# A Review Paper on Various Methods of Removal of Fluoride from Water

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***Abstract*— Groundwater is the most important source of water to meet the requirement of consumption for drinking water, irrigation. India is the largest user of groundwater in the world. It uses an estimated 230 cubic kilometers of groundwater per year - over a quarter of the global total. More than 60% of irrigated agriculture and 85% of drinking water supplies are dependent on groundwater. Fluorine is widely dispersed in nature. It is about 0.06 to 0.09 % of component on Earth's crust and is estimated to be the 13th most abundant element on our planet. It is the most electronegative of all chemical elements, and as a result, it never exists in elemental form, but rather combines with other elements. Fluoride is distributed universally throughout soils, plants, and animals, and is assumed to be an essential element in animals, including humans. Fluoride has an important role in bone mineralization and formation of dental enamels. Fluoride, when consumed in inadequate quantities (less than 0.5 ppm), causes health problems such as dental caries, lack of formation of dental enamel, and reduced bone mineralization, especially among children (WHO 1996). In contrast, when Fluoride is consumed in excess (more than 1 ppm), health problems may result, which equally affect the young and old (WHO 1996). At higher fluoride concentrations, metabolic processes are affected in humans, and overexposed individuals may suffer from skeletal or dental fluorosis, non-skeletal manifestations, or combinations of these maladies (Susheela et al. 1993).**

**Among the three forms of environmental media (air, soil, and water), groundwater is the major source of fluoride exposure in humans. . To sustain life, freshwater must be continuously available to humans. Throughout history, humans have relied on groundwater as a source of drinking water, and even today, more than half of the world's population depends on sources of groundwater for survival. The levels of natural fluoride that occur in groundwater range from 0.5 to 48 ppm, or more (Susheela 2003). Common symptoms of fluoride toxicity in humans are stained teeth, paralyzing bone disease, stooped backs, crooked hands and legs, blindness, and other deformities. W.H.O has stated that fluoride should be in the range of 0.1 to 0.5ppm. The Indian Standard for fluoride contents is 1 ppm. This shows that the requirement of fluoride content changes and it depends on the geographical condition and the age of human beings. In this paper we have reviewed various techniques used for removing the fluoride content from the water. India is one among the 23 nations in the world, where fluoride contaminated groundwater is creating health problems. The state of Art Report of UNICEF confirms the fluoride problem in 177 districts of 20 states in India**.

***Keywords*—*Fluoride, Groundwater analysis, fluorosis, adsorbents***

## INTRODUCTION

Fluoride is an essential constituent for both humans and animals depending on the total amount ingested or its concentration in drinking water. The presence of fluorine in drinking water, within permissible limits of 0.5–1.0 mg/l, is beneficial for the production and maintenance of healthy bones and teeth, while excessive intake of fluoride causes dental or skeletal fluorosis which is a chronic disease manifested by mottling of teeth in mild cases, softening of bones and neurological damage in severe cases. 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 groundwater only when conditions favour their dissolution or high fluoride containing effluents are discharged to the water bodies from industries. Fluoride contamination in groundwater has been recognized as one of the serious problems worldwide. Fluoride is classified as one of the contaminants of water for human consumption by the World Health Organization (WHO), in addition to arsenic and nitrate, which cause large-scale health problems. Various minerals, e.g., fluorite, biotites, topaz, and their corresponding host rocks such as granite, basalt, syenite, and shale, contain fluoride that can be released into the groundwater. Thus, groundwater is a major source of human intake of fluoride. Besides the natural geological sources for fluoride enrichment in groundwater, various industries are also contributing to fluoride pollution to a great extent. The industries which discharge wastewater containing high fluoride concentrations include glass and ceramic production, semiconductor manufacturing, electroplating, coal fired power stations, beryllium extraction plants, brick and iron works, and aluminum smelters. The effluents of these industries have higher fluoride concentrations than natural waters, ranging from ten to thousands of mg/L. The fluoride content in ground water tends to increase due to heavy withdrawal of water for agriculture purpose, poor recharging, low rainfalls and pollution from industrial effluents. India has declared fluorosis as an epidemic and has banned the use of water for drinking and cooking if the fluoride content is more than 1.5 mg/L. Latest guidelines from the Bureau of Indian Standards (BIS) suggest that the fluoride limit in ground water used for drinking and cooking purposes should not be greater than 1mg/L.

Fluorosis can be prevented by the removal of excess fluoride from drinking water by chemical treatment which is a difficult task and requires favorable socio-economical conditions of knowledge, motivation, prioritization, technical and organizational set-ups. Most of these methods are based on principles of precipitation, such NaS the use of lime softening, alum-lime addition and adsorption/ion exchange methods using materials such as activated alumina, bone char, synthetic calcium hydroxyl apatite and bauxite. In addition ion exchange, electro\;;dialysis and reverse osmosis techniques have also been attempted to remove fluoride However, due to lack of favorable conditions (like low fluoride removal capacity, high treatment cost, lack of user friendly technologies and government initiatives etc), many initiatives on defluoridation of water have resulted in failures and frustrations. Nalgonda technique developed by NEERI is commonly preferred at all levels because of

its low price and ease of handling. Various processes tried so far for the removal of excess fluoride from water are adsorption, ion exchange, precipitation, and membrane process. However, most of these methods have high operational and maintenance cost, low fluoride removal capacities, lack of selectivity for fluoride, undesirable effects on water quality, generation of large volumes of sludge and complicated procedures involved in the treatment.
The amount of fluoride concentration and there health outcome is shown in the table below.

| Fluoride concentration, mg/L | Health outcome |
|---|---|
| <0.5 | Dental caries |
| 0.5–1.5 | Optimum dental health |
| 1.5–4.0 | Dental fluorosis |
| 4.0–10 | Dental and skeletal fluorosis |
| 4.0–10 | Dental and skeletal fluorosis |
| >10.0 | Crippling fluorosis |

## I. Methodology

The various methodology used for the removal of fluoride from the groundwater are mainly adsorption and membrane techniques.

*1. Adsorption*

Adsorption is the process considered to be efficient to defluoridate the water. Researches were carried on different adsorbents, viz. activated carbon, processed bone char powder, activated alumina, magnesia, activated bauxite, fly ash, granular calcite, alum, lime, etc.

*1.1 Adsorption using activated Char coal as an adsorbent*

A.R. Tembhurkar et al. (2006) have studied that activated charcoal can be fruitfully utilized for the removal of fluoride. The uptake of fluoride ions is possible between pH of 2.0 and 8.0, however, pH of 2 gives maximum fluoride removal since neutralization of OH- ions by large number of H+ ions takes place at less pH values.They have studied that the percentage of fluoride removal was found to be a function of adsorbent dose and contact time at a given initial solute concentration. The removal increased with time and adsorbent dose, but with higher initial solute concentration decreased with time and adsorbent dose.

*1.2 Adsorption using Alumina and aluminium based adsorbents*

Pietrelli (2005) suggested about the fluoride adsorption of metallurgical grade alumina (MGA). According to them, the best removal was observed at pH 5-6 hence it was favorable to promote stable fluoro-alumina complex. The fluoride adsorption onto MGA sites decreased drastically at higher pH values, which was attributed to compete with hydroxide ions on the binding to the MGA surface. The fixed bed study resulted in the adsorption capacity of 12.21 mg/g.

H. Lounici (2003) studied the electro-activation as a technique to improve the fluoride adsorption capacity of alumina. According to them the fluoride adsorption capacity of electro-activated alumina was 55% more than that of the conventional alumina.

M. Srimurali (2008) studied activated alumina for the removal of fluoride from water. They concluded that the various parameters plays an important role in adsorption capacity. An increase in in pH, alkalinity, carbonates and calcium resulted is a decrease in sorption capacity. Presence of chlorides, sulphates, potassium, sodium and magnesium has marginal influence on sorption capacity.

Tripathi (2006) studied the kinetics of fluoride removal by activated alumina. They concluded that the removal of fluoride was found to be very rapid during the initial period i.e most of the fluoride removed during 10-60 min and reaches to maximum 92% in 3 hours. The removal of fluoride increases with increase in pH upto 6.5 them decreases with the increasing pH. The optimum pH was found to be 6.5, which is suitable for the drinkable purpose.

*1.3 Adsorption using bauxite*

M. G. Sujana et al. (2010) studied the feasibility of utilizing bauxite for fluoride removal from synthetic and natural fluoride bearing groundwater samples. They concluded that the adsorption of fluoride was highly dependent on pH, temperature and initial adsorbate and other anion concentrations in the solutions. The optimum pH range for fluoride on bauxite surface was found to be 5 to 7, which makes it suitable for water treatment. The kinetic study reveals that the F- adsorption on bauxite surface followed first order. The bauxite has also shown encouraging results with ground water sample collected from villages nearby hot water springs in Orissa, India. Since bauxite is an abundantly available mineral in many parts of the world, it can provide a simple, effective and yet low cost method for removing Fluoride from contaminated water

Nigamananda Das et al. (2005) studied the potential of activated titanium rich bauxite for adsorptive removal of excess fluoride from drinking water. They have concluded that bauxite can be thermally activated to a be a adsorbent. The optimum temperature of thermal activation for maximum adsorption capacity is found in between 300 to $450^0$ C. The uptake of fluoride is dependent on contact time, pH and concentration of adsorbate, pH remains the most important factor.

*1.4 Adsorption using iron based adsorbent*

Bhatnagar et al. (2011) stated that iron shows better affinity toward the iron. Maximum adsorption occurred at the pH of 3.7 and decreased with increase in pH. At the pH attribute 3.7, the intensity of fluoride was attributed to the weak ionized character of HF, because a fraction of fluoride becomes unavailable for adsorption. However, at pH > 3.7, the reactive sites became undeveloped due to lack of fluoride became undeveloped due to lack of fluoride adsorption due to increased negative reaction between fluoride ions and deprotonated sites negatively charged.

*1.5 Adsorption using calcium based adsorbent*

Nath and Dutta (2010) have investigated the defluoridation capability of crushed limestones approximately 3-4 mm diameter for pre acidified fluoride water by acetic acid (AA) and citric acid (CA) in batch study. The CA (0.05M) and AA (0.033M) reduced the fluoride concentration from 10 to 1.5 mg/l with the contact time of 12 hours without affecting the taste and odor of water having pH 5.7 to 7. Further they have studied the limestone defluoridation in a fixed bed reactor for fluoride water pre-acidified with edible organic acids, viz. Acetic acid (AA) and citric acid (CC). The fluoride removal process was enhanced by both the acid treatment such as AA and CC and remove up to 90% from 10 mg/l fluoride containing distilled water and ground water.

Fan et al. (2003) studied fluoride adsorption on to a number of minerals such as fluorite, calcite, quartz, iron activated quartz and compared their fluoride uptake capacities. Fan et al. (2007) took advantage of the extremely sensitive analysis available for the radioisotope $^{18}$F ($10^{-13}$ mg) to look closely at the deposition of fluoride on calcite, hydroxyapatite and fluorite along with quartz and iron (III)-activated quartz from very dilute solution (0.025–6.34 ppb). Their experimental data suggested that among the selected materials, calcite is a surface fluoride adsorbent within that low fluoride concentration range and less effective than all the other solids except untreated quartz. The fluoride did not appear to exchange with carbonate beyond an initial surface reaction.

Turner et al. (2005) extended this lead to a range of fluoride concentrations in which the solubility product of calcium fluoride is readily exceeded. Results indicated that fluoride adsorption occurs immediately over the entire calcite surface with fluorite precipitating at step edges and kinks, where dissolved Ca2þ concentration is highest. Surface-sensitive techniques, including atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) as well as z potential measurements, confirmed that although precipitation occurred so did adsorption.

*2. Membrane techniques*

Membrane techniques comprising of reverse osmosis, nanofiltration, dialysis and electro-dialysis are briefly discussed in the following sections:

*2.1 Reverse osmosis(RO) and nanofiltration*

RO is a physical process in which the anions are removed by applying pressure on the feed water to direct it through the semi permeable membrane. RO works at higher pressure with more prominent rejection of dissolved solids. The membrane rejects the ions taking into account the size and electrical charge. RO membrane process is the reverse of natural osmosis as a consequence of applied hydraulic pressure to the high concentration side of the solution, it forces solvent filter through the membrane, against a pressure gradient into the lower-concentration solution. In RO, utilizing a mechanical pump, pressure is applied to a solution via one side of the semi-permeable membrane to overcome inalienable osmotic pressure. The process likewise removes soluble and particulate matter, incorporating salt from seawater in desalination. In the 80's, RO membrane separation technique was effectively connected for the treatment of industrial wastewater particularly for the removal and recovery of fluoride from its effluents. More than 90% of fluoride can be removed regardless of initial fluoride concentration using RO membrane separation process.

Ndiaye et al. was utilized RO separation process for defluoridation of industrial wastewater observed that the rejection of fluoride ion was regularly higher than 98%, considering that the RO membrane was completely recovered after every arrangement of analyses. Berhanu Assefa et al. concentrated the fluoride retention of RO membranes of Ethiopian Rift Region were in the range of 94 to 99 %. Diawara et al. utilized low pressure reverse osmosis for removing fluoride and salinity of brackish ground water of Senegal village where 97 to 98.9% of fluoride rejection happened. Gedam et al. study uncovered that 95 to 98 % of fluoride was removed from ground water of Moradgaon village of Chandrapur district by using Polyamide RO membrane.

*2.1.2. Dialysis and electro-dialysis*

Dialysis separates solutes by transport of the solutes through a membrane rather than using a membrane to retain the solutes while water passes through it as in reverse osmosis and nanofiltration. The membrane pores are much less restrictive than those for nanofiltration, and the solute can be driven through by either the Donnan effect (Donnan, Hichour et al. (1999) studied the Donnan dialysis process in a counter current flow system in which the anion-exchange membrane was loaded with sodium chloride and the feed was 0.001 M NaF together with other sodium salts. Fluoride migrated into the receiver as other ions migrated into the feed. This technique was later used to defluoridate solutions made to simulate high fluoride African ground waters (>30 mg/L fluoride) and whatever other ions were present the fluoride in the feed could be brought below 1.5 mg/L (Hichour et al., 2000)

**CONCLUSION:**

In the paper, the various techniques for the removal of fluoride from water have been reviewed. Their results and conclusions are discussed in the paper. As a whole, it can be stated that the choosing a technique for removal of fluoride depends on various factors. Funds are the major factor which governs the selection of method for removal of fluoride. Rural areas are mostly affected by fluoride contamination. Due to non-availability of funds expensive techniques can't be selected for the removal of fluoride. Further studies can be done on cheap techniques for removal of fluoride.

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