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Fluoride and environment

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ABSTRACT

The presence of fluoride in exceeding limits and related problems of drinking water prevailing in many parts of India is well documented. Fluoride in drinking water is known for having 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, as well as available methods of defluoridation in detail.

Keywords: Fluorine, Environment

1. 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. FLUORIDE IN ENVIRONMENT

Fluorine (F_2) 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, CaF_2; Cryolite, Na_3AlF_6; Fluorapatite, $3Ca_3(PO_4)_2$ $Ca(F_2,Cl_2)$. Other minerals containing fluoride are given in the Table 1.

Table1. Fluoride bearing minerals[45]

Mineral	Chemical formula	% fluorine
Sellaite	MgF_2	61 %
Villianmite	NaF	55 %
Fluorite (Fluorspar)	CaF_2	49 %
Cryolite	Na_3AlF_6	45 %
Bastnaesite	$(Ce,La)(CO_3)F$	9 %
Fluorapatite	$Ca_3(PO_4)_3F$	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 solution[1]. 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, CO_3 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. 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 ppm[1]. Similarly occurrence of fluoride bearing waters was reported by many in A.P[3]., Rajasthan[4], Punjab and Haryana[5], Maharastra[6], Tamil Nadu[7], Karnataka[8], Madhya Pradesh[9], Gujarat[10] and Uttar Pradesh[11].

4. 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.

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

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 thrust. 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 summarized[2] in Table 2.

Table 2. Concentrations of fluorides and biological effects

Concentration of fluoride, ppm*	Medium	Effect
0.002 1	Air Water	Injury to vegetation 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. 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 developed [1]*. 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 studies[12], 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 fluorid e/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 issued [1]. Filter alum was used[13] 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 0.2 kg 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 io n exchange[13], but investigations by others[14] have shown that the process is one of the adsorption and follows the Langmuir isotherm model.

Activated Alumina can be regenerated with HCl, H_2SO_4, 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 data[14] 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 supplies[15]. 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 supplies[16]. The process was reportedly one of the ion exchange in which carbonate radical of the apatite comprising bone, $Ca_3(PO_4)_2$. $CaCO_3$, was replaced by fluoride to form an insoluble fluorapatite. Bone char produced by carbonizing bone at temperature of 1100-1600 ºC 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 reported[21]. Alkali digested alum impregnated paddy husk carbon was an efficient defluoridating agent[22]. 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 carbon[24]. 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 only[1].

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 necessary[27]. Magnesia and calcined magnesite have also been used for fluoride removal from water and fluoride removal capacity was reported to be better at high temperature[28].

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 impregnable with alum solution have been found to act as defluoridating agents. Alum treated cation exchange resins were used for defluoridation[31-33]. 'Avaram Bark' based cation exchange resins, had been reported to work effectively in removing fluoride from water[33]. 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 given[6] 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, A27	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 compared 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
	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.

6. 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 ppm[1]. Similarly occurrence of fluoride bearing waters was reported by many in A.P[3], Rajasthan[4], Punjab and Haryana[5], Maharastra[6], Tamil Nadu[7], Karnataka[8], Madhya Pradesh[9] , Gujarat[10] and Uttar Pradesh[11]
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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