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FLUORIDE AND ENVIRONMENT- A REVIEW

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Abstract

The presence of fluoride in exceeding limits and its related problems of drinking water prevailing in many parts of India is well documented. Fluoride in drinking water is known for both beneficial and detrimental effects on health. Many solutions to these problems were also suggested. Fluoride from water or wastewater can be removed by an ion exchange/adsorption process or by a coagulation, precipitation process. The ion exchange/adsorption can be applied to either concentrated or diluted solutions and they are capable of achieving complete removal under proper conditions. The method suitable for a given situation needs to be judiciously selected considering the various aspects. The paper presents the current information on fluoride in environment and its effects on human health and available methods of defluoridation in detail.

1.0.Introduction

Water is one of the major elements essential for sustenance of all forms of life and is available in abundance in nature covering approximately three fourths of the surface of the earth. The chemical nature of water is one of the most important criteria that determines its usefulness for a specific need and as such not all the waters are fit for drinking; hence the problems of scarcity of drinking water. The presence of fluoride, in quantities in excess of limits is a serious matter of concern from a public health point of view. Like any other pollutant the fluoride pollution can also occur due to both natural and man made reasons.

Fluoride in drinking water is known for both beneficial and detrimental effects on health. The fact that the problems associated with the excess fluoride in drinking water is highly endemic and widespread in countries like India prompted many researchers to explore quite a good number of both organic and inorganic materials adopting various processes from coagulation, precipitation through adsorption, Ion exchange etc.. Some are good under certain conditions while others are good in other conditions. Leaching of Fluoride from the earth crust is the chief source of fluoride content in ground water; however the other sources like food items also add to increase the overall ingestion of fluoride into the human body. The current information on fluoride in the environment and its effects on human health, and available methods of defluoridation is presented in the following sections.

2.0.Fluoride in Environment

Fluorine (F₂) is a greenish diatomic gas. Fluorine is so highly reactive that it is never encountered in its elemental gaseous state except in some industrial processes. The fluoride occurs notably as Sellaite, fluorspar, Ca F₂; Cryolite, Na₃ Al F₆; Fluorapatite, 3Ca₃(PO₄)₂ Ca(F,Cl). Other minerals containing fluoride are given in the table 1.

Table1. Fluoride bearing minerals⁴⁶

Mineral	Chemical formula	% fluorine
Sellaite	MgF ₂	61 %
Villianmite	NaF	55 %
Fluorite (Fluorspar)	CaF ₂	49 %
Cryolite	Na ₃ AlF ₆	45 %
Bastnaesite	(Ce,Ln) (CO ₃)F	9 %
Fluorapatite	Ca ₃ (PO ₄) ₃ F	3-4 %

As fluorspar it is found in sedimentary rocks and as Cryolite in igneous rocks. These fluoride minerals are nearly insoluble in water. Hence fluorides will be present in ground water only when conditions favour their solution¹. It is also present in sea water (0.8-1.4 ppm), in mica and in many drinking water supplies.

It is evident from the information available that a certain quantity of fluorine is essential for the formation of caries-resistant dental enamel and for the normal process of mineralisation in hard tissues. The element is metabolized from both electrovalent and covalent compounds. Low fluoride concentrations stabilize the skeletal systems by increasing the size of the apatite crystals and reducing their solubility. About 95% of the fluoride in the body is deposited in hard tissues and it continues to be deposited in calcified structures even after other bone constituents (Ca, P, Mg, CO₃ and citrate) have reached a steady state. Age is an important factor in deciding to what extent fluorine is incorporated into the skeleton. The uptake almost ceases in dental enamel after the age of about 30 years.

3.0. Incidence of fluorides in river waters and ground waters in India.

Many rivers flowing through more than half a dozen states in India reported to have fluoride contents varying from 0.1 to 12.0 ppm¹. Similarly occurrence of fluoride bearing waters was reported by many in A.P.³, Rajasthan⁴, Punjab and Haryana⁵, Maharastra⁶, Tamilnadu⁷, Karnataka⁸, Madhya Pradesh⁹, Gujarat¹⁰ and Uttar Pradesh¹¹.

4.0. Effect of Fluoride ingestion in human beings

Fluorosis - a disease caused by ingestion of fluoride in excess through water, food, and air and is a serious health problem. Fluoride ingested with water goes on accumulating in bones up to age of 55 years. At high doses fluoride can interfere with carbohydrates, lipid protein, vitamin, enzyme and mineral metabolism.

1.1 Flouride Bearing Illness

Long term consumption of water containing 1 mg of fluoride per liter leads to dental fluorosis. White and yellow glistening patches on the teeth are seen which may eventually turn brown. The yellow and white, patches when turned brown present itself has horizontal streaks. The brown streaks may turn black and affect the whole tooth and may get pitted, perforated and chipped off at the final stage. Dental fluorosis not only poses cosmetic problems but has serious social problems too, in terms of matrimonial problems of the children.

4.2. Skeletal fluorosis

This has been observed in persons when water contains more than 3-6 mg/L of fluoride. Skeletal fluorosis affects young and old alike. Fluoride can also damage the foetus- if the mother consumes water and food, with a high concentration of fluoride during pregnancy/breast feeding, infant mortality due to calcification of blood vessels can also occur.

- Severe pain in the backbone
- Severe pain in the joints
- Severe pain in the hip region
- Stiffness of the backbone.
- Immobile /Stiff joints
- Increased density of bones, besides calcification of ligaments
- Construction of vertebral canal and intervertebral foramen-pressure on nerves
- Paralysis

4.3. Non-Skeletal Manifestations

This aspect of fluorosis is often over looked because of the misconception prevailing that fluoride will only affect bone and teeth. Flouride, when consumed in excess can cause several ailments besides skeletal and dental fluorosis viz.

1. Neurological Manifestations:

Nervousness, depression tingling sensation in fingers and toes, excessive thirst. Tendency to urinate frequently (polydypsia and poly urea are controlled by brain-appears to be adversely affected)

2. Muscular Manifestations

Muscle weakness, stiffness, pain in the muscle and loss of muscle power.

3. Allergic Manifestations

Very painful skin rashes, which are perivascular inflammation—present in women and children pinkish, red or bluish red spots on the skin that fade and clear up in 7- 10 days, they are round or oval shape.

4. Gastro intestinal problems

Acute abdominal pain, diarrhea, constipation, blood in stools, bloated feeling (gas) tenderness in stomach, feeling of nausea and mouth sores.

5. Head-ache

6. Loss of teeth (edentate) at an early age.

The relation between concentration of fluoride and the biological effects are summarized² in table.2.

Table.2. Concentrations of fluorides and biological effects

Concentration of fluoride, ppm*	Medium	Effect
0.002	Air	Injury to vegetation
1	Water	Dental caries reduction
2 or more	Water	Mottled enamel
8	Water	10% osteosclerosis
50	Food and water	Thyroid changes
100	Food and water	Growth retardation
120	Food and water	Kidney changes
*In water-medium, ppm can be taken as equivalent to mg/L		

5.0. Fluoride removal.

Fluoride from water or wastewater can be removed by ion exchange/adsorption process or by coagulation, precipitation process. The ion exchange/adsorption can be applied to either concentrated or diluted solutions and they are capable of achieving complete removal under proper conditions.

5.1. Precipitation methods:

Method involving the addition in sequence, of an alkali, chlorine and aluminium sulphate or aluminium chloride or both was developed¹. It is cheap and is used extensively in India.

Though lime softening accomplishes fluoride removal, its high initial cost, large dosage and alkaline pH of the treated water renders it unsuitable for field application. Large dosage and alkaline pH of the treated water renders it unsuitable for field application.

5.2. Activated alumina:

Activated alumina is a granular, highly porous material consisting essentially of aluminum trihydrate. It is widely used as a commercial desiccant and in many gas drying processes.

The studies¹², perhaps the earliest, have demonstrated the high potential of activated alumina for fluoride uptake. An initial concentration of 5 mg/L was effectively brought down to 1.4 mg/L before regeneration and to 0.5 mg/L on regeneration with 2N HCl. The bed was regenerated with a

solution of 2% Na OH, 5% NaCl, 2N HCl, 5% NaCl and 2N HCl. The removal capacity of the medium was found to be about 800 mg/L of fluoride/L of Alumina. Many modifications of process was suggested by subsequent workers, several patents based on the use of Aluminum oxide for fluoride removal were issued¹. Filter alum was used¹³ to regenerate activated alumina bed. The capacity of alumina to remove fluoride was reported to be proportional to the amount of filter alum used for regeneration up to a level of about 0.2kg of alum per litre of alumina. At this level the fluoride removal capacity was approximately 500 mg of fluoride per litre of alumina. Similar studies employing activated alumina was later conducted by many workers and all these works confirmed the ability of activated alumina for higher uptake of fluoride from water. Some researchers have concluded that removal was the result of ion exchange¹³, but investigations by others¹⁴ have shown that the process is one of the adsorption and follows the Langmuir isotherm model.

Activated Alumina can be regenerated with HCl, H₂SO₄, Alum or NaOH. The use of NaOH needs to be followed by a neutralization to remove residual NaOH from the bed. Fluoride removal by activated alumina is strongly pH dependent. Batch adsorption data¹⁴ showed very little removal at pH 11.0 and optimum removal at pH 5.0. Hence raw water pH & regenerated bed pH need to be adjusted accordingly.

The ability of activated alumina to remove fluoride depends on other aspects of the chemistry of water as well. Such factors as hardness, silica and boron, etc., if present in water will interfere with fluoride removal and reduce the efficiency of the system.

The use of activated alumina in a continuous flow fluidized system is an economical and efficient method for defluoridating water supplies¹⁵. The process could reduce the fluoride levels down to 0.1 mg/L. The operational, control and maintenance problems, mainly clogging of bed, may be averted in this method.

5.3. Bone Char:

The uptake of fluoride onto the surface of bone was one of the early methods suggested for defluoridation of water supplies¹⁶. The process was reportedly one of the ion exchange in which carbonate radical of the apatite comprising bone, Ca(PO₄)₆.CaCO₃, was replaced by fluoride to form an insoluble fluorapatite. Bone char produced by carbonizing bone at temperature of 1100-1600°C had superior qualities than those of unprocessed bone and hence replaced bone as defluoridating agent

5.4. Degreased and alkali treated bones:

Degreased and alkali treated bones are effective in the removal of fluoride from initial fluoride concentration ranging from 3.5 mg fluoride/L to 10 mg fluoride/L to less than 0.2 mg fluoride/L.

5.5. Synthetic tricalcium phosphate

The product is prepared by reacting phosphoric acid with lime (Bulusu). It has a capacity to remove 700 mg fluoride/L. The medium is regenerated with 1% NaOH solution followed by a mild acid rinse^{12,16-18}.

5.6.Florex

A mixture of tri-calcium phosphate and Hydroxy -apatite, commercially called Florex, showed a fluoride removal capacity of 600 mg of fluoride per litre and is regenerated with 1.5% sodium hydroxide solution. Owing to high attritional losses, Florex was not successful and the pilot plants using this material were abandoned^{19,20}.

5.7.Activated Carbon

Most of the carbons prepared from different carbonaceous sources showed fluoride removal capacity after alum impregnation. High Fluoride removal capacities of various types of activated carbons had been reported²¹.

Alkali digested alum impregnated paddy husk carbon was an efficient defluoridating agent²². Alkali digested (1% KOH) & alum soaked (2% alum) carbon removed 320 mg fluoride per kg & showed maximum removal efficiency at pH 7.0.²³

Investigations have shown that carbonized saw dust when quenched in 2% alum solution forms an excellent defluoridating carbon²⁴. The defluoridating process is stoichiometric and equilibrium is established between carbon & fluoride. On exhaustion (after continued use) the carbon can be regenerated by passing 0.2 to 0.5% alum solutions.

Activated carbon prepared by other workers from cotton waste, coffee waste, coconut waste etc., was tried for defluoridation but all these materials proved to be of academic interest only¹.

5.8.Lime:

The fluorides in waters containing Magnesium, when treated with lime, are adsorbed on Magnesium hydroxide flocs enabling fluoride removal^{12,25,26}. In this case the water must be treated to a caustic alkalinity of 30 mg fluoride/L, a pH of 10.5 or above and as such recarbonation is necessary²⁷. Magnesia and calcined magnesite have also been used for fluoride removal from water and fluoride removal capacity was reported to be better at high temperature²⁸.

5.9.Ion Exchange Resins

Strong base exchange resins remove fluorides either on hydroxyl cycle or chloride cycle along with anions^{29,30}. Since the proportional quantity of fluoride as compared to other anions is very small, the effective capacity of such resins works out quite low. Some inorganic ion exchangers, eg. complex metal chloride silicates, formed from barium or ferric chloride with silicic acid, also exchanged fluoride for chloride.

Cation exchange resins impregnated with alum solution have been found to act as defluoridating agents. Alum treated cation exchange resins were used for defluoridation³¹⁻³³. ‘Avaram Bark’ based cation exchange resins, had been reported to work effectively in removing fluoride from water³⁴.

Polystyrene anion exchange resins in general and strongly basic quaternary ammonium type resins in particular are known to remove fluorides from water along with other anions^{29,30}. The fluoride removals by various anion exchange resins are given⁶ in the table 3.

Table.3. Fluoride removal by anion exchange resins

Resin	Form	Calculated capacity	Test water Fluorides, mg/L	Cost of treatment/m ³ Rs	Capital cost per m ³ Rs
Tulsion, A-27	Hydroxyl	32	2.8	7.95	1422
Deaceodite, FF-1P	Hydroxyl	130	2.8	2.35	1000
Lewatit, MIH-59	Hydroxyl	96	2.8	3.00	1043
Amberlite, IRA-400	Hydroxyl	232	2.8	1.55	939

Table 3 indicates that the resins studied yields 20 – 145 bed volume of defluoridated water per cycle. Subsequent experience showed that these resins lose their fluoride removal capacity on prolonged use (10 – 15 cycles) and a total replacement becomes necessary. A layer of white deposits was developed over the resin beds, and this may be the reason for this drop in the capacity.

Thus the anion exchange resins were found to be of relatively low capacity for fluoride removal. The cost of anion resins is Rs. 20 to 35 per litre. The results indicate that anion exchange resins are not economical for removing fluorides from water. Besides, the strong base anion exchange resins impart a taste to the treated water that may not be acceptable to the consumers.

Cation Exchange Resins:

Performance of Saw dust carbon (Defluoron-1), Carbion, Wasoresin – 14 and a polystyrene cation exchange resin for fluoride removal were compared³⁵ and the results of the study are summarized in the table.4.

Table.4. Fluoride removal by cation exchange resins

Medium	Calculated capacity	Test water Fluorides,	Bulk density g/L	Cost of treatment/m ³	Capital cost per m ³
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	mg/L	mg/L		Rs	Rs
Carbion	320	4.3	680	0.65	258
Wasoresin-14	262	4.3	730	0.74	315
Polysteren resin	420	4.3	850	0.56	197
Sulphonated saw dust carbon	370	4.3	620	0.60	285

During the above studies the bed was regenerated with 200 ml of 1% alum solution and washed with tap water when the residual fluoride concentration reached 1.5 of fluoride/1.

5.10. Magnesia

Investigations were conducted to study the usefulness of magnesia in fluoride removal¹. Crystalline magnesium hydroxide was obtained by reacting a magnesium salt with milk of lime. The precipitate was filtered, washed and dried. The dried product was calcined at 1000°C for 3 hours to obtain magnesia. Varying quantities of magnesia were added to one litre aliquots of test water and stirred for 30 min using a jar test machine. Fluoride contents were estimated on one hour settled sample.

A typical groundwater containing 10 mg/L fluorides, 60 mg/l hardness, 500 mg/L alkalinity and 7.6 pH was studied using magnesia (MgO) concentrations of 10 - 1,500 mg/L. The treated water showed a pH above 9. The average fluoride concentration in the filtrate was 5.8 mg F/L where the dose was 1,000 mg/L. The fluoride at 100, 250 and 500 mg/L doses were 9.5, 8.9 and 8.4 mg F/L, respectively. A dose of 1,500 mg/L magnesia and a contact period of 3 hr was required to reduce the fluoride content in the water to 1 mg/L.

The study established that magnesia removed the excess fluorides, but large doses were necessary. Moreover the pH of the treated water was beyond 10 and its correction by acidification or recarbonation was necessary. All this adds to the cost and complexity of operations. The acid requirement can be to the extent of 300 mg/L expressed in terms of CaCO₃/L.

The high initial cost, large concentrations required, alkaline pH of the treated water and complexity of the preparation of magnesia are the inhibitive factors to render it acceptable in the field.

5.11. Serpentine:

Serpentine is a mineral name, which applies to the material containing one or both of the minerals, chrysotile and antigorite¹. The composition of the mineral closely corresponds to the formula Mg₆Si₄O₁₀(OH). The material is green or yellow and is available in Andhra Pradesh. To test the capacity of serpentine to remove fluorides from waters, the green and yellow varieties were studied for their defluoridation capacity. Extensive laboratory investigations were conducted with a view to popularize the mineral, if found suitable as a defluoridating medium. A comparative evaluation was made using green and Yellow varieties of serpentine and the results are given in the table 5.

Table.5. Comparative performance of green and yellow varieties of serpentine (-100 mesh powder) jar tests

	GREEN VARIETY						YELLOW VARIETY					
Dose, g/L	0	10	20	40	60	80	0	10	20	40	60	80
Fluorides, mg/F/L	6.2	4.8	4.2	2.6	2.5	1.9	6.2	4.6	3.7	2.7	2.2	1.8
pH	8.8	8.4	8.6	8.7	8.8	8.9	8.4	8.4	8.6	8.8	8.8	8.9

It is concluded that cost of defluoridation is prohibitive with serpentine.

Materials like clays, minerals, ion exchange resins, activated carbons, activated alumina, sulphonated coals and serpentine were tried for the removal of excess fluorides from water. In- situ chemical treatment with lime, magnesium salts, iron and aluminum salts were also studied. Those that showed an encouraging trend on a bench scale were studied in detail. These include ion exchange resins, saw dust carbon, coconut shell carbon defluoron-1 carbion, magnesia, serpentine and defluoron-2. Ion exchange resins, saw dust carbon, defluoron-1, magnesia and serpentine did not prove useful beyond bench –scale.

5.12.Lime stone, special soils and clay etc.:

Recently limestone and heat-treated soil were tried for fluoride removal⁶⁶. Limestone was used in a two-column continuous flow system (limestone reactor) to reduce fluoride concentrations from wastewaters to below the MCL (Maximum contaminant level) of 4 mg/L. Calcite was forced to dissolve and fluorite to precipitate in the first column. The degassing condition in the second column caused the precipitation of the calcite dissolved in the first column, thus returning the treated water to its approximate initial composition.

In laboratory experiments, the fluoride concentration of the effluent from all tested feed waters containing initial fluoride amounts from 10 to 100 mg/L. And a steady state of the system performance was quickly achieved, For instance, in an experiment when the input fluoride concentration was 100 mg/L, effluent concentrations from both columns were below 4 mg/L after only 8 pore volumes had passed. The proposed reactor has potential application to reduce concentrations from wastewaters of anionic elements similar in charge and size to carbonate ion, such as Selenate and arsenate and cations similar in size and charge to Ca^{2+} , such as Cd^{2+} .

Pleistocene soil available locally in Xinzhou, China was able to remove fluoride from local ground water. X-ray diffraction analysis revealed that the soil is composed principally of quartz (50-60%), Illite (30-40%), goethite (5-10%) and feldspar (5-10%). A substantial improvement in both permeability and the fluoride removal capacity of the soil was achieved by heating it in a Muffle furnace. A granular material can then be obtained by crushing the heated product.

The experimental results showed that heating at 400-500°C has the optimal effect on the enhancement of the material's fluoride removal capacity. A preliminary column experiment showed that 4.0 kg of 400°C heat-treated soil can treat more than 300L of 5 mg/L fluoride feed water before the effluent fluoride concentration reaches 1.0 mg/L. Once the soil's fluoride-sorption capacity had been reached, the material could be regenerated in a cost effective way: rinse the soil first with sodium

carbonate solution, then with dilute HCl and finally with distilled water twice. After being air-dried the material is ready for reuse.

Attempts were made to use local Kenyan soil derived from volcanic ash (ex: Ando soils or soils with andic properties) as a fluoride sorbent³⁷. The ability of Kenyan Ando soil to adsorb fluoride was determined experimentally. These results were extended to possible technical application using a one dimensional solute transport model. Based on the result it is concluded that the use of Ando soils appears to be an economical and efficient method for defluoridation of drinking water on a small scale in rural areas of Kenya and other regions along the Rift zone. Further research is warranted to evaluate its practical applications and social acceptance.

Fluoride sorption studies were carried out on two clay minerals, montmorillonite KSF and kaolin, and a silty clay sediment series (SCSS, used in earthenware making)³⁸. The function of fluoride concentration, clay concentration and pH in clay-water suspensions was studied. Kaolinite, a dioctahedral two layered (Silica + alumina) Silicate(1:2 type), exhibited very little tendency for Fluoride sorption while montmorillonite, 2:1 type material characterized by Octahedral sheet of alumina sandwiched between two tetrahedral sheets of silica, showed significant Fluoride sorption. The Fluoride sorption on montmorillonite KSF was found to be greatest at $\text{pH } 1.9 \pm 0.3$, the natural pH of montmorillonite-water suspension. At $\text{pH } 4.0 \pm 0.36$, the percentage fluoride sorption on montmorillonite decreased, followed by an increase around pH 5-6, after which the percentage decreased with increasing pH. The applicability of the Freundlich isotherm was also verified in case of montmorillonite KSF at low fluoride concentrations. As a result of fluoride adsorption, increased release of Fe^{2+} , Cl^- , NO_3^- ions from montmorillonite matrix was observed. There was no effect on SO_4^{2-} or PO_4^{2-} solubility. Fluoride adsorption on SCSS was also significant and decreased regularly with increasing pH.

On the basis of experimental data a plausible mechanism of fluoride sorption by clay minerals is suggested. Based on the results of fluoride sorption mentioned above, a pilot study on defluoridation of water employing clay (SCSS) as an adsorbent was also undertaken which yielded promising results.

Removal of fluoride by adsorption on to low-cost materials like kaolinite, bentonite, charfines, lignite and nirmali seeds was investigated³⁹.

5.13. Fly Ash:

Retention of fluoride ion in dynamic experiments on columns packed with fly ash was studied⁴⁰ at 20°C with a series of aqueous solutions containing 1,5,10,20,50 and 100 mg fluoride/L. The flow rate through a 450-g bed was $\leq 2\text{ml/hr}$. At the lowest fluoride concentration (1 mg/L), the fluoride level in the effluent initially increased and then gradually decreased down to 0 mg/L after 120 hours. With higher fluoride concentrations in the feed solutions, the fluoride concentration in the effluent steadily decreased reaching 0 mg/L after 120-168 hours. The fly ash was an effective sorbent especially at high concentrations.

5.14. Electro coagulation/Electrochemical methods:

Electro coagulation process with aluminum bipolar electrodes was used for defluoridation process⁴¹. The influence of parameters such as inter-electrode distance, fluoride concentration, temperature and pH of the solution were investigated and optimized with synthetic water in batch mode. The optimization process continued with Oued Souf water (South Algeria) where the influence of current density and area/volume ratio on the defluoridation process was evaluated. The electro coagulation process with aluminum bipolar electrodes permitted the defluoridation of Sahara water without adding salts to the treated water. The aluminum-fluoride weight ratio attained was 17/1.

A technology of defluoridation through Electrochemical route has been developed⁴². The basic principle of the process is the adsorption of fluoride with freshly precipitated aluminum hydroxide, which is generated by the anodic dissolution of aluminum or its alloys, in an electrochemical cell. The process utilizes 0.3 to 0.6kwh of electricity per 1000 litres of water containing 5- 10 mg/L of fluoride. The anode is continuously consumed and needs to be replenished. The process generates sludge at the rate of 80- 100 gm per 1000 litres (on dry basis).

Constraints in the above technology: Electricity is the main raw material and hence wherever electricity is not available a suitable solar panel can be installed.

5.15. Rare earth based materials:

New water treatment processes have been developed for removal of hazardous anions such as Fluoride, Arsenic, Selenium species, and phosphate from water using rare earth based materials which have not been efficiently utilized by industry in spite of their abundance⁴³. The state-of-the-art of rare earths in terms of cost, use and health effects and the environmental problems associated with hazardous anions in terms of treatment and toxicity are generally described. Solid lanthanum and Yttrium ions have been used as adsorbents for removing hazardous anions. Either lanthanum or Yttrium ions have been loaded on porous silica or alumina beads to improve economic and engineering performance; such rare earth impregnated materials have been successfully applied to the treatment of synthetic as well as industrial wastewaters.

A rare earth metal-based inorganic adsorbent, Cerium-Iron adsorbent (CFA), was developed and its performance for fluoride removal from water was evaluated⁴⁴. The characteristics of the adsorbent were summarized. Experimental results show that rare earth metal adsorbents had a relatively high adsorption capacity and good kinetic property for fluoride ion removal. The highest capacity was obtained at pH 3, then it decreased with the increase of pH. The pH effect however, became inconspicuous when the pH was over 5. The results show that the adsorption of fluoride on CFA adsorption follows Freundlich isotherm in the tested range of fluoride concentrations. The adsorption capacity could almost be recovered by regenerating it with 1 mol/L NaOH solution.

An adsorbent, which is a mixture of rare earth oxides was found to adsorb fluoride rapidly and effectively⁴⁵. The effect of various parameters such as contact time, initial concentration, pH and adsorbent dose on adsorption efficiency was investigated. More than 90% of the adsorption occurred within the first 5-10 minutes. Adsorption was found to be dependent on the initial fluoride concentration and adsorption behavior followed Langmuir adsorption model. The optimum pH was

found to be about 6.5. The presence of other ions such as nitrate and sulphate did not affect the adsorption of fluoride significantly (adsorption efficiency reduced from 85 to 79%) indicating the selective nature of the adsorbent. The adsorbed fluoride could be easily desorbed by washing the adsorbent with a pH 12 solutions. This study clearly shows the applicability of naturally occurring rare earth oxides as selective adsorbent for fluoride from solutions

6.0. Conclusions

1. The chief source of fluoride content in ground water is the leaching of fluoride from the fluoride-bearing minerals of the earth's crust.
2. Many rivers flowing through more than half a dozen states in India are reported to have fluoride contents varying from 0.1 to 12.0 ppm¹. Similarly occurrence of fluoride bearing waters was reported by many in A.P.³, Rajasthan⁴, Punjab and Haryana⁵, Maharashtra⁶, Tamilnadu⁷, Karnataka⁸, Madhya Pradesh⁹, Gujarat¹⁰ and Uttar Pradesh¹¹
3. Fluoride in drinking water is known for both beneficial and detrimental effects on health. The problems associated with the excess fluoride in drinking water are highly endemic and widespread in countries like India.
4. Fluorosis - a disease caused by ingestion of fluoride in excess through water, food, and air is a serious health problem. Fluoride ingested with water goes on accumulating in bones up to age of 55 years. Depending upon the amount and period of ingestion, illness of varying degree like dental fluorosis, skeletal fluorosis and non-skeletal fluorosis would occur. Calcification of certain ligaments, rendering movement of joints difficult, is usually associated with at least 10 mg/L of fluoride in drinking water.
5. The detrimental effects of excessive fluoride can be controlled by defluoridation of natural waters. A number of methods of defluoridation are available; however not all the methods are suitable for all circumstances and hence proper justification is required for selection an appropriate method for a given situation.
6. Certain under-exploited but abundantly available materials like rare earth materials have indicated excellent potential for fluoride uptake. Attempts may be made to develop cost effective, simple to use technologies based on these material..

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