A comparative Study on Fluoride Removal Capacity from Drinking Water by Adsorption using Nano-sized Alumina and Zirconia Modified Alumina Prepared by Chemical Route

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Nano-sized alumina (Al₂O₃) [abbreviated as AO] and zirconia modified alumina (Al₂O₃-ZrO₂) [abbreviated as AZO] were synthesized by chemical route using Al(NO₃)₃, ZrO₂ and triethanol amine [N(C₂H₅OH)₃]. The precursor materials were calcined for 950°C for 4 hr. to obtain phase pure nano powder. The synthesized nano powders were characterized by X-ray Diffraction (XRD), Fourier Transform-Infra Red (FTIR) spectroscopy, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analyses. From XRD the average crystallite sizes were calculated using Scherrer’s formula and were found to be 10 nm and 16 nm, while from SEM the grain size was found to 0.37 µm and 0.93 µm. Fluoride removal experiments were carried out taking different concentration of fluorides, 3 mg/L, 5 mg/L, 10 mg/L and 20 mg/L of water using different adsorbent dose. The contact time of adsorption were set to be 30 mins, and 1 hr. The adsorption mechanism was also investigated throughout this study.

Keywords:
Chemical synthesis
Nano alumina
Defluoridation
Adsorption mechanism

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1- Introduction
Fluoride is the normal constituent of water samples. Geological and man-made sources are the fluoride sources in drinking water [1]. But the major source is geological one. Sometime fluoride levels in surface water exceeds 0.3 mg/L [1] such as streams flowing over granite rich fluoride minerals and various industries viz. glass & ceramic production, electroplating, semiconductor manufacturing, brick & iron works etc. also contribute to untreated fluoride rich industrial waste water in the rivers [2-4]. In the earth’s crust, fluoride mineral present in limestone, sandstone, and granite rocks [1]. Some of them are sellaite (MgF₂), fluor spar (CaF₂), cryolite (Na₃AlF₆) and fluorapatite [Ca₅(PO₄)₂Ca(F,Cl₂)]. Weathering of these minerals and fumarolic & volcanic processes increase the fluoride concentration in the ground water. In groundwater, the natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer,
the porosity and acidity of the soil and rocks, the temperature, the action of other chemical elements, and the depth of the aquifer [5].

Incidence of high fluoride ground water has been reported from 29 countries [6]. According to a recent estimate, 6 million people are seriously affected by fluorosis and another 62 million are exposed to it in India alone [7-8]. In India more than 16 states are facing acute fluorosis problems [9-12].

Fluoride is considered an essential element for animals and humans because of the role it plays in bone and dentin mineralization. Excessive fluoride exposure may cause irreversible demineralization of bone and tooth tissues, a condition known as fluorosis, and long-term damage to the brain, liver, thyroid and kidney [13-15].

The world health organization (WHO) guidelines suggest optimum level of fluoride concentration at 1 & 1.2 mg/L for warmer and cooler climates respectively. This difference is due to greater water consumption in warmer climates. But the maximum level of fluoride in drinking water is 1.5mg/L [16]. Due to high toxicity of fluoride to mankind there is an argent need to difluoride drinking water for safe drinking. Conventional methods for fluoride removal are chemical additive methods (Nalgonda process) [17], Adsorption [18], ion exchange [19], reverse osmosis [20], electro dialysis [21], Donnan dialysis [22] etc. But chemical additive methods & contact precipitation are not used in field application due to high sludge formation, alkaline pH and large dosage. Reverse osmosis, electro dialysis, Donnan dialysis are advanced large scale treatment technology and costly. Hence they are very difficult to use in less advanced regions. Adsorption is the most widely used method for the removal of fluoride from water due to simplicity and cost effectiveness [23].

Different materials, which have been used for defluoridation such as activated alumina [24], amorphous alumina [25], activated carbon [26], low-cost adsorbents such as calcite, clay charcoal, tree bark, saw dust, rice husk, ground nut husk [27-30], fly ash [31] and rare earth oxides [32]. However, the lowest limit for fluoride reduction by most of the adsorbents is greater than 2 mg/L. So they are not suitable for fluoride removal. Bulusu et al. (1979) developed a technique in which fluoride can be removed from drinking water by treatment with alkali, chlorine and aluminium sulphate or aluminium chloride or both [33]. Though this technique has been extensively used in India, but due to its high cost, alkaline pH and large dosage, it was not suitable for field application. Although activated alumina is considered to be a good adsorbent for the defluoridation of water, but it could remove fluoride from water only up to 70% at pH 7 [34]. Alum impregnated alumina shows 92% fluoride removal at pH 6.5 but after desorption study impregnation of alum on alumina is required again for regeneration of the reagent and further defluoridation [23]. Another problem is alum will dissolve in the drinking water which is not safe for consuming purpose. Liu et al prepared Al-Ce hybrid adsorbent and studied it for defluoridation. Its maximum adsorption capacity was 91.4 mg/g at 25°C that was observed at pH 6.0[35]. The potential of nano alumina for fluoride removal and was found to be 140 mg/g [36]. The fluoride removal was occurred on Al2O3/CNTs at pH 5.9-9.0. The adsorption capacity for Al2O3/CNTs was 13.5 times higher than AC-300 carbon and four times higher than that of γ-Al2O3 at equilibrium fluoride concentration of 12 mg/L. The mass of fluoride adsorption for Al2O3/CNTs at pH 6 reached 28.7 mg/g at equilibrium concentration of 50 mg/L [25].

The detailed literature survey have shown that alumina/modified alumina function as quite efficient adsorbent for the removal of Fluoride from drinking water. In this context study of adsorption of Fluoride from drinking water using nanosized alumina and zirconia modified alumina synthesized by a novel chemical technique would be of great interest in this area of research.

In this present work nanosized alumina and zirconia modified alumina were synthesized by a simple aqueous based solution method for the removal fluorinated water. Different parameters such as contact time, different fluoride concentrations, and adsorbent dose were studied.

2. Experimental Procedure

Materials

Syntheses of nano-sized alumina and zirconia modified alumina

The chemicals required are Al(NO3)3·9H2O (E. Merck India Limited, 99%), triethanolamine (TEA) (Qualigen Fine Chemicals, India) and HNO3 (S. D. Fine Chemicals, India). Required amount of Al(NO3)3·9H2O was dissolved in distilled water. Precipitation occurred due to addition of TEA. The precipitate was dissolved by adding HNO3 maintaining pH at 3-4. The clear solution of TEA complexed metal nitrate was evaporated on a hot plate at 180°C with constant stirring. Continuous heating of the solution causes foaming & puffing. The evaporation of nitrate ions
provides an in situ oxidizing environment for the conversion of the hydroxyl groups of TEA to carboxylic acids. After complete dehydration and evolution of nitrate to nitrogen dioxide a voluminous, organic based, chocolate brown fluffy powder was left i.e. precursor powder. Well ground precursor powders were calcined at 900ºC for 4 hours. White color powder was obtained after calcination.

For the preparation of nano sized zirconia modified alumina (AZO) the chemical required are Al(NO₃)₃ 9H₂O (E. Marck India Ltd. 98%), triethanolamine (TEA) (Qualigen Fine Chemicals, India) and HNO₃ (S.D. Fine Chemicals India). Zirconium hydrous oxide forms zirconium nitrate in contact with 2:1 HNO₃ solution. The aqueous solution of Al(NO₃)₃ and Zr(NO₃)₄ mixed in 1:1 ratio with appropriate amount of TEA (the total metal ion to TEA mole ratio was maintained at 1:3) heated on hot plate at a temperature 180ºC. The solution was heated until it formed fluffy black mass. Obtained black mass was then calcined for 4 hr. at a temperature 900ºC.

Fluoride solution preparation
Appropriate amount of sodium fluoride (NaF) (Merk India, CAS No. 7681-49-4) with purity 99%. was added to distilled water to prepare the standard fluoride solution i.e. 1g/L. Different concentrations were prepared by appropriate dilution from the freshly prepared standard solution.

Removal of fluoride from fluoridated water
Desired concentration of fluoride solutions were taken in plastic bottles. All experiments were done in a shaker (Paragon RPM-0249 TXT-7203) at 158 RPM. After shaking the suspension were settled and filtered through whatman-42 filter paper. A double beam UV-visible spectrophotometer (Perkin Elmer, Model: UV 240) was used for spectrophotometric determination of fluoride at 600-620 nm as a blue colored alizarin lanthanum fluoride complex. Orange solution of alizarin 3-methyl amine-N,N-diaceic acid dihydrate forms a red chelate with lanthanum(III) ion; when small quantities of fluoride are added, this red chelate yields the blue colored ternary complex, whose color intensity was proportional to the concentration of fluoride. The fluoride concentrations of the filtered solutions after adsorption were measured using spectrophotometer. At the time of analysis, 2 mL of reagent solution was added to 1 mL of fluoride solution (2:1 volume ratio). All experiments are done at room temperature (35°C).

3. Powder characterization
The synthesized nanomaterials were characterized by X-ray Diffraction (XRD) (Model PW 1710 and PW 1810, Philips Research Laboratories) using CuKα radiation. Infra-red spectra were collected using FTIR (Perkin Elmer Spectrum Version 10.400) spectrometer using KBr disks containing 1% sample. Elemental composition is determined by Energy Dispersive X-ray (EDX) analysis (Model JFM 5800 Jeol, Tokyo, Japan) in vacuum, in the specimen chamber of an EDX coupled Scanning Electron Microscope (SEM). Scanning electron micrograph is recorder using SEM.

4. Results and discussion
XRD study
X-ray diffraction study was performed for the samples calcined at 950ºC for 4 hr. The calcinations time, the duration and the heating rate were carefully monitored in order to restrict crystallite growth. The X-ray diffractogram of the samples calcined at 950ºC as shown in Fig. 1 indicated by black line for synthesized alumina (AO) was found to be monophasic [PCPDFWIN VERSION 2.02© copyright 1999 by ICDD Powder Diffraction database, File card no. 86-1410] with monoclinic structure, S.G. c2/m (12). Nano sized AO as synthesized was observed to be γ-Al₂O₃ as was evidenced by previous work [37]. The XRD pattern of zirconia modified nanosized alumina (AZO) as shown in Fig. 1 indicated by red line was found to be well matched with the earlier report [38]. In AZO, A₂O₃ was determined as γ-phase and ZrO₂ was determined as t-phase. The XRD patterns of both the compounds also confirmed the amorphousness of the crystallite. These amorphous type crystal structures were actually purposely done to get the high surface area as well as pore-volume so that adsorption process was expected to be high. The average crystallite sizes as calculated from Scherrer’s formula [39] were observed to be 10 nm and 16 nm as listed in Table 1. The lattice parameters were calculated using the following equation:

\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]

(1)

The lattice parameters calculated are listed in Tab. (2). The unit cell volume is found to be 240.38Å³ and 101.43 Å³ respectively for A₂O₃ and Al₂O₃-ZrO₂.

SEM study
The SEM images of pure nano-alumina are shown in Fig. 3 (a) and (b). The powders were well-defined as
Table 1. Diseases caused by fluoride contamination [13-15]

<table>
<thead>
<tr>
<th>Diseases</th>
<th>Fluoride concentration</th>
<th>Symptoms</th>
<th>Whom affected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dental fluorosis</td>
<td>&gt;1mg/L</td>
<td>Yellow streaks on teeth; teeth become denser, harder &amp; more brittle</td>
<td>children</td>
</tr>
<tr>
<td>Skeletal fluorosis</td>
<td>&gt;3mg/L</td>
<td>Pain in back; bone abnormalities; crippling; bones becomes denser, harder and more brittle</td>
<td>Both adults &amp; children</td>
</tr>
<tr>
<td>Non skeletal fluorosis</td>
<td>Excess intake of fluoride</td>
<td>Gastro intestinal problems; allergies; anemia; urinary tract problem</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. Lattice parameters and crystallite sizes of nanosized Al2O3 and Al2O3-ZrO2 mixed system

<table>
<thead>
<tr>
<th>Compositions</th>
<th>a value (in Å)</th>
<th>b value (in Å)</th>
<th>c value (in Å)</th>
<th>Volume (in Å³)</th>
<th>Crystallite size (in nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3</td>
<td>12.36</td>
<td>3.05</td>
<td>6.37</td>
<td>240.38</td>
<td>10</td>
</tr>
<tr>
<td>Al2O3-ZrO2</td>
<td>5.07</td>
<td>4.05</td>
<td>4.94</td>
<td>101.43</td>
<td>16</td>
</tr>
</tbody>
</table>

Figure 1. X-ray diffractograms of nano-alumina (AO) and zirconia modified alumina (AZO)
Figure 2. Scanning Electron Micrograph of nano alumina (a) and alumina-zirconia (b) calcined at 950°C for 4 h

Figure 3. FTIR spectrum of nano-alumina calcined at 950°C 4 hr.
shown in Fig. 2. Most of the particles were discrete in nature. From the SEM study it could be seen that the highest intense peak in XRD study i.e. the crystal lattice having (hkl) value (-712) and (111) aggregates in a definite direction which was also observed in this SEM micrographs for AO and AZO as shown in Fig. 2 (a) and Fig. 2 (b) respectively. The grain size of the synthesized powders were calculated using Image Tools sofware. The average size was found to be 0.37 µm and 0.93 µm respectively for AO and AZO.

**IR study**

The IR spectra of pure nano alumina (AO) are shown in Fig. 3. In IR spectra of pure nano-alumina (before adsorption), the peak at 3500 cm⁻¹ is attributed to the atmospheric water vapor. An absorption band at 1637 cm⁻¹ was also observed which is in accordance with the reported literature that alumina presents an absorption band at 1620 cm⁻¹ [40]. The peak at 1085 cm⁻¹ corresponds to the Al–O stretching vibration [41]. The stronger broadening band between 1000 cm⁻¹ and 400 cm⁻¹ was a characteristic absorption band of alumina.

**Effect of adsorbent dose and initial fluoride concentration vs time for % of fluoride removal**

The percent of removal of fluoride was investigated as a function of adsorbent dose, fluoride concentration, and contact time shown in the Table 3. The adsorbent dose taken were 0.025, 0.05, 0.1, 0.2, 0.3, 0.4, 0.6, and 0.8 g in every 100 fluorinated water solution having different fluoride concentration 3mg/L, 5 mg/L, and 20 mg/L for the contact time 30 minutes, 1 hr. as listed in Table 3.

To compare the fluoride adsorption capacity of AO and AZO, the % of fluoride removal is plotted against adsorbent dose for different fluoride containing water -contact time such as 3 mg/L -30 min, 3 mg/L -1 hr., 5 mg/L-30 min, 5 mg/L-1 hr., and 20 mg/L-1 hr. are plotted as shown in Fig. 4 (a), (b), (c), (d), and Fig. 4 (e) respectively. In the case of 3 mg/L-30 min the % of Fluoride removal did not go above 70%. For 0.8 g/100 ml adsorbent dose highest of 67.0% Fluoride removal was obtained for AZO adsorbent in case of 3 mg/L-30 min condition. Similar results were found in case of 3 mg/L-1 hr condition for both the adsorbents studied. However, for last stated condition AZO showed better results as compared to AO; for AZO 68.3%, 65.0%, and 64.6% Fluoride were found to be removed at adsorbent doses 0.4g/100 ml, 0.6 g/100 ml, and 0.8 g/100 ml respectively as listed in Tab. 3. For the concentration level 3 mg/L of Fluoride, the results were remarkably high throughout and a maximum of 98.0% of removal was observed at an adsorbent dose of 0.4 g/100 ml of AO for the contact time of 30 min only. However, at higher Fluoride concentration level, 20 mg/L AZO was found to be

### Table 3. Summary of percent of Fluoride removal, adsorbent doses, contact time on different concentration of Fluoride solution using AO and AZO as adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent dose (g/100 ml)</th>
<th>3 mg/L-30 min</th>
<th>3 mg/L-1 hr.</th>
<th>5 mg/L-30 min</th>
<th>5 mg/L-1 hr.</th>
<th>20 mg/L-1 hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AO</td>
<td>AZO</td>
<td>AO</td>
<td>AZO</td>
<td>AO</td>
</tr>
<tr>
<td>0.025</td>
<td>33.0</td>
<td>38.0</td>
<td>36.6</td>
<td>37.7</td>
<td>57.0</td>
</tr>
<tr>
<td>0.05</td>
<td>34.0</td>
<td>32.3</td>
<td>33.8</td>
<td>35.0</td>
<td>58.0</td>
</tr>
<tr>
<td>0.1</td>
<td>37.3</td>
<td>39.8</td>
<td>37.2</td>
<td>44.4</td>
<td>75.0</td>
</tr>
<tr>
<td>0.2</td>
<td>35.5</td>
<td>39.9</td>
<td>40.3</td>
<td>48.5</td>
<td>82.0</td>
</tr>
<tr>
<td>0.3</td>
<td>33.6</td>
<td>35.1</td>
<td>33.0</td>
<td>64.5</td>
<td>88.0</td>
</tr>
<tr>
<td>0.4</td>
<td>31.2</td>
<td>31.0</td>
<td>30.5</td>
<td>68.3</td>
<td>98.0</td>
</tr>
<tr>
<td>0.6</td>
<td>34.8</td>
<td>30.0</td>
<td>32.7</td>
<td>65.0</td>
<td>89.0</td>
</tr>
<tr>
<td>0.8</td>
<td>30.3</td>
<td>67.0</td>
<td>31.8</td>
<td>64.6</td>
<td>85.0</td>
</tr>
</tbody>
</table>
working well for 1 hr contact time for all the adsorbent dose studied as shown in Tab. 3. Fluoride removal capacity was found to be maximum up to a certain dose and there after started decreasing as shown in Fig. 4 (b), (d), and (e) respectively for 3mg/L, 5 mg/L and 20 mg/L.

**Effect of pH**

An important parameter is pH, which can control adsorption process of the ions and oxide surface. The effect of pH on the percentage removal of Fluoride were studied on 5 ppm and 20 ppm Fluoride solution using the adsorbent doses 0.4 g/100 ml for 30 min. and 1 hr. contact time respectively as these sets were seemed to obtain highest Fluoride removal capacity. The pH of the Fluoride containing water was adjusted using 0.01 (M) NaOH and 0.01 (M) HCl solutions.

![Figure 4. Effect of adsorbent dose vs percentage of Fluoride removal at different Fluoride concentration and different shaking time](image-url)
Probable fluoride removal mechanism –

\[ \text{AlOH}_{\text{surface}} + \text{H}^+ \rightleftharpoons \text{AlOH}_2^+ \]

\[ \text{AlOH}_2^+\text{surface} + \text{F}^- \rightleftharpoons \text{AlF}_{\text{surface}} + \text{H}_2\text{O} \]

The amount of fluoride removed decreased in the acidic pH range may be due to the formation of weak hydrofluoric acid or combined effect of both chemical and electrostatic interaction between the oxide surface and fluoride ion. Fluoride removal decreases sharply at the alkaline pH range might be due to the stronger competition with hydroxide ions on adsorbent surface even though the oxide surface is positively charged above the pH 6.5 [23].

5. Conclusion

Nano-sized \( \gamma \)-alumina along with nano-sized zirconia modified alumina were prepared successfully by a novel and easy chemical approach. The phase formation temperatures were found to be as low as 950°C for just 4h heating in static air. XRD analyses showed that \( \gamma \)- phase alumina was detected in both the samples as evidenced by previous literature [37]. Further analysis of XRD revealed that an approximate crystallite size of 10 nm and 16 nm respectively for AO and AZO were calculated using Scherrer’s formula. The IR studies also revealed the corresponding metal oxygen stretching frequencies. The scanning electron micrographs showed distinct grains with average sizes of 0.37\( \mu \)m and 0.93\( \mu \)m respectively for AO and AZO. More than 98% of Fluoride removal capacity was detected while using 0.4g/100ml of each of the adsorbent at 5 ppm of F- solution level at pH ~ 6.7 when 30 minutes shaking time was maintained. To check the effect of pH, F-solutions of different pH were taken for further studies and were found to decrease the F-removal capacity on increasing pH, especially an abrupt decrease was found after pH 7. A probable mechanism was also proposed and justified for such type of adsorption.

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References


