Chapter 5
Chapter-5

Synthesis and characterization of nano Calcium hydroxide Calcium carbonate mixture and its Applicability for Defluoridation

5.1: INTRODUCTION

There are several applications of nano materials. Most of current applications represent evolutionary developments of existing technologies. Such as, reduction in size of electronic devices etc. Nanoscience and technology help the protection of air, water, soil and ground water from pollution. Particles in nano size act as anti bacterial, anti fouling, anti dust catching[1-4].

Environmentally fluoride has received much attention on account of the fact that it is known for both beneficial and detrimental effect on health. If drinking water containing fluoride of more than 1.5 mg/L causes Fluorosis which is a bone disease mainly by intake of drinking water in which fluoride concentration exceeds 1.5 mg/L. The threshold recommended fluoride level in water by WHO is 1.5 mg/L [5], causes tenderness of bones including pain. Because, as fluorine is the most electronegative element which reacts with calcium ions of bone and tooth in body which are having highest amount of calcium ions. That means, the body attracts the maximum amount of fluoride and deposits as calcium fluorapatite crystals which causes tenderness of bones (fig-1). Some times, Dental fluorosis [Fig.2] may also occur. The maximum ill effects of fluoride water are detected in the neck, spine, knee, pelvic and shoulder joints,
which is called as skeletal fluorosis [Fig.1]. The literature indicated that many parts of India are widely effected by fluorosis [Fig.3].

Fig.1: Skeletal fluorosis [6] (fluoride and fluorosis and nalgonda web pages)
Fig. 2: Dental fluorosis

Moderate effects of Fluoridated water
Arrows point to discolored, cracked or pitted areas
Fluorosis is endemic in 19 states of India. 65 million people, including six million children, are today affected.

- Fluoride levels in India's groundwater vary from 1 mg/l to 48 mg/l. (The World Health Organization guideline for maximum permissible level of fluoride in drinking water is 1.5 mg/l.)

- A 1999 study by New Delhi-based Fluorosis Research and Rural Development Foundation has identified 59,111 problem villages with fluoride levels above 1.5 mg/l.

- A 1997 study by the Rajasthan Voluntary Health Association shows that almost 35,000 people in the state are consuming water having more than 10 mg/l of fluoride.

- A 2001 study by S L Choubisa of M L Sukhadia University in Rajasthan shows high prevalence of dental fluorosis in various districts of the state: 63.4 per cent in Bhamwara, 77.2 per cent in Dungarpur, and 72.5 per cent in Udaipur.

- A recent white paper prepared by the Gujarat government shows that 3,826 villages have fluoride levels above 1.5 mg/l.

- Out of the total 1,152 villages in Andhra Pradesh, 624 have high fluoride in the drinking water.

- In village Tilaipam of Tanur district in Madhya Pradesh, 14.4 per cent of children and adolescents below age 20 have dental mottling, and 51.2 per cent are afflicted with genu valgum (knock knees).

- Groundwater surveys in Unnao district of UP conducted by Jal Nigam (1992) and Jal Nigam (1997) have identified 500 problem villages with fluoride levels above one mg/l.

Fig. 3: Fluorosis in India [7](downtoearth web page)
Various defluoridation technologies have been developed to reduce the fluoride concentration in water viz., adsorption, ion exchange, precipitation and membrane process such as reverse osmosis [8], nanofiltration [9], electrodialysis [10], and Donnan dialysis [11], were also investigated to reduce fluoride level in water. Among the methods, adsorption technique seems to be a promising technique for fluoride removal, because of ease of operation and selectivity. The efficiency of the technique depends on the nature of adsorbents. The adsorbents like activated alumina [12], clay [13], hydroxyapatite [14], activated carbon [15], metal ion impregnated fiber [16], ion exchange resin [17], quick lime [18] and other sorbents [14, 19], nano-hydroxyapatite /chitosan [20], normal MgO [21] were successfully employed for fluoride removal. Now a days a traditional less expensive defluoridation technique used is Nalgonda technique [6].

In the Nalgonda Technique, two chemicals, alum (aluminium sulphate or kalium aluminium sulphate) and lime (calcium oxide) are added to and rapidly mixed with the fluoride contaminated water, induced by a subsequent gentle stirring, “cotton wool”-like flocs develop (aluminium hydroxides) and are subject to removal by simple settling. The main contents of the fluoride is removed along with the flocs, probably due to a combination of sorption and ion exchange with some of the produced hydroxide groups. The removal process, which is still not fully understood, has been designated as a co-precipitation [22]. In some methods, activated alumina is used. These methods cause Alzheimer’s disease due to presence of excess aluminium in water.
Among the sorbents studied so far, they are mostly expensive and technically oriented, so they are not useful to common men. The mixture of nano calcium hydroxide and calcium carbonate was found to be a better sorbent because of its low cost, availability and higher defluoridation capacity (DC) as previously reported by the authors[21,19].

5.2: Present work

In continuation of our studies, herein we present the synthesis of nano calcium hydroxide and calcium carbonate mixture adopting by coprecipitation method. In this, Calcium nitrate, sodium hydroxide, sodium fluoride and all other chemicals used were of analytical grade and used without further purification.

5.3: Methods

Synthesis of nano calcium carbonate and calcium carbonate mixture

0.2M Calcium nitrate solution is treated with 0.4 M NaOH solution until precipitate is obtained [23]. The precipitate is stirred mechanically for 30 minutes and filtered, washed with methyl alcohol 3 to 4 times and the precipitate is calcinated to 600°C for 6 hours in air by keeping it auto-regulated muffle furnace to get the mixture of nano calcium hydroxide and calcium carbonate powder, which contains traces of CaCl₂. Nano calcium hydroxide and calcium carbonate powder has been used as such, in batches.

In this batch adsorption process, sodium fluoride solution of known concentration was agitated with powder of nano calcium hydroxide and
calcium carbonate in an incubator till equilibrium is reached. The process was optimized for initial fluoride concentration (4 – 20 mg/L), dose (50mg), size of nanopowder particle (12nm-20nm), Agitation period (120 min) and temperature (303 K) of working solutions. The solution was filtered by using micro filter (whatmann 44) and the fluoride concentration in the filtrate was measured for 4 mg/L, 12 mg/L, 20 mg/L colorometrically using zirconium-alizarin-s reagent as an indicator and the exact amount of residual fluoride are ascertained by referring to the colour standards. The colour developed by the reaction between fluoride and a zirconium – dye lake can be compared visually with the known standard fluoride solutions. Awaiting period of 1 hour after addition of zirconium-alizarin-s reagent is necessary for satisfactory colour development. The visual colorimetric method requires inexpensive laboratory glassware.

it requires ultra filtration and this disadvantage outweighs its advantage of higher DC. Nano calcium hydroxide and calcium carbonate powder is used to remove fluoride from water as calcium fluoride sludge. So it was prepared and tested for its applicability as a defluoridating agent which was not studied so far. The sorbents were tested with standard fluoride solutions.

5.4: Instrumentation

Characterization of nano calcium hydroxide and calcium carbonate

The nano calcium hydroxide and calcium carbonate powder derived from combustion method has been characterized by using X-ray powder diffraction (XRD) and scanning electron microscope (SEM). The X-ray
powder diffraction pattern confirms the crystallinity and phase purity (Figures 4, 5a&5b). The scanning electron microscope (SEM) results (Figures 6&7) reveal that the combustion derived powder is an agglomeration of fine particles, the grains and grain boundaries are larger with intergranular pores. The particle size of the powder is calculated from the broadening of the XRD peak using Scherrer’s formula. The results showed that the particle sizes are in the range of 12-20 nm with a large surface area.

Powder X-ray diffraction (XRD), scanning electron microscope (SEM), Energy dispersive X-ray (EDX) were used for structural, morphological and compositional characterization of calcium hydroxide and calcium carbonate nanoparticles.

Fig.4: XRD pattern of mixture of CaCO₃, Ca(OH)₂
Fig. 5: (a) XRD pattern of calcium carbonate (12.85 nm); (b) XRD of calcium hydroxide (16.65 nm)
Fig. 6: SEM image of nano calcium Hydroxide and calcium carbonate mixture (closeup)
Fig. 7: SEM image of nano calcium Hydroxide and calcium carbonate mixture
5.5: RESULTS AND DISCUSSION

a) Effect of contact time
Table.1 illustrates the effect of DC of powder of nano calcium hydroxide and calcium carbonate as a function of contact time in the range of 1 hr–24 hrs with 4-20 mg/L as initial fluoride concentration at room temperature. The DC of all the sorbents increased linearly up to 30 min and thereafter it remained almost constant indicating the attainment of sorption equilibrium. Therefore 30 min was fixed as minimum contact time for the maximum defluoridation of the sorbent.

b) Various other parameters
We propose this low cost method to remove fluoride from water by using nano calcium hydroxide and calcium carbonate. It requires less time, less consumption of materials, and non-toxic in nature. Hardly 100 milligrams of mixture of nano calcium hydroxide and calcium carbonate is sufficient to remove fluoride from one litre of water containing 4 – 20mg/L fluoride. In this method, the various parameters [Tables.2, 3], which alter the defluoridation of water are studied. The main phenomenon involved in this method is more chemisorptions and ion exchange of fluoride ion on the nano calcium hydroxide and calcium carbonate compared to the bulk MgO substance (Rao Sudhakar, M. et al. 2004). The Traces of CaCl₂ formed also involves in defluoridation. This process gives less sludge of CaF₂ by absorbing the fluoride, so it can be filtered and removed easily. The chemical reactions involved in this process are shown below.
In this process, the OH⁻ ions increase as a result of the reaction of CaCO₃ and Ca(OH)₂ with Fluoride ion in the solution that leads to increase in pH of the solution to 11. This can be buffered to the required WHO standard drinking water pH 6.5 to 8.5 by adding 100 mg/litre of Citric acid, which is also a low cost (0.04 Indian Rupee per litre) and non-toxic chemical. It is observed that little amount of mixture of nano calcium hydroxide and calcium carbonate (50 mg/L) is sufficient for removing fluoride from water containing fluoride ion up to 20 mg/L [Tables 1, 2, 3]. But, in case of normal MgO, the amount of MgO required for removing fluoride is about high nearly of 1 gram/L [21]. Other parameters such as effect of time of contact of nano CaCO₃ and Ca(OH)₂ with water and initial weight of mixture used are studied. As seen from figure 8 and table 1, the time required to remove fluoride to acceptable level by 50 mg of nano powder is about 6 hours in case of 4 ppm solution and about 8 hours in case of both 12 and 20 ppm solutions. The pH of NaF solution increases with the increase of initial weight of mixture nano powder used for defluoridation as seen from figure 9 and table 2 is due to increase in the reaction kinetics which leads to formation more of OH⁻ ions.

The change of pH with time of contact of nanomixture with NaF solution slightly increases up to 8 hours due to the more and more defluoridation reaction and further leaving for long time nearly 16 hours,
the PH is decreased as shown in figure 10 and table 3, it could be due to the absorption of CO₂ from atmosphere.

Table 1: Change of fluoride concentration with Time when 50 mg of nanopowder was used

<table>
<thead>
<tr>
<th>Initial Fluoride Concentration</th>
<th>After 2 hours</th>
<th>After 4 hours</th>
<th>After 6 hours</th>
<th>After 8 hours</th>
<th>After 12 hours</th>
<th>After 16 hours</th>
<th>After 20 hours</th>
<th>After 24 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 mg/L</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>12 mg/L</td>
<td>1.2</td>
<td>1</td>
<td>0.8</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>20 mg/L</td>
<td>1.6</td>
<td>1.2</td>
<td>1.0</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 2: Change of PH with increase of amount of nanomixture

<table>
<thead>
<tr>
<th>Initial concentration of fluoride in solution (mg/L or ppm)</th>
<th>PH of the solution</th>
<th>Weight of the nanomixture taken for study (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>8.6</td>
<td>3</td>
</tr>
<tr>
<td>12</td>
<td>9.2</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>10.6</td>
<td>50</td>
</tr>
<tr>
<td>50</td>
<td>11.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: PH variation of the solution with time of contact with nanomixture

<table>
<thead>
<tr>
<th>Initial Concentration of Fluoride ion in solution (mg/L or ppm)</th>
<th>PH of the solution</th>
<th>Time of contact (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>11</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>10.9</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>12</td>
<td>10.9</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>6</td>
</tr>
<tr>
<td>12</td>
<td>10.9</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>8</td>
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<tr>
<td>12</td>
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<td>8</td>
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<tr>
<td>4</td>
<td>11</td>
<td>16</td>
</tr>
<tr>
<td>12</td>
<td>10.9</td>
<td>16</td>
</tr>
</tbody>
</table>
**Fig-8** the variation of concentration of fluoride ion contact of nano mixture with NaF solution at various ion concentrations of initial NaF solution.

**Fig-9** the variation of pH of the solution with weight nano Ca(OH)$_2$+CaCO$_3$ mixture.

Fluoride concentration, ppm

![Graph of Fluoride concentration](image)

Time, hours

Flouride concetration, ppm

![Graph of pH variation](image)

Weight of nano Ca(OH)$_2$+CaCO$_3$ mixture, mg

pH of the solution

- ■ 4 ppm
- ● 12 ppm
- ▲ 20 ppm
5.6: CONCLUSIONS

Defluoridation of drinking water is required to the healthy living of human being in this earth. We have synthesized a low cost and non-toxic nanopowder comprising of CaCO$_3$ and Ca (OH)$_2$. Since little amount of this nano powder (50mg) is sufficient to remove fluoride from 1 litre of drinking water to acceptable limit, (so it can be easily affordable by common man even in remote villages of India.or government can provide this nano powder and citric acid in the form of tablets). This method is most useful when compared to existing costly methods where normal MgO is used (1 g/litre).

These results were published as Defluoridation of water by nanotechnology. Water Sci.& Technol:water. Supply-WSTWS (UK).(2009).485-492, 9.5 copy enclosed at the end.
5.7 Experimental

**Synthesis of standard sodium fluoride solutions:**- 221 mgs of anhydrous NaF is dissolved in distilled water and diluted to litre.

\[1\text{ml} = 0.1\text{mg of Fluoride}\]

**Working standard solution:**- 100ml stock fluoride is diluted to 1lit with distilled water

\[1\text{ml} = 0.01\text{mg of Fluoride}\]

**A) Preparation of Zirconium Alizarin Reagent[24]:**- 300mg of zirconium chloride ortho hydrate is dissolved in 50ml double distilled water containing 1lit volumetric flask and dissolve Alizarin Red S in 50ml of double distilled water and slowly added this to Zirconyl Fluoride solution following stirring for few minutes until this solution becomes clear.

**B) Mixed acid solution** :- Dilute 100ml conc.HCl is approximately to 400ml of distilled water. Carefully 33.3ml of H$_2$SO$_4$ is added to 400ml of distilled water. Mixed the two acids after cooling carefully.

**C) Preparation of standards:**- A series of 1ml, 2ml, 3ml, 4ml of standard fluoride solutions are prepared by diluting various volumes of standard working fluoride solutions in 100ml nesslers tubes and diluted to 100ml by distilled water. Then 5ml acid zirconyl Alizarin Red is mixed thoroughly. The colour developed by the reaction between fluoride and a zirconium – dye lake can be compared visually with the known standard fluoride solutions. Awaiting period of 1 hour after addition of reagent is necessary.
for satisfactory colour development. The visual colorimetric method requires inexpensive laboratory glassware.

<table>
<thead>
<tr>
<th>Standard</th>
<th>mg. of fluoride</th>
</tr>
</thead>
<tbody>
<tr>
<td>1ml</td>
<td>0.40</td>
</tr>
<tr>
<td>2ml</td>
<td>0.80</td>
</tr>
<tr>
<td>3ml</td>
<td>1.20</td>
</tr>
<tr>
<td>4ml</td>
<td>1.6</td>
</tr>
<tr>
<td>5ml</td>
<td>2.0</td>
</tr>
</tbody>
</table>

D) Alizarine visual method

It is a colorometric method based on the reaction between the fluoride and zirconium dye lake. The reaction between fluoride and the dye resulted in the dissociation of a portion of it into a colorless complex ion $(\text{ZrF}_6^2-)$. Due to the increase in fluoride concentration the color produced becomes progressively lighter or different depending on the fluoride content. Sample and standards are adjusted same temperature in such way that the deviation between them is not more than $20^\circ$C. 100 ml clear sample or a portion diluted to 100ml and to the standards in Nessler's tubes add 5ml of Alizarine Zirconil Reagent from a volumetric pipette. Mix thoroughly. and compare samples with the colors of standards after 1hour.

E) Preparation of nanocalcium hydroxide and calcium carbonate

Co precipitation method. aqueous solution of 0.2moles of of calcium(II) nitrate is taken in 2lit.clean beaker and treated with 0.4 mole of sodium hydroxide solution until precipitate occur stirred the mixture for 1hr and filtered ,washed with methyl alcohol 3 to 4 times and then the precipitate is calcinated
F) Calcination

The precipitate is calcinated to 600°C for 6 hours in air by keeping it auto-regulated muffle furnace to get the mixture of nano calcium hydroxide and calcium carbonate powder, which contains traces of CaCl₂. Nano calcium hydroxide and calcium carbonate powder has been used as such, for further crystallization. The co precipitated agglomerates were grinded for few minutes using mortar and pestle to have very fine particles. The sizes of the particles were calculated by X-ray powder diffraction patterns and scanning electron micro graph studies [26]

\[
\text{Ca(NO}_3\text{)}_2 + 2\text{NaOH} \rightarrow \text{Ca(OH)}_2 + 2\text{NaNO}_3
\]

G) Batch study

In the batch adsorption process sodium fluoride solution of known concentration was agitated with powder of nano calcium hydroxide and calcium carbonate in an incubator till equilibrium is reached. The process was optimized for initial fluoride concentration (4 – 20 mg/L), dose (50mg), size of nanopowder particle (12nm-20nm), Agitation period (120 min) and temperature (303 K) of working solutions. The solution was filtered by using micro filter (whatman 44) and the fluoride concentration in the filtrate was measured for 4 mg/L, 12 mg/L, 20 mg/L colorometrically using zirconium- alizarin-s reagent as an indicator and the exact amount of residual fluoride are ascertained by referring to the colour standards as said in Alizarine visual method.
Calculation

Fluoride mg/ml = [ml standard which compares]/V1

Where V1 = volume of solution taken in neslers tube

V2 = the volume of standard fluoride with which it is compared
5.8 References


7. web page (http://www.downtoeart.org.in/html/20030415_map.htm)


   (2007).


   (2007).


24. D. Chandrika, Testing methodologies for Fluoride., web page