

# REMOVAL OF FLUORIDE DIFFERENT TECHNIQUES FROM THE DRINKING WATER

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## ABSTRACT

**KEY WORDS:** - Fluoride removal, Laterite soils, water, Adsorbents

Occurrence of fluoride at excessive levels in drinking-water in developing countries is a serious problem. Its detection demands analytical grade chemicals and laboratory equipment and skills. Similarly, the prevention of fluorosis through management of drinking-water is a difficult task, which requires favourable conditions combining knowledge, motivation, prioritization, discipline and technical and organizational support. Many filter media and several water treatment methods are known to remove fluoride from water. The ability of lateritic soils to remove fluoride from water has been study. Important issues considered in the study include the relation between the mineral composition of soils & their ability to remove fluoride, The effect of thermal treatment of the soil on fluoride removal, the pre dominant fluoride containing species remain in the treated water and the possible mechanism of fluoride removal by lateritic soils. Fluorine is estimated to the most abundant element in the earth's crust and is widely dispersed in nature in the form of fluorides. Fluoride found naturally in soil, water, and foods. High-level exposure to fluoride can lead to Fluoride poisoning. Fluoride contamination in drinking water due to natural & anthropogenic activities has been accepted as one of the major problems worldwide imposing a serious threat to human health. The present review emphasizes on efficacy of different methods for the removal of fluoride from water.

## INTRODUCTION

Fluoride is a naturally found mineral in all water sources, including fresh water, ground water & ocean water. It also found naturally in a wide range of food items including tea, fish and rice and our normal diet. Fluoride is an extremely negative aspect and has an extraordinary tendency to induce attraction by charged ions like metallic elements. Although fluoride is an essential constituent for both humans and animals, yet it can be either beneficial or detrimental to human health depending on the level of fluoride in drinking water. When the amount of fluoride increases from the permissible limit, it can induces intense impact on human health in the form of dental and skeletal fluorosis. Fluoride has beneficial effects on teeth at low concentrations in drinking- water, but excessive exposure to fluoride in drinking- water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects. These range from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases. Early stages of skeletal fluorosis start with pain in bones and joints, muscle weakness, stiffness of joints, chronic fatigue. During later stages of fluorosis, calcification of the bones takes place, osteoporosis in long bones & symptoms of osteosclerosis appear where the bones become denser and develop abnormal crystalline structure. In India, fluorosis is common in places such as Jammu, Uttar Pradesh, Rajasthan, Gujarat, Tamil Nadu, Andhra Pradesh, Karnataka, Kerala, and Orissa.

## Permissible limit of fluoride in drinking water prescribed by various organizations.

- |  |         |
|--|---------|
| 1. World Health Organization (International standard of drinking water)                        | 0.6-1.5 |
| 2. US Public Health Standards  | 0.8     |
| 3. The Committee on public health engineering manual and Code of practice, Government of India | 1.0     |
| 4. BIS   | 0.6-1.5 |
| 5. ICMR  | 1.0     |

## Effects of Fluoride Toxicity

**Acute Effects-** Nausea, vomiting, Hypocalcaemia, Hypotension, Hyper salivation, Mixed metabolic and respiratory acidosis

**Chronic Effects-** Dental Fluorosis, Skeletal Fluorosis Hypersensitivity reactions, Dyspepsia, gastric irritation, Muscular spasm, Birth defects.

The use of earth ground water with high fluoride concentrations poses a health threat to millions of people around the world and some cost effective technologies are required to eliminate excess fluoride in water. De- fluoridation of drinking water is the only pragmatic approach to solve the fluoride pollution problem as the use of alternate water sources and improvement of nutritional status of population at risk have their own limitations and are expensive affairs. The methods developed for this purpose are divided as follows depending upon the mode of action. Several methods have been developed to efficiently remove F from water, including Nano filtration, Reverse osmosis (RO), coagulation, electrocoagulation, electrochemical oxidation, ion exchange and adsorption .This review article is aimed at providing precise information on efforts made by various researchers in the field of fluoride removal from drinking water.

**The fluoride removal techniques has been divided in following two type –**

(1) Common Methods

(2) New Technologies.

### 1. Common Methods –

Among the common methods, techniques used are Contact precipitation, Coagulation, Distillation, Electro-coagulation, Ion exchange, Adsorption, Membrane Filtration.

### New Technologies

Among the new technologies, techniques used are The Water pyramid solutions, The Solar Dew Collector system, Memstill technology, Crystal factor and Boiling with Brushite and Calcite

## COMMON METHODS FOR DEFLORIDATION OF WATER

### A. Contact Precipitation

Contact precipitation is a technique in which fluoride removed from water through the addition of calcium and phosphate compounds. The presence of a saturated bone charcoal medium acts as a catalyst for the precipitation of fluoride either as CaF<sub>2</sub> or fluorapatite. Tests at community level in Tanzania have shown promising results of high efficiency. Reliably good water quality and low cost are reported advantages of this method.

### B. Coagulation

Lime and alum are the most commonly used coagulants. Addition of lime leads to precipitation of fluoride as insoluble calcium fluoride and raises the pH value of water.



As lime leaves a residue of 8.0 mg F-/L ,it is used only in conjunction with alum treatment to ensure the proper fluoride removal.

In the first Step precipitation of fluoride occurs by lime dosing which is followed by a second step in which alum is added to cause coagulation. When alum is added to water, essentially two reactions occur. In the first reaction, alum reacts with some of the alkalinity to produce insoluble Al(OH)<sub>3</sub>. In the second reaction, alum reacts with fluoride ions present in the water. The best fluoride removal occurs at pH range of 5.5-7.5.



The Nalgonda technique of de fluoridation is based on combined use of alum and lime in a two step process and has been claimed for fluoride removal.

Adaptable to domestic use and Simplicity of design, construction, operation and maintenance are reported advantages of this method. But the major cause for concern with this technology is that if the dose of alum is not adhered to, there is a possibility of excess aluminium contaminating the water. The maximum contamination of aluminium permitted is 0.03 mg to 0.2 mg/L for water according to BIS, as an excess is suspected to cause Alzheimer's disease. Advantages and disadvantages of these methods are-

#### **Advantages**

1. Simplicity of design, construction, operation and maintenance cost.
2. Beside fluoride turbidity, colour, odour, pesticides and organic substance are also removed in this method.
3. It can be used at domestic and community level because it is cost effective.

#### **Disadvantages**

1. There is a possibility of excess aluminium contaminating the water. The maximum concentration of aluminium permitted is 0.03 mg to 0.2 mg/litre of water according to Bureau of Indian Standards (BIS), as an excess is suspected to cause Alzheimer's disease.
2. Discarding the sludge from the Nalgonda process is a serious environmental health problem. The sludge is toxic as it contains the removed fluoride in a concentrated form and therefore, sludge disposal is a problem.
3. Periodic analysis of feed and treated water is required to calculate the correct dose of chemicals to be added.

#### **C. Distillation**

Distillation units can also be used for treating the drinking water. Electrodialysis (ED) is a desalination technology which uses an electric voltage and anion-exchange and cation-exchange membranes placed in alternating order to separate low salinity water from high salinity water. Large scale electrodialysis plants are already used for making drinking water out of brackish water with high fluoride concentration. But it is a large scale treatment technology which are difficult to use in less advanced regions.

#### **D. Electrocoagulation**

Electrocoagulation is an electrochemical technique, in which a variety of unwanted dissolved particles and suspended matter can be effectively removed from an aqueous solution by electrolysis Continuous flow experiments with mono polar aluminium electrodes for fluoride removal were undertaken to investigate the effects of the different parameters. The highest treatment efficiency was obtained for the largest current and the removal efficiency was found to be dependent on the current density, the flow rate and the initial fluoride concentration when the final pH ranged between 6 and 8. The results obtained showed that the continuous flow electrocoagulation technology is an effective process for de fluoridation of potable water

supplies and could also be utilized for the de fluoridation of industrial Waste Water. Advantages and disadvantages of these methods are

### Advantages

1. Equipment is simple to handle and cost effective.
2. Treated water is colourless and odourless.
3. It produces low sludge that is promptly settlable and simple to de-water since it essentially content metallic oxides or hydroxides.

### Disadvantages

1. The 'sacrificial electrodes' are Dissolve into wastewater streams
2. Gelatinous hydroxide may tend to solubilize now and again
3. An impermeable oxide film may be frame on the cathode prompting loss of productivity of the EC unit.

### E. Ion Exchange

Ion exchange technique has proved to be an efficient method for fluoride removal. Fluoride can be remove from water with a strongly basic anion-exchange resin containing quaternary ammonium groups. The removal takes place according to the following reaction.



The fluoride ions replace the chloride ions of the resin. This process continues until all the sites on the resin are occupied. The resin is then back washed with water that is supersaturated with dissolved sodium chloride salt. New chloride ions then replace the fluoride ions leading to recharge of the resin and starting the process again. The driving force for the replacement of chloride ions from the resin is the stronger electro-negativity of the fluoride ions. The main advantage of this technique is High productivity (90-95 % fluoride removal) but this Technique is exceptionally costly and pH of treated water is low and contains high concentration of chloride. Regeneration of resin is also an issue on the ground that it prompts fluoride rich waste, which must dealt with before last disposal. The point of interest and restriction of ion exchange technique are given below.

### Interest

1. High productivity (90-95 % fluoride removal).
2. Retains the superiority of water.

### Restriction

1. Technique is exceptionally costly.
2. pH of treated water is low and contains high concentration of chloride.
3. Interference because of the presence of other anions like sulphate, carbonate, phosphate and alkalinity.
4. Regeneration of resin is an issue on the ground that it prompts fluoride rich waste, which must dealt with before last disposal.
5. It requires longer reaction period.

### F. Adsorption

Adsorption is one of the most widely used techniques for water de fluoridation due to the high efficiency, low cost and easy application Several adsorbent materials have been tried in the past to find out an efficient and economical de fluoridation techniques. These divided into two categories.

1. Chemical adsorbents
2. Bio-adsorbents

## CHEMICAL ADSORBENTS

Among chemical adsorbents following are the main Activated Alumina, Bone-char, Activated Charcoal, Brick Powder, Hydrated Cement, Activated Titanium Rich Bauxite, Red mud, Calcite Clay Chips, Doping of poly-anilines, Aluminium containing compounds, Cynodon Dactylon, Kaolinite, Nano Hydroxyapatite, Chitin composite, Poly pyrrole, Lacterite, Bentonite Clay, China Clay.

### 1. Activated Alumina

Activated alumina has a very high surface area and can bind inorganic ions such as fluoride on its surface sites.  $Al-OH + F^- \rightarrow Al-F + OH^-$  This reaction is pH sensitive and works best in the optimum pH range of 5-6. When all surface sites are Occupied the filter cannot take up more fluoride and needs to be regenerated. This is done by treating the activated alumina with a strongly alkaline solution (e.g. NaOH) to reverse the reaction, followed by a strong acid ( $H_2SO_4$ ) to re-establish a positive surface charge.

### 2. Bone Char/Hydroxyapatite

Fluoride removal with bone char is based on an adsorption process. The effectiveness of bone char for fluoride removal is due to its hydroxyapatite content. The fluoride ions bind to surface sites on the hydroxyapatite, thereby releasing  $OH^-$  into solution.  $Ca_5(PO_4)_3OH + F^- \rightarrow Ca_5(PO_4)_3F + OH^-$  Once the uptake capacity has been reached and most surface sites are occupied, the ability to find fluoride decreases rapidly. At this point the filter material needs to be regenerated or replaced.

### 3. Activated Charcoal

The performance of activated carbon for the removal of fluoride from aqueous solution is promising. Batch adsorption studies were undertaken to assess the suitability of commercially available activated charcoal to remediate fluoride contaminated water. Removal of fluoride by using activated charcoal is one of the good methods as by this maximum fluoride removal was observed i.e. 94% at optimum conditions.

### 4. Brick Powder

Brick powder has economical and effective adsorbents in removing fluoride from water to acceptable levels. De fluoridation of ground water using brick powder as an adsorbent was studied in batch process in the optimum condition of pH and dose of adsorbents, the percentage defluoridation from synthetic sample, increased from 29.8 to 54.4% for brick powder and from 47.6 to 80.4% for commercially available activated charcoal with increasing the contact time starting from 15 to 120 min.

### 5. Hydrated Cement

Their studies to investigate the potential of cement hydrated at various time intervals for the removal of excess F from aqueous solution by using batch adsorption studies. It was found that 92.37% removal of fluoride occurs using hydrated Portland cement granules of 1.4-3 mm size.

### 6. Activated Titanium rich bauxite

Activated titanium rich bauxite has also been employed for adsorptive removal of excess fluoride from drinking water. Nearly complete desorption of adsorbed fluoride from loaded bauxite was achieved by treating with aqueous solutions of  $pH > 11.1$  ( $NaOH$ ) or  $0.015 \text{ mol/dm}^3$ .

### 7. By using Granular red mud

Among various industrial by-products, red mud is a solid waste residue formed after the caustic digestion of bauxite ores during the production of alumina. Each year, about 90 million tonnes of red mud are produced globally. Red mud is mainly composed of fine particles containing aluminium, iron, silicon, titanium oxides and hydroxides. The red colour is caused by the oxidized iron present, which can make up to 60% of the mass of the red mud. Toxic heavy metal and metalloid ions and fluoride have been removed by using red mud as a potent adsorbent. Besides fluoride, nitrate and phosphate anion have also been eradicated by red mud.

### 8. By Calcite

Fluoride removal by crushed limestone (99% pure calcite) was investigated by batch studies and surface sensitive techniques from solutions with fluoride concentrations from 150 mg/L (3mg/L) to 110 mg/L (2100mg/L). Results indicate that fluoride adsorption occurs immediately over the entire calcite surface with fluoride precipitating at step edges and kinks, where as dissolved  $Ca^{+2}$  concentration is highest.

## 9. Using Fired Clay Chips

Fired clay chips have been used by Moges and Zwege for fluoride removal from water. The maximum capacity of the adsorbent was found to be 0.2mgF<sup>-</sup>/g of the adsorbent. Studies show that 5-20mg/L of fluoride solution can be reduced to less than 1.5mg/L thus showing nearby 70-90% removal capacity.

## 10. De-fluoridation of Water via Doping of Polyanilines

Some polymeric substances viz. polyaniline and poly n-methylaniline also act as effective de-fluoridation agent. From these polymers doping technique has been applied and the influence of pH, dosage of polyanilines, initial fluoride concentration and temperature on the amount of fluoride removed by the polyanilines were studied. The amount of fluoride removed at pH 7.0 by 50mg/50mL dose was found to be 0.78mg/g.

## 11. Using Aluminium Containing Compounds

KarthiKeyan et al., applied batch adsorption technique to study the suitability of aluminiumtitanate (AT) and bismuth aluminate (BA) to remove fluoride ions from water. The amount of fluoride ions adsorbed at 30°C from 4mg/L of fluoride ion solution, by AT and BA were 0.85 and 1.55 mg/g respectively.

## 12. Cynodon Dactylon

Thermally activated carbon obtained for cynodon dactylon has been studied by Alagumuthu et al., to remove fluoride from aqueous solution. The batch adsorption studies were carried out at neutral pH as functions of contact time, adsorbent dose, adsorbate concentration, temperature and effect of co-anions, which are commonly present in water. The rate of adsorption was rapid during initial 105 minutes and attained equilibrium.

## 13. Using Laterite

Sarkar and Banerjee assessed the suitability of laterite soil particles as potential adsorbent for fluoride removal through batch operation mode. The process attains equilibrium at 195 min, removing 78.2% fluoride from 10mgdm<sup>-3</sup> fluoride solution using fine particles size at 303K.

## 14. Using Bentonite

The magnesium incorporated bentonite clay works effectively over wide range of pH and shows a maximum fluoride removal capacity of 2.26mgg<sup>-1</sup> at an initial fluoride concentration of 5mgL<sup>-1</sup>, which is much better than the unmodified bentonite.

## 15. Adsorption on China Clay

China clay has been used as adsorbent for removal of fluoride from water. Fluoride removal is favoured by low concentration, high temperature and acidic pH. The alumina constituent of china clay is responsible for maximum adsorption of fluoride in the pH range of interest.

**BIO-ADSORBENTS** - These are following- Thermally activated carbon prepared from neem and kikar leaves, Serpentine, Rice Husk, Eichhornia Crassipes

### 1. By Bio-thermally Activated Carbon prepared from neem (*Azadirachta indica*) and kikar (*Acacia Arabica*) leaves

Thermally activated neem leaves carbon and thermally activated kikar leaves carbon (AKC) have been used as bio adsorbent for fluoride removal. These bio adsorbents were prepared by heating the leaves at 400 degree C in electric furnace and was found useful for the removal of fluoride.

### 2. Using Rice Husk

Static studies have aimed for investigation of fluoride removal efficiency under the varying conditions of the major parameters of adsorption. Maximum fluoride removal was observed to be 75% at optimum conditions. Rice husk is a cheap and easily available bio adsorbent, whose adsorptive capability has been explored to remove fluoride from drinking water by batch adsorption.

### 3. By Eichhornia Crassipes

Eichhornia Crassipes and the activated carbon derived from this plant were examined to assess their capacity for the removal of fluoride from waste water by batch techniques

## G. Membrane Process

Although various conventional techniques of water purification described earlier are being used at present to solve the problem of ground water pollution, none of them is user friendly and cost effective technique due to some or the other limitation and has either no or very long pay back period. In the recent years, membrane process has emerged as a preferred alternative to provide safe drinking water without posing the problems associated with other conventional methods. Under the membrane techniques following techniques have been discussed

1. Reverse osmosis
2. Nano filtration
3. Ultrafiltration and
4. Electrodialysis.

## H. Fluoride Water

Filters A fluoride water filter eliminates fluoride and other toxins from our drinking water, and provides safe and healthy supply of drinking water at an affordable cost. Two technologies consistently remove fluoride from water.

- (1) Reverse Osmosis Water Filters
- (2) Cartridge Filters

## 2. NEW TECHNOLOGIES

Besides the methods mentioned above several new methods have been introduced in recent years. These new technologies include –

### a. Crystalactor

In Netherland a new type of Contact precipitator, named the Crystalactor, is developed by DHV. The Crystalactor is a fluidized-bed type crystallizer also called a pellet reactor. In the reactor fluoride is removed from the water while calcium fluoride pellets with a diameter of 1mm are produced for treating drinking water, the crystalactor is only advisable in case of high fluoride concentrations (>10 or 20mg/L).

### b. Memstill® Technology

Memstill® technology combines multistage flash and multi effect distillation modes into one membrane module. The memstill technology can produce drinking water at a cost well below that of existing technologies like reverse osmosis and distillation with the memstill® technology also anions like fluoride and arsenic are removed.

### c. The Water Pyramid Solution

Aqua-Aero Water Systems has developed the water pyramid concept for tropical, rural areas. The water pyramid makes use of simple technology to process clean drinking water out of salt, brackish or polluted water. One of the pollutants could be fluoride. Most of the energy needed to clean the water is obtained from the sun.

### d. The Solar Dew Collector System

Solar Dew developed a new porous membrane to purify water using solar energy. The technique is similar to the water pyramid.

### e. Boiling With Brushite and Calcite

Larsen and Pearce suggested a new method using a suspension of the minerals brushite and calcite (Calcium Carbonate) followed by boiling. On a laboratory scale, this method gave good results. It was concluded that boiling a brushite/calcite suspension rapidly converts the two salts to apatite which incorporates fluoride if present in solution. This process may be exploited to de-fluoridate drinking water.

## CONCLUSION

The removal of fluoride from the drinking water. A deep insight of the survey of literature for de-fluoridation techniques. Each of the discussed techniques can remove fluoride under specified conditions. The fluoride removal efficiency varies according to many site specific chemical, geographical and economic conditions, so actual applications may vary from the generalizations made. Any particular process, which is suitable at a particular region may not meet the requirements at some other place. Therefore, any technology should be tested using the actual water to be treated before implementation in the field.

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