina and also to simulate the field conditions. Besides prolongation of the experiments beyond 2mgF/L to reach initial fluoride value (Co) is considered impracticable with such studies in view of the time that takes for each run to approach Co in the effluent; and hence full and Co breakthrough capacities of the F-1 activated alumina and γ- alumina as a function of the test water is not attempted experimentally.

Exhausted F-1 activated alumina and γ- alumina bed is regenerated using acid/alkali treatment. Any innovative technique that can reduce the cost of regeneration operation will contribute to making adsorption more efficient and more attractive.

Systematic studies were carried out for the critical evaluation of the application of F-1 activated alumina and γ- alumina for defluoridation of ground waters and to assess their relative merits and demerits. The results are presented and discussed in following pages.
5.2. Critical Analysis Of Data And Design Considerations

5.2.1. General characteristics of activated alumina

An understanding of the mechanisms of fluoride adsorption is important to the quantitative design of an alumina adsorption system particularly in terms of its regeneration capability.

The main component of activated alumina is aluminium oxide, which is an amphoteric compound. When this compound is mixed with an acid solution, the following surface reaction can occur:

\[(\text{Al}_2\text{O}_3)_n \text{ Al}_2\text{O}_3 + 3\text{H}_2\text{O} \leftrightarrow (\text{Al}_2\text{O}_3)_n \text{ Al} (\text{OH})_3 \] ...

\[ (1) \]

It is apparent from the preceding reaction that the product of aluminium hydroxide complex, \((\text{Al}_2\text{O}_3)_n, \text{ Al} (\text{OH})_3\) will raise the pH of the solution. On the contrary, when activated alumina is introduced into alkali solution, the surface reaction can be described as follows:

\[(\text{Al}_2\text{O}_3)_n \text{ Al}_2\text{O}_3 + 3\text{H}_2\text{O} \leftrightarrow (\text{Al}_2\text{O}_3)_n 2\text{H}_3\text{AlO}_3 \] ...

\[ (2) \]

The complex form of activated aluminium, \((\text{Al}_2\text{O}_3)_n 2\text{H}_3\text{AlO}_3\), will lower the pH of the solution. Therefore, the type of aluminium complex formed strictly depends upon the acidity and alkalinity of the solution in which the process of fluoride adsorption is to take place.

Upon hydration, hydroxide groups develop at the alumina surface. These hydroxide groups behave amphotERICALLY as shown in Fig. 5.3.
The surface acidity constants the equilibrium reaction in the adsorption process with alumina can be represented by:

\[ \text{AlO}H_2^+ = \text{AlOH} + H^+: K_{a1}^{\text{int}} \] ...........................................(3)

\[ \text{AlOH} = \text{AlO}^- + H^+: K_{a2}^{\text{int}} \] ...........................................(4)

where AlO\(\text{H}_2\)\(^+\), AlOH, \(\text{AlO}^-\) = positive, neutral, and negative surface hydroxo groups, respectively. The strength of the surface groups is expressed by the intrinsic acidity constants (\(K_{a1}^{\text{int}}\) and \(K_{a2}^{\text{int}}\)) as

\[ \{\text{AlOH}\} \{H^+\} \]

\[ K_{a1}^{\text{int}} = \frac{\{\text{AlOH}\}}{\{\text{AlO}H_2^+\}} \] ...........................................(5)

\[ \{\text{AlO}^-\} \{H^+\} \]

\[ K_{a2}^{\text{int}} = \frac{\{\text{AlO}^-\}}{\{\text{AlO}H_2^+\}} \] ...........................................(6)

the total number of surface Bronsted acid sites, \(N_t\) (or acidity capacity), can be expressed as the following summation:

\[ N_t = \{\text{AlO}H_2^+\} + \{\text{AlOH}\} + \{\text{AlO}^-\} \] ...........................................(7)
To evaluate the surface acidity constants and the acidity capacity, it is necessary to obtain the surface concentrations of the terms in Eqs.5 and 6. This can be accomplished by an alkalimetric titration technique when the surface charge is determined at any given pH value. From Eq. 5, it is seen that at pH < pH_{pc} (pH of zero point charge), \( N_t \equiv \{\text{AlOH}_2^+\} + \{\text{AlOH}\} \), and at pH > pH_{pc} (pH of zero point charge), \( N_t \equiv \{\text{AlO}^-\} + \{\text{AlOH}\} \). The quantities, \( \{\text{AlOH}_2^+\} \) and \( \{\text{AlO}^-\} \) are determined from an alkalimetric titration; i.e., \( \{\text{AlOH}_2^+\} = \sigma_+ \) and \( \{\text{AlO}^-\} = \sigma_- \), where \( \sigma_+ \) and \( \sigma_- \) are the positive and negative surface charge, respectively.

The pK_{al}^{int}, pK_{al2}^{int}, and total number of acid sites of the two adsorbents \( \gamma \)-alumina and F1-activated alumina are determined and the corresponding data is presented in Table 5.2.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Solid</th>
<th>pK_{al}^{int}</th>
<th>pK_{al2}^{int}</th>
<th>( N_t )</th>
<th>S</th>
<th>pH_{pc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>F-1 activated alumina</td>
<td>4.2</td>
<td>10.5</td>
<td>5.6</td>
<td>300</td>
<td>7.5</td>
</tr>
<tr>
<td>2.</td>
<td>( \gamma )-Al_{2}O_{3}</td>
<td>7.7</td>
<td>9.3</td>
<td>6.4</td>
<td>130</td>
<td>8.6</td>
</tr>
</tbody>
</table>

\( N_t = 10^{13} \) sites/cm²

\( S = m^2/g \)
5.2.2. Effect Of Operational Conditions On The Removal Of Fluoride Using Different Types Of Alumina

The effect of pH, the dosage of adsorbent, and the rate of uptake of the fluoride i.e., kinetic effects of the concentration, are studied by both batch studies and column studies. In regeneration studies, the data from batch studies are utilized to study the effect of different solutions on regeneration using column technique and column regeneration studies were conducted. These studies are verified with the ground water samples procured from nalgonda, Andhra Pradesh, which is the most severely-affected region by fluorosis in the state. Detailed analysis of this data is presented in the following pages.

5.2.3. Batch studies

5.2.3.1. Effect of contact time

In Fig. 5.4 and 5.5 are shown plots of typical data on the removal of fluoride by F-1 activated alumina and γ- alumina at various pH’s as a function of time for an initial concentration of 5 ppm. The data are presented in the Table 5.3.

It is evident from the data that the relatively rapid initial rate of removal takes place within 30 min and the system approaches equilibrium in 180 minutes of contact between solution and the adsorbent. Preliminary investigations showed that the removal beyond 180 minutes and up to 1200 minutes was almost insignificant and hence in all studies, 180 minutes was considered as practical time to attain near equilibrium conditions, while for practical fluoride removal operations 30 min contact time is recommended.
Fig. 5.4 Rate of uptake of fluoride at different pH values, at $\sigma = 0.000625$ mg/mg and initial fluoride 5 ppm by F-1 activated alumina.

Fig. 5.5 Rate of uptake of fluoride at different pH values, at $\sigma = 0.000625$ mg/mg and initial fluoride 5 ppm by $\gamma$-alumina.
Table 5.3: Effect of contact time and pH on the removal of fluoride by F-1 activated alumina and γ-alumina at $\sigma = 0.000625$ mg/mg at an initial conc. of 5 ppm

<table>
<thead>
<tr>
<th>S. No</th>
<th>Parameter</th>
<th>pH 3.00</th>
<th>pH 4.00</th>
<th>pH 5.00</th>
<th>pH 6.00</th>
<th>pH 7.00</th>
<th>pH 9.00</th>
<th>pH 11.00</th>
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<tr>
<td></td>
<td></td>
<td>F-1</td>
<td>F-1</td>
<td>F-1</td>
<td>F-1</td>
<td>F-1</td>
<td>F-1</td>
<td>F-1</td>
</tr>
<tr>
<td>1</td>
<td>A</td>
<td>2.82</td>
<td>4.02</td>
<td>2.43</td>
<td>3.8</td>
<td>1.76</td>
<td>3.19</td>
<td>2.56</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>43.7</td>
<td>19.6</td>
<td>51.4</td>
<td>25</td>
<td>64.8</td>
<td>36.2</td>
<td>48.8</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.27</td>
<td>0.12</td>
<td>0.32</td>
<td>0.2</td>
<td>0.41</td>
<td>0.23</td>
<td>0.31</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>1.93</td>
<td>3.01</td>
<td>1.4</td>
<td>2.7</td>
<td>0.87</td>
<td>2.43</td>
<td>1.63</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>61.5</td>
<td>39.8</td>
<td>72</td>
<td>46</td>
<td>82.6</td>
<td>51.5</td>
<td>67.4</td>
</tr>
<tr>
<td></td>
<td>C</td>
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<td>0.25</td>
<td>0.45</td>
<td>0.3</td>
<td>0.52</td>
<td>0.32</td>
<td>0.42</td>
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<tr>
<td>3</td>
<td>A</td>
<td>1.68</td>
<td>2.74</td>
<td>1.17</td>
<td>2.5</td>
<td>0.62</td>
<td>2.22</td>
<td>1.37</td>
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<tr>
<td></td>
<td>B</td>
<td>66.4</td>
<td>45.2</td>
<td>76.6</td>
<td>50</td>
<td>87.6</td>
<td>55.6</td>
<td>72.6</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.42</td>
<td>0.28</td>
<td>0.48</td>
<td>0.3</td>
<td>0.55</td>
<td>0.35</td>
<td>0.45</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>1.42</td>
<td>2.54</td>
<td>1.01</td>
<td>2.2</td>
<td>0.51</td>
<td>2.01</td>
<td>1.16</td>
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<tr>
<td></td>
<td>B</td>
<td>70.4</td>
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<td>90</td>
<td>60</td>
<td>76.8</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.44</td>
<td>0.31</td>
<td>0.5</td>
<td>0.4</td>
<td>0.56</td>
<td>0.37</td>
<td>0.48</td>
</tr>
<tr>
<td>5</td>
<td>A</td>
<td>1.35</td>
<td>2.43</td>
<td>0.81</td>
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<td>0.4</td>
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<td>0.96</td>
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<tr>
<td></td>
<td>B</td>
<td>74</td>
<td>51</td>
<td>85</td>
<td>60</td>
<td>91</td>
<td>62.8</td>
<td>80.8</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.46</td>
<td>0.32</td>
<td>0.53</td>
<td>0.4</td>
<td>0.6</td>
<td>0.4</td>
<td>0.51</td>
</tr>
<tr>
<td>6</td>
<td>A</td>
<td>1.24</td>
<td>2.32</td>
<td>0.75</td>
<td>1.86</td>
<td>0.4</td>
<td>1.7</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>75</td>
<td>54</td>
<td>85</td>
<td>62.8</td>
<td>93</td>
<td>67</td>
<td>82.4</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.47</td>
<td>0.34</td>
<td>0.53</td>
<td>0.39</td>
<td>0.6</td>
<td>0.4</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Note: $\sigma =$ initial fluoride conc./dosage of adsorbent added, mg/mg
A = fluoride in equilibrium, mg/l
B = % removal of fluoride
C = mg F removed/mg of adsorbent x 10^2
F-1 = F-1 activated alumina and $\gamma =$ γ-alumina
5.2.3.2. Effect of pH and Surface loading

As per the surface characteristics of alumina and defluoridation mechanism discussed later the efficiency of defluoridation by the adsorbent is expected to vary with pH and surface loading, the ratio (σ) of fluoride concentration (F₀) to activated alumina dose (X₀) or \( \sigma = \frac{F_0}{X_0} \), the author has critically analyzed the data of the adsorption of fluoride by F-1 activated alumina and γ-alumina under different conditions.

The residual fluoride concentration under different pH values and contact times at the surface loading of \( \sigma = 0.000625 \text{ mg/mg} \) has been systematically studied and the corresponding data are presented in Table 5.2. These data indicate that the residual fluoride concentration varies as a function of both pH and contact time, and maximum removal can be achieved at pH 5 with a contact time of 30 min. At pH 5, 88% and 56% of the initial fluoride concentration is removed within 30 min by F-1 activated alumina and γ-alumina respectively.

5.2.3.2.1. Effect of pH on rate of reaction

The rate of reaction of adsorption process under different pH conditions is also examined assuming the following first order equation for the fluoride removal

\[
\frac{-dF}{dt} = k(F) \hspace{1cm} (12)
\]
in which \( \frac{dF}{dt} \) = rate of change in fluoride concentration in solution, in milligrams per liter; \( k \) = reaction rate constant per hour; \( F \) = fluoride concentration remaining in solution, in milligrams per liter; and \( t \) = time, in hours.

The rate constants \( (K) \) obtained by Eq (12) under same conditions with different pH values (Fig. 5.6 and 5.7) after a contact time of 180 min indicate that the adsorption rate varies with pH. For F-1 activated alumina the adsorption rate constant increased from pH 3 onwards, reached maximum of 0.87/hr at pH 5, and reached lowest 0.19/hr at pH 11.0.

![Graph showing fluoride adsorption rate constant as function of pH.](image)

Fig 5.6 Fluoride adsorption rate constant as function of pH, at \( \sigma = 0.000625 \) mg/mg and initial fluoride 5 ppm by F-1 activated alumina.

For \( \gamma \)-activated alumina the adsorption rate constant increased from pH 3 onwards, reached maximum of 0.36/hr at pH 5, and reached lowest 0.10/hr at pH 11.0.
Fig 5.7 Fluoride adsorption rate constant as function of pH, at $\sigma = 0.000625$ mg/mg and initial fluoride 5 ppm by $\gamma$-alumina

5.2.3.3. Effect of alkalinity

The effect of alkalinity on removal of fluoride is shown in Fig 5.8 and 5.9. As can be observed, the fluoride removal capacity of the adsorbents decreased with an increase in alkalinity. Due to higher affinity of hydroxyl ions to the aluminium oxide compared to fluoride ions in waters with higher alkalinity, the hydroxyl ions occupy the active adsorption sites on the aluminium oxide and prevent adsorption of fluoride due to which adsorption of fluoride may be decreasing with increase in alkalinity.
Fig. 5.8 Residual fluoride concentration versus contact time at various alcalinities and for initial conc. of 5 ppm by F-1 activated alumina.

Fig. 5.9 Residual fluoride concentration versus contact time at various alcalinities and for initial conc. of 5 ppm by γ-alumina.

5.2.3.4. Concentration Ratio (σ) Effect

In addition to pH, the value of σ is likely to affect the extent of fluoride removal. The effect of changing the σ values on the removal efficiency of F-1 activated alumina and γ-alumina at the optimum pH is critically analyzed at an initial fluoride concentration $C_0$ of 5 mg/l and 10 mg/l at 0.5 g/l, 1.0 g/l, 2.0 g/l, 4.0 g/l, and 8.0 g/l dosages of F-1 activated alumina and γ-alumina.
Plots are drawn for residual fluoride concentration versus time curves at different $\sigma$ values, are presented in Fig. 5.10 to 5.13. It can be derived from the graphs that the effectiveness of fluoride removal is dramatically affected by the value of $\sigma$, and by decreasing $\sigma$ values, i.e., increasing F-1 activated alumina/ $\gamma$-alumina dose will help in the removal of higher amounts of fluoride. In Fig. 5.9, for instance, for an initial concentration of 5 ppm the removal of fluoride increases from 34% to 90% after a 30 min contact time as the value of $\sigma$ decreases from 0.0100 mg/mg-0.000625 mg/mg for F-1 activated alumina, and, as shown in Fig 5.10, from 20%-56% after 30 min contact time for $\gamma$-alumina.

Experiments using an initial fluoride concentration of 10 mg/l are shown in Fig. 5.12 and 5.13. The investigations with higher initial fluoride concentration indicate that F-1 activated alumina is capable of effectively removing fluoride ion from a liquid phase, but its efficiency is dependent upon the ratio of the initial fluoride ion concentration to the activated alumina dose or $\sigma$.

![Diagram](image)

Fig. 5.10 Residual fluoride concentration versus contact time at pH 5 and various $\sigma$ values for initial conc. of 5 ppm by F-1 activated alumina.
Fig. 5.11 Residual fluoride concentration versus contact time at pH 5 and various $\sigma$ values for initial conc. of 5 ppm by $\gamma$-alumina.

Fig. 5.12 Residual fluoride concentration versus contact time at pH 5 and various $\sigma$ values for initial conc. of 10 ppm by F-1 activated alumina.
Fig. 5.13 Residual fluoride concentration versus contact time at pH 5 and various σ values for initial conc. of 10 ppm by γ-alumina.

In Fig. 5.14 and 5.15 the residual fluoride concentration at different σ values are plotted. It can be seen from the figures that the residual fluoride concentration decreases with decreasing σ value, i.e., % removal increases with decreasing surface loading and it reaches a maximum at a particular surface loading i.e., σx value (0.0025 mg/mg for 5 ppm whereas for is 0.005 mg/mg for 10 ppm initial concentration for both F-1 activated alumina and γ-alumina. Further, it is also observed that change in residual fluoride concentration or change in the % fluoride removal will be insignificant after the surface loading σ exceeds σx value for that system. This σx determines the effective fluoride removal zone. When the operational surface loading is greater than the specific σx value of that system, the removal of fluoride by the adsorption process becomes very difficult, while the removal of fluoride with activated alumina proceeds rapidly as the σ is less than specific loading value (σx) which has to be taken into consideration in the reactor loading.
Fig. 5.14 Residual fluoride concentration at different $\sigma$ values and pH 5 for F-1 activated alumina.

Fig. 5.15 Residual fluoride concentration at different $\sigma$ values and pH 5 for $\gamma$-alumina.
Similarly, the kinetic constants are also plotted in Fig 5.16 for different \( \sigma \) values, it is observed that the reaction rate increases with decreasing \( \sigma \) value and the change in rate constant will be insignificant after the \( \sigma \) exceeds the \( \sigma_k \) value.

![Graph](image)

Fig. 5.16 Fluoride adsorption rate constant as function of \( \sigma \) for F-1 activated alumina/\( \gamma \)-alumina at 5.0 ppm

### 5.2.3.5. Adsorption models

By way of concise description, AA is a porous light material with a surface comprised largely of active sites, which compete with various solutes (Bulusu and Nawlakhe, 1988). Because the sites at or near the exterior of AA are most readily available for competition with solvent and other solutes other than fluoride, rapid initial adsorption occurs thereon. Several types of isothermal adsorption relations may occur. The most common relationship, between (q) the amount of solute adsorbed per unit weight of solid adsorbent and (C) the concentration of solute remaining in solution at equilibrium, obtains for systems in which adsorption from solution leads to the deposition of an apparent single layer of solute molecules on the surface of the solid. Occasionally, multimolecular layers of solute may be adsorbed.
In order to understand the adsorption of fluoride on activated alumina, two models commonly employed for adsorption study were chosen. The models are presented herein in both the standard form and the linearized form:

Langmuir isotherm: 
$$q_e = \frac{Q^0 b F_e}{1+bF_e}$$ 

or 
$$\frac{1}{q_e} = \frac{1}{Q^0 b} + \frac{1}{F_e}$$ ...

(16)

Freundlich Isotherm: 
$$q_e = K F_e^n$$ or 
$$\log q_e = \log K + n \log F_e$$ ...

(17)

in which $q_e$ = concentration of fluoride ion adsorbed per unit weight of activated alumina, in milligrams per gram; $F_e$ = concentration of fluoride ion in solution at equilibrium condition, in milligrams per liter; $Q^0$ = maximum concentration of fluoride ion adsorbed per unit weight of activated alumina solids in forming complex monolayer on the surface of activated alumina, in milligrams per gram; and $K$, $b$, and $n$ = constants. A plot of the left-hand term of Eq. 16 against $1/F_e$ or of the left-hand term of Eq. 17 against $\log F_e$, gives a straight line of slope $1/(Q^0 b)$ and intercept $1/Q^0$ for data which agree with the Langmuir model, and give a slope $(1/n)$ and intercept $\log K$ for data which accord with the Freundlich model.
Fig 5.17. Data according to Langmuir isotherm for F-1 activated alumina at initial conc.=5 ppm, pH=5.0

Fig 5.18. Data according to Langmuir isotherm for γ-alumina at initial conc.=5 ppm, pH=5.0

Fig 5.19. Data according to Freundlich isotherm for F-1 activated alumina at initial conc.=5 ppm, pH=5.0
Fig 5.20. Data according to Freundlich isotherm for γ-alumina at initial conc.=5 ppm, pH=5.0

The straight relationship between log \(1/q_e\) and log \(1/C_e\) or log \(q_e\) and log \(C_e\) are depicted in Figs 5.17 to 5.20, respectively. These figures clearly show that the data fit the Langmuir adsorption model better than the Freundlich adsorption model. This indicates that adsorption of fluoride ion by these adsorbents is a single-layer adsorption process and its maximum adsorption capacity is equal to 4.34 mg/g, according to Fig. 5.17 for F-1 activated alumina, and according to Fig. 5.17 the γ-alumina gave a negative value indicating very little adsorption. The Freundlich constants \(K\) and \(1/n\) are 1.191 mg/g and 0.8009 l/g for F-1 activated alumina. Since the value of the constant, \(1/n\) (adsorption intensity) is less than unity, it indicates a favorable adsorption (Ghorai and Pant, 2004). Whereas for the γ-alumina the \(K\) and \(1/n\) values are 0.11 mg/g and 2.286 l/g, since the value of \(1/n\) is greater than unity the adsorption process is unfavorable for the adsorbent. However, adsorption isotherms are equilibrium tests and thus do not indicate the actual performance of the F-1 activated alumina and γ-alumina.
Column operations are essential for industrial scale designing of the technical systems. The objective of the column experiments was to study the effect of process parameters such as raw water, inlet flow rate, initial fluoride concentration, and bed height at various throughput volumes. Runs were made at different flow rates and at various initial concentrations to study the change in the uptake capacity of fluoride. Samples of the outlet bulk solution were collected at a fixed time interval and examined for the fluoride concentration.

Column type continuous flow separations have distinct advantage over batch type operation because rate of adsorption depends on the concentration of solute in the solution to be treated. For column operations, the adsorbent F-1 activated alumina and γ-alumina is continuously in contact with a fresh solution. Consequently, the concentration in the solution in contact with a given layer of F-1 activated alumina and γ-alumina in a column is relatively constant.

5.2.4.1. Analysis of experimental data

5.2.4.1.1. Breakthrough curve

A plot of exit concentration as a function of lapse time or volume throughput reacted is known as breakthrough curve. 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.

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 total quantity sorbed in the column for a given feed concentration is equal to the area under the breakthrough curve obtained from the plot of adsorbed concentration versus effluent volume. 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 breakpoint. In the present study, the shape of the breakthrough curves at various flow rates as shown in Fig 5.21 and 5.22 indicate that adsorption is mainly mass transfer controlling.

5.2.4.2. Effect of flow rate

The effect of flow rate is studied at 3 and 5 ml/min while the inlet fluoride concentration is kept constant at 5 mg/l for both the experiments. Initially the adsorption is 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, \( \frac{C_t}{C_0} \) against volume throughput is shown in Fig. 5.21 and 5.22 for two different flow rates 3, and 5 ml/min. The maximum fluoride removal for these two flow rates is found to be at 3 ml/min hence further experiments are carried out at this flow rate.

![Breakthrough curves](image)

Fig. 5.21 Breakthrough curves for two different flow rates at \( C_0 = 5 \) ppm for F-1 activated alumina
Fig. 5.22 Breakthrough curves for two different flow rates at $C_0 = 5$ ppm for $\gamma$-alumina

5.2.4.3. Effect of initial fluoride concentration

Removal of fluoride with respect to volume of flow past the column at different initial concentrations of 5.0 and 10.0 mg/l for various regeneration cycles is shown in Fig. 5.23 and 5.24. Fluoride adsorbed by AA in the packed column depends on the volume of flow passed. The effluent volume shows whether fluoride uptake by AA is subjected to saturation limits. Sharper breakthrough curves were obtained with AA at 5 mg/l of inlet fluoride concentration and at all flow rates. At lower flow rate relatively higher uptake is observed for adsorption at the beginning of operation due to the magnitude of the concentration driving force. As solution continues to flow, the concentration of fluoride in the effluent rapidly increases. Finally, the bed becomes saturated with fluoride and the concentration of solute in the effluent rises to the inlet fluoride concentration.
Fig. 5.23 Breakthrough curves for different initial fluoride concentration, 5 ppm and 10 ppm for F-1 activated alumina.

Fig. 5.24 Breakthrough curves for different initial fluoride concentration, 5 ppm and 10 ppm for γ-alumina.
5.2.4.4. Effect of bed height

To study the effect of bed height on fluoride removal sorbent dose, 10, and 20 g is placed in the column. Fluoride spiked distilled water (Co = 5 mg/l) is passed through the column. As can be seen from Fig. 5.25 and 5.26, an increase in the bed height from 5 to 10 cm for corresponding F-1 AA doses of 10 and 20 g, respectively, the breakthrough curve becomes gentler. Thus, it is recommended to operate the unit at a minimum contact of 5 min when the bed depth is 10 cm.

Fig. 5.25 Breakthrough curves for two different bed heights at Co = 5 ppm for F-1 activated alumina
Fig. 5.26 Breakthrough curves for two different bed heights at for $C_0 = 5$ ppm for $\gamma$-alumina

5.2.4.5. Effect of pH

For both F-1 activated alumina and $\gamma$-alumina, a notable difference exists between the $C_t/C_0$ values at the highest pH (8.0 ± 0.1) and lowest pH (3.0 ± 0.1) values tested. The $C_t/C_0$ values for F-1 activated alumina are lower than for $\gamma$ alumina at any given pH and time indicating a higher removal by F-1 activated alumina. As can be observed from the Fig 5.27 to 5.32 for both F-1 activated alumina and $\gamma$-alumina maximum removal is obtained at pH 5.0 as observed in batch studies.

The fluoride removal capacity of F-1 activated alumina at pH 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0 is 2160, 2520, 3060, 2610, 2070, and 1890 mg F/Kg respectively. The fluoride removal capacity of $\gamma$-alumina at pH 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0 is 1710, 1530, 1350, 1170, and 1080 mg F/Kg respectively. As can be observed from these values maximum efficiency is obtained at
pH 5.0 as observed in batch studies previously. From these values it can be observed that the removal capacity of F-1 activated alumina is higher than \( \gamma \)-alumina at all pH values.

In order to achieve increased capacities, it is necessary to destroy the naturally occurring alkalinites to obtain values below 10 mg/l or pH around 6 through acidification of natural water.

![Breakthrough curves](image)

Fig. 5.27 Breakthrough curves for a pH of 3.0 at \( C_0 = 5 \) ppm for F-1 activated alumina and \( \gamma \)-alumina
Fig. 5.28 Breakthrough curves for a pH of 4.0 at \( C_0 = 5 \) ppm for F-1 activated alumina and \( \gamma \)-alumina

Fig. 5.29 Breakthrough curves for a pH of 5.0 at \( C_0 = 5 \) ppm for F-1 activated alumina and \( \gamma \)-alumina
Fig. 5.30 Breakthrough curves for a pH of 6.0 at $C_0 = 5$ ppm for F-1 activated alumina and $\gamma$-alumina.

Fig. 5.31 Breakthrough curves for a pH of 7.0 at $C_0 = 5$ ppm for F-1 activated alumina and $\gamma$-alumina.
5.2.4.6. Effect of alkalinity on removal of fluoride

In Fig.5.33 to 5.37, the removal of fluoride by F-1 activated alumina and γ-alumina at various alkalinitities is compared. The removal of the fluoride decreased with increased alkalinity. Thus, the fluoride removal capacity of F-1 activated alumina at 100 mg/l, 200 mg/l, 400 mg/l, 600 mg/l, and 800 mg/l as CaCO₃, is 1710, 1530, 1350, 1170, and 1080 mgF/Kg respectively, showing a 17%, 26%, 35%, 43% and 48% decrease in its removal capacity compared to its removal capacity at pH 7.0.

Whereas γ-alumina showed a fluoride removal capacity of 270, 180 and 90 mgF/Kg at 100, 200 and 400 mg/l alkalinity respectively, showing a 50%, 70% and 84% decrease in its
removal capacity compared to its removal capacity at pH 7.0. At alkalinity above 400 mg/l, the γ-alumina did not remove any fluoride.

Due to higher affinity of hydroxyl ions to the aluminium oxide compared to fluoride ions, these ions occupy the active adsorption sites on the aluminium oxide and prevent adsorption of fluoride. Hence, the adsorption of fluoride decreases with increase in alkalinity.

Fig. 5.33 Breakthrough curves for an alkalinity of 100 mg/l at Co= 5 ppm for F-1 activated alumina and γ-alumina
Fig. 5.34 Breakthrough curves for an alkalinity of 200 mg/l at $C_0 = 5$ ppm for F-1 activated alumina and $\gamma$-alumina.

Fig. 5.35 Breakthrough curves for an alkalinity of 400 mg/l at $C_0 = 5$ ppm for F-1 activated alumina and $\gamma$-alumina.
Fig. 5.36 Breakthrough curve for an alkalinity of 600 mg/l at $C_0=5$ ppm for F-1 activated alumina.

Fig. 5.37 Breakthrough curve for an alkalinity of 800 mg/l at $C_0=5$ ppm for F-1 activated alumina.
5.2.5. Regeneration Studies

Batch studies are utilized to find the most effective regenerating solution.

5.2.5.1. Batch regeneration studies

Experiments on removal of fluoride from used F-1 activated alumina and γ-alumina are conducted using distilled water, 1 N HCl, 1 N NaOH, 1 % Alum Fig 5.32 to 5.35. As can be observed from Fig. 5.38 and 5.41. A higher percentage of removal of fluoride is obtained with sodium hydroxide with 1 gm of adsorbent each.

![Graph showing fluoride in equilibrium vs. time with lines for F-1 AA and Alumina](image)

Fig 5.38. Removal of Fluoride from used F-1 activated alumina and γ-alumina using Distilled Water (dosage 1gm)
Fig. 5.39. Removal of Fluoride from used F-1 activated alumina and γ-alumina using 1 N HCl (dosage 1 gm)

Fig. 5.40. Removal of Fluoride from used F-1 activated alumina and γ-alumina using 1N NaOH (dosage 1 gm)
The order of removal of fluoride from used F-1 activated alumina and γ-alumina adsorbent using different reagents followed the following order: NaOH > Distilled water > 1% Alum > HCl.

Further experiments were conducted using sodium hydroxide at 1 gm of the adsorbents and at various normality's of sodium hydroxide. The removal of fluoride using 1 N NaOH, 0.5 N NaOH, 0.25 N NaOH by adding 1.0 g of F-1 activated alumina and γ-alumina are shown in Fig 5.42 to Fig 5.44. Highest removal of fluoride was observed at 0.5 N NaOH for both F-1 activated alumina and γ-alumina.
Fig. 5.42. Removal of Fluoride from used F-1 activated alumina and γ-alumina using 1N NaOH (dosage 1.0 gm)

Fig. 5.43. Removal of Fluoride from used F-1 activated alumina and γ-alumina using 0.5 N NaOH (dosage 1 gm)
Further regeneration studies were conducted with 0.5 N NaOH. After regeneration with sodium hydroxide, the adsorbent had a pH of 11.0-12.0; hence, the adsorbent pH was brought down to pH 7.0 by using 0.1 N HCl.

The following reaction may take place in regeneration/reactivation cycle:

\[
\text{AlF (S)} + \text{OH}^- \rightarrow \text{AlOH (S)} + \text{F} \\
\text{AlOH (S)} + \text{H}_2\text{SO}_4 \rightarrow \text{AlHSO}_4 + \text{HOH}
\]

Al represents alumina surface.

5.2.5.2. Column Regeneration studies

In column studies the removal efficiency of F-1 activated alumina and γ-alumina at neutral pH (7.0) was tested for several runs each time regenerating with 0.5N NaOH and neutralizing with 0.1 N H\textsubscript{2}SO\textsubscript{4}. 0.5N NaOH is run through the column till a 0.2 mgF/l is obtained and then
neutralized by running 0.1 N H$_2$SO$_4$, till pH 7.0 is attained and then washed with distilled water followed by drying in the oven for 3 h.

In regeneration studies, as shown in Fig. 5.45, the uptake capacity of F-1 activated alumina was same even after 3 regeneration cycles, after the 3$^{rd}$ regeneration cycle 5% loss in fluoride removal capacity was observed. For $\gamma$-alumina, the fluoride removal capacity decreased tremendously after the first regeneration, showing a loss of 45% and after 2$^{nd}$ regeneration, a loss of 70%, and during the 3$^{rd}$ run it lost its mechanical strength, became powdery, and blocked the column.

![Graph](image)

Fig. 5.45. Removal of Fluoride using F-1 activated alumina and $\gamma$-alumina (4$^{th}$ run)

For F-1 activated alumina used in column studies the regeneration with 0.5 NaOH took 5-6 hrs to attain 0.2mg/L fluoride in all the five runs as shown in Fig. 5.46.

For $\gamma$-alumina used in column studies the regeneration with 0.5N NaOH took 6 hrs to attain 0.2mg/L fluoride in all the three runs as shown in Fig. 5.47.
Fig 5.46. Removal of Fluoride using 0.5N NaOH from used F-1 Activated Alumina

Fig 5.47. Removal of Fluoride from used γ-alumina using 0.5N NaOH

The γ-alumina mechanical strength is less compared to F-1 activated alumina due to which it is losing its spherical shape and is becoming powder.

5.2.6. Studies with nalgonda sample

Studies are conducted with samples brought from nalgonda where the fluorosis problem is very severe. The samples have 4.31 ppm of fluoride. As shown in Fig 5.48 the F-1 activated alumina
removed 1780 mgF/kg in the first run, 2nd and 3rd run. The γ-alumina removed only 458 mgF/kg and after the second run its fluoride removal capacity is exhausted this might be due the presence of interfering ions. F-1 activated alumina has a very good potential for removal of fluoride even from field samples.

![Graph](image)

Fig 5.48. Breakthrough curve for nalgonda sample using F-1 activated alumina and γ-alumina -

1st run

The characteristics of influent and effluent nalgonda sample were checked the change in characteristics of the sample is negligible before and after passing through the column as is seen in Table 5.4. During the study it is observed that when the sample pH is adjusted to 6.0 the removal of fluoride from the nalgonda sample by F-1 activated alumina was comparable to the removal capacity achieved when synthetic fluoride sample is passed through the adsorbent column.
Table 5.4. Influent and effluent characteristics of nalgonda water samples

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameters</th>
<th>Influent value</th>
<th>Effluent value F-1 activated alumina</th>
<th>γ-alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>pH</td>
<td>7.29</td>
<td>8.34</td>
<td>7.68</td>
</tr>
<tr>
<td>2.</td>
<td>Conductivity, ms/cm</td>
<td>0.3</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>3.</td>
<td>Alkalinity, mg/l as caco₃</td>
<td>200</td>
<td>176</td>
<td>126</td>
</tr>
<tr>
<td>4.</td>
<td>Total Hardness, mg/l as caco₃</td>
<td>80</td>
<td>78</td>
<td>65</td>
</tr>
<tr>
<td>5.</td>
<td>Chlorides mg/l</td>
<td>14.99</td>
<td>15.36</td>
<td>13.46</td>
</tr>
<tr>
<td>6.</td>
<td>Fluoride, mg/l</td>
<td>4.31</td>
<td>1.0 (3ml/min)</td>
<td>1.0 (3ml/min)</td>
</tr>
</tbody>
</table>

5.2.7. Mechanism Of Fluoride Removal By Activated Alumina And Final Conclusions

Surface Complex Formation—Many mechanisms (conceptual and numerical) have been proposed to describe the adsorption of anions onto hydrous solids (Stumm et al. 1980; Huang 1981; Kingston 1981). Most of these mechanisms involve the solution of multi-variable equations derived from electrical double layer theory.

Based upon the results and the surface acidity information presented above, the adsorption of fluoride onto activated alumina can be described by the following equation:
(1) $\Delta \text{OH} + F^- = \Delta F + \text{OH}^-$; $^8K_1$ (at pH$>$7) ..................................... (13)

This equation implies that OH$^-$ is released from the activated alumina surface into the bulk phase upon fluoride adsorption. The pH of resultant solution after carrying out the adsorption process under different experimental conditions are measured and plotted in Fig. 5.49 and 5.50 with 2 adsorbents.

![Fig. 5.49 Changes in pH upon Fluoride adsorption by F-1 activated alumina](image)

![Fig. 5.50 Changes in pH upon Fluoride adsorption by $\gamma$-activated alumina](image)
In all these cases, it is observed a marked rise in pH with increasing surface loading which may be due to the release of OH$^-$ ions during the process of fluoride adsorption. It is also observed that the extent of OH release is more pronounced at pH 6-7 while maximum fluoride removal is observed at pH 5. This suggests that different adsorption mechanism may be in operation at pH values lower than 6, which can be represented by following Eq.

\[(\text{II}) \quad \text{AlOH}_2^+ + F^- = \text{AlF} + \text{H}_2\text{O}; \quad sK_0 \text{ (at pH < 6)} \]

According to studies the calculated $p^S K_0$ values are constant over the pH range 3-5, then decrease as pH becomes greater than 5. Apparently, a change in reaction mechanisms occurs between pH 6 and 7. At lower pH values, i.e., pH 5.0 the amount of fluoride adsorbed at high initial fluoride concentration (e.g., 10 mg F/L in 1 g/L alumina) exceeded the total available surface sites, $N_t$.

In view of this in lower pH ranges < 4.0 the adsorption reaction may be polynuclear surface complex formation as per the following reaction mechanism:

\[(\text{III}) \quad \text{AlOH} + 2F^- = \text{AlF}_2^- + \text{OH}^-; \quad sK_{12} \]

As fluoro-alumino complexes, AlF$_x^{3-x}$ ($x = 1-6$) are stable in the low pH region, at high surface loading, it is possible to form polynuclear surface complexes, as per above mechanism.

However due to formation of negative fluoro complex at high surface loading at pH< 4, activated alumina will be rendered soluble by forming alumina-fluoro complexes and aluminium in water and will be toxic and the water will not be suitable for consumption. These complexes are stable in the acidic pH region and become unstable as pH increases. As a result, the role of pH in minimizing alumina-dissolution as opposed to maximizing fluoride removal
should be considered. It is suggested that alumina adsorption systems for fluoride removal should be operated at pH values where alumina-fluoro complexes are unstable. This can prevent alumina from dissolving.

The reaction between fluoride and activated alumina can be described by the formation of surface complexes £F or £F₂; depending upon the surface loading. At high surface loading polynuclear surface complexes such as £F₂ may form. The formation of the £F surface complex takes place through two independent steps, one involving the £OH with the release of OH⁻; the other involving the £OH₂⁺ without OH⁻ or H⁺ release.
5.2.8. Conclusions

5.2.8.1. Batch studies

The results of batch studies indicate that:

1. The relatively rapid initial rate of removal takes place within 30 min and the system approaches equilibrium in 180 minutes of contact between solution and the adsorbent. At pH 5, 88% and 56% of the initial fluoride concentration is removed within 30 min by F-1 activated alumina and γ-alumina respectively.

2. For F-1 activated alumina the adsorption rate constant increases from pH 3 onwards, reaches maximum of 0.87/hr at pH 5, and reaches lowest of 0.19/hr at pH 11.0. For γ-activated alumina the adsorption rate constant increases from pH 3 onwards, reached maximum of 0.36/hr at pH 5, and reached lowest of 0.10/hr at pH 11.0.

3. The optimum pH for the removal of fluoride in water occurs at pH 5.

4. At the optimum pH for fluoride removal, the rate of adsorption of fluoride ion in water is a function of the ratio of the initial fluoride concentration to the activated alumina dose (σ). For an initial concentration of 5 ppm the removal of fluoride increases from 34% to 90% after a 30 min contact time as the value of σ decreases from 0.0100 mg/mg - 0.000625 mg/mg for F-1 activated alumina, and from 20%-56% after 30 min contact time for γ-alumina.

5. The residual fluoride concentration decreases with decreasing σ value, i.e., % removal increases with decreasing surface loading and it reaches a maximum at a particular surface loading i.e., σ_s value at 0.0025 mg/mg for 5 ppm whereas the σ_s is 0.005 mg/mg for 10 ppm.
initial concentration for both F-1 activated alumina and γ-alumina. The change in residual fluoride concentration or change in the % fluoride removal will be insignificant after the surface loading $\sigma$ exceeds $\sigma_x$ value for that system and this factor has to be taken into consideration in reactor system.

6. The adsorption of fluoride by F-1 activated alumina and γ-alumina fit the Langmuir adsorption model better than the Freundlich adsorption model. This indicates that adsorption of fluoride ion by these adsorbents is a single-layer adsorption process and its maximum adsorption capacity is equal to 4.34 mg/g, the γ-alumina gave a negative value indicating less adsorption. The Freundlich constants $K$ and $1/n$ are 1.191 mg/g and 0.8009 l/g for F-1 activated alumina, indicating a favorable adsorption process. Whereas for the γ-alumina the $K$ and $1/n$ values are 0.11 mg/g and 2.286 l/g, a indicating that adsorption process is unfavorable for the adsorbent.

5.2.8.2. Column studies

1. The effect of flow rate indicates that the breakthrough curve becomes steeper when the flow rate is increased while the break point time and adsorbed ion concentration decreases. The maximum fluoride removal is obtained at 3 ml/min.

2. With an increase in the bed height from 5 to 10 cm for corresponding F-1 AA doses of 10 and 20 g, respectively, the breakthrough curve becomes gentler

3. The fluoride removal capacity is maximum at pH 5.0 for both the alumina.
4. The adsorption of fluoride is found to decrease with increase in alkalinity, which may be due to higher affinity of hydroxyl ions to the aluminium oxide compared to fluoride ions, the hydroxyl ions may occupy the active adsorption sites on the aluminium oxide and prevent adsorption of fluoride.

5. In regeneration studies a higher percentage of removal of fluoride from exhausted F-1 activated alumina and γ-alumina is obtained with 0.5 N NaOH. The order of removal of fluoride from used F-1 activated alumina and γ-alumina adsorbent using different reagents followed the following order: NaOH > Distilled water > 1% Alum > HCl.

6. The uptake capacity of F-1 activated alumina is unchanged for 3 regeneration cycles, 5% loss in fluoride removal capacity was observed in the 4th run. For γ-alumina, the fluoride removal capacity decreased tremendously after the first regeneration, showing a loss of 45% and after 2nd regeneration, a loss of 70%, and during the 3rd run it lost its mechanical strength, became powdery, and blocked the column.

7. Studies with ground water samples from nalgonda where the fluorosis problem is very severe, the F-1 activated alumina removed 1780 mgF/kg in the first run, 2nd and 3rd run. The γ-alumina removed only 458 mgF/kg and after the second run its fluoride removal capacity is exhausted this might be due the presence of interfering ions. F-1 activated alumina has a very good potential for removal of fluoride even from field samples.
8. During the study it is observed that when the sample pH is adjusted to 6.0 the removal of fluoride from the nalgonda sample by F-1 activated alumina was comparable to the removal capacity achieved when synthetic fluoride sample is passed through the adsorbent column. In order to achieve increased capacities, it is necessary to destroy the naturally occurring alkalinitities to obtain values below 10 mg/l or pH around 6 through acidification of natural water.

9. The probable mechanism of adsorption of fluorides by activated alumina at different experimental conditions is discussed.

10. From these studies it is established F-1 activated alumina with a greater surface area of 300 m²/g is found to be an efficient adsorption medium, for the removal of fluoride from ground waters. Based on systematic studies it was observed that experimental conditions like pH, alkalinity, surface loading, and zone of adsorption (σₙ), flow rate, bed height, are critical parameters in the reactor operation which have to be evaluate in reactor designing and operations. Although pH 5.0 is optimum for alumina for acquiring higher removal capacity of fluorides, the pH of the residual water after adsorption of fluoride shifts to > 7.0. In view of this it is recommended that for actual practice for effective and efficient removal of fluorides the ground waters alkalinity has to be destroyed by acidifying the untreated waters to preferably pH 5.0 with dilute H₂SO₄ as the final treated waters pH will be raised to pH > 7.0 which will be within the drinking water standard.