

# Application of nanostructured materials in fluoride removal from contaminated groundwater

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**Abstract:** Fluoride is a water pollutant of great environmental concern due to its wide abundance and devastating effects on human health. Defluoridation of drinking water is one of the effective solutions for mitigating fluoride pollution. Extensive research has been done so far on various methods for removal of fluoride from water and wastewater. Precipitation processes involve the addition of chemicals and formation of fluoride precipitates. Strong base exchange resins remove fluorides either on hydroxyl cycle or chloride cycle along with anions. Researchers had paid their attention on adsorption technology since last two decades for fluoride removal. Adsorption processes are generally more popular because of their efficiency, convenience, simplicity of design and for their eco-friendly nature. Adsorbents used in fluoride removal are bone charcoal, tricalcium phosphate, florex, activated carbon, magnesia, activated alumina, plant materials, limestone, special soils and clay, fly ash etc. Nanomaterials have gained attention recently and have been widely used as sorbents due to properties such as high surface-to-volume ratio and short diffusion route. Hydrous titanium dioxide ( $\text{TiO}_2$ ), Aluminum–cerium (Al–Ce) hybrid adsorbent, Aluminium hydroxide impregnated limestone, sulfate-doped  $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$  nanoparticles,  $\text{Fe}_3\text{O}_4$  nanoparticles were used for fluoride removal. Micro/nano-hierarchical web consisting of activated carbon fibres and carbon nano fibres impregnated with Al used as an adsorbent for fluoride removal from wastewater. The future research should be focused on evaluating the efficiency of adsorbents in terms of cost and feasibility for removal of fluoride.

**Key words:** Fluoride, Adsorption, Nanomaterials, Remediation, Groundwater

## 1. INTRODUCTION

Fluoride is a water pollutant of great environmental concern due to its wide abundance and devastating effects on human health. Fluoride releases into the environment naturally through the weathering and dissolution of minerals, in emissions from volcanoes and in marine aerosols, via coal combustion and from industrial wastes (Ayoob and Gupta, 2006). WHO has prescribed the range of fluoride from 0.6 to 1.5mg/l in drinking water as suitable for human consumption (WHO, 1984, 2002). WHO estimated that more than 260 million people living all over the world consume water with fluoride concentration above 1mg/l.

High fluoride contents in the groundwater have been found in many parts of the developing countries and fluorosis is endemic in around 25 countries of the world. The affected zones include arid parts of northern China, India, Srilanka, African countries, Northern Mexico and central Argentina. Out of 85 million tons of fluoride deposits on the earth's crust, 12 million are found in India (Teotia and Teotia, 1994). In India, about 62 million people in 17 states are affected with dental, skeletal and or non-skeletal fluorosis (Susheela, 1999). Out of 6 lakh villages in India, atleast 50% have fluoride content in groundwater with a concentration more than 1.0 ppm (Gupta, 1995). Many rivers flowing through different states of India are reported to have fluoride contents varying from 0.1 to 12.0 ppm (Bulusu et al., 1979).

Very low doses of fluoride (<0.6 mg/l) in water can induce tooth decay. However, higher doses (>1.5 mg/l), can lead to dental fluorosis or mottled enamel and excessively high concentration (>3.0 mg/l) of fluoride may cause skeletal fluorosis (Yadav and Khan, 2010). General clinical symptoms includes severe pain in the backbone and joints, muscle weakness, increased density of bones, arthritis, brittle bones, paralysis, cancer, infertility, brain damage, thyroid disorder etc.

During later stages, calcification of the bones takes place, osteoporosis in long bones and symptoms of osteosclerosis can be seen where the bones become denser and develop abnormal crystalline structure. (Ibrahim et al., 2011).

## 2. FLUORIDE REMOVAL TECHNOLOGIES: NANOMATERIAL APPLICATION

Fluoride poisoning can be prevented or minimized by using alternative water sources (surface water, rainwater, and low-fluoride groundwater), by improving the nutritional status of populations at risk and by removing excessive fluoride from drinking water. Defluoridation of groundwater is one of the feasible options to overcome the problem of excessive fluoride in drinking water. The methods developed for this purpose are divided as follows depending upon the mode of action.

### 2.1 Based on precipitation–coagulation (*Nalgonda technique*)

Precipitation processes involve the addition of chemicals and formation of fluoride precipitates. Among these, one of the effective methods are precipitations with calcium and aluminium salts. Precipitation chemicals must be added daily in batches and precipitation techniques produce a certain amount of sludge every day. Lime and alum are the most commonly used coagulants (John, 1996; Parker and Fong, 1975). Nalgonda Technique is an economical and simple method for fluoride removal which involves addition of aluminium salts, lime and bleaching powder followed by rapid mixing, flocculation, sedimentation, filtration and disinfection (Nawalakhe et al., 1975). Aluminium salt is only responsible for removal of fluoride from water. Lime facilitates the formation of dense floc for rapid settling.

However, the process removes only a smaller portion of fluoride (18–33%) in the form of precipitates and converts a greater portion of ionic fluoride (67–82%) into soluble aluminium fluoride complex ion, which is a neurotoxin. Hence adoption of Nalgonda technique for defluoridation of water is not desirable. The residual aluminium in excess of  $0.2 \text{ mg.L}^{-1}$  in treated water can cause pathophysiological, neurobehavioral, structural and biochemical changes (Nayak, 2002). The maintenance cost of the plant is very high, and the process is not automatic and large space is required for the drying of sludge (Meenakshi and Maheshwari, 2006).

### 2.2 Based on electrochemical method

A technology of defluoridation through electrochemical route has been developed. The process utilizes  $0.3$  to  $0.6 \text{ kw.h}^{-1}$  of electricity per  $1000 \text{ L}$  of water containing  $5$ -  $10 \text{ mg.L}^{-1}$  of fluoride. The anode is continuously consumed and needs to be replenished. The process generates sludge at the rate of  $80$  -  $100 \text{ g}$  per  $1000 \text{ L}$  (on dry basis). However, high cost of electricity in third world countries like India makes the use of this method unsuitable (Feng et al., 2003).

### 2.3 Based on Ion exchange mechanism

Strong Base Exchange resins remove fluorides either on hydroxyl cycle or chloride cycle along with anions (Runaska et al., 1951). Some inorganic ion exchangers, eg. complex metal chloride silicates, formed from barium or ferric chloride with silicic acid, also exchanged fluoride for chloride. Polystyrene anion exchange resins and strongly basic quaternary ammonium type resins are known to remove fluorides from water along with other anions.

Cation exchange resins impregnable with alum solution have been found to act as defluoridating agents. “Avaram bark” based cation exchange resin works effectively in removing fluoride from water (Meenakshi and Maheshwari, 2006). Few examples of ion exchange resins are given in Table 1.

*Table 1. Fluoride removing ion exchange resins*

<b>Anion exchange resins</b>	<b>Cation exchange resins</b>
Tulsion, A-27	Carbion
Deaceodite, FF-1P	Wasoresin-14
Lewatit, MIH-59	Polysteren resin
Amberlite, IRA-400	Sulphonated saw dust carbon

However, the process has some limitations like the efficiency is reduced in presence of sulphate, carbonate, phosphate and alkalinity; regeneration of resin is a problem because it leads to fluoride rich waste, which has to be treated separately before final disposal; the technique is expensive because of the high cost of resin; pre-treatment required to maintain the pH, regeneration and waste disposal; treated water has a very low pH and high levels of chloride; the process can make the water totally demineralised and hence is not hygienic.

#### **2.4 Based on membrane process**

In spite of various conventional techniques of defluoridation described earlier, the reverse osmosis (RO) membrane process has emerged as a preferred alternative to provide safe drinking water without posing the problems associated with other conventional methods (Pervov et al., 2000). Applications of reverse osmosis to purification of water are discussed by several researchers (Schneider and Middlebrooks, 1983). Nanofiltration makes use of the same overall phenomenon as reverse osmosis. For nanofiltration, the membranes have slightly larger pores than those used for reverse osmosis and offer less resistance to passage both of solvent and of solutes. As a consequence, pressures required are much lower, energy requirements are less, removal of solutes is much less exhaustive, and flows are faster. 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, 1911) or an applied electric field.

The process has some limitations like it removes all the ions present in water, hence, some essential minerals are also removed and remineralisation is required after treatment. The process is also comparatively expensive; the water can become acidic and needs pH correction; huge amount of water gets wasted as brine which has disposal issues.

#### **2.5 Based on adsorption process**

Many researchers are being focused on adsorption technology since last two decades for contaminated ground and surface water treatment. Adsorption appears to be an effective method for fluoride removal because it is eco-friendly, simple and cost effective option for the common people using groundwater as a main source. Activated alumina, activated carbon, activated alumina coated silica gel, calcite, activated saw dust, activated coconut shell carbon and activated fly ash, groundnut shell, coffee husk, rice husk, magnesia, serpentine, tricalcium phosphate, bone charcoal, activated soil sorbent, carbion, defluoron-1, defluoron-2, etc. are different kinds of adsorbents reported in the previous research works (Min et al., 1999; Wang and Reardon, 2001; Nava et al., 2003). Several bone formulations, synthetic tricalcium phosphate and hydroxy apatite etc. were investigated for their fluoride removal efficiency.

Biosorption is an emerging technique for water treatment utilizing abundantly available biomaterials. Various biosorbents have been developed for fluoride removal. Chitin and chitosan are attractive adsorbents because of their unique properties like biodegradability, biocompatibility and low cost, in addition to their particular physical and mechanical properties, resulting from the presence of chemical reactive groups (hydroxyl, acetamido or amino functions) in polymer chains (Yao et al., 2009).

Sujana et al. (2013) synthesized new biopolymer beads, composite of hydrous ferric oxide (HFO) and alginate, characterized and examined it, with aim of fluoride removal from water. The authors concluded that pH had significant effect on fluoride adsorption efficiency of the beads. The biomass of the natural plant *Tinospora cordifolia* demonstrated a good capacity of fluoride biosorption, highlighting its potential for the drinking water treatment process (Pandey et al., 2012). Fungal biosorbent prepared from *Fusarium moniliforme* for removal of fluoride was investigated by Merugu et al. (2012). A new type of adsorbent was prepared from orange waste by a simple method of saponification reaction with lime water and used for the removal of some metal ions and, after that, for fluoride removal from water (Paudyal et al., 2012). Gopal et al. (2004) and Yadav et al. (2013) studied the removal of fluoride from water using sawdust, groundnut husk and sand. The obtained results indicate that these chemically treated natural adsorbents can remove fluoride effectively. Conducting the experiments on water defluoridation with bauxite, Sajidu et al. (2008) reported that up to 93.8% fluoride was removed from fluoride solution with initial concentration of 8 mg/L when adsorbent dose of 2.5 g/200 mL were used. Sivasankar et al. (2010) showed the defluoridation capacities of activated tamarind fruit shell (ATFS) and MnO<sub>2</sub> coated tamarind fruit shell (MTFS). Alagumuthu and Rajan (2010) studied zirconium-impregnated cashew nut shell carbon (ZICNSC) to assess its capacity for the adsorption of fluoride from aqueous solutions. The method is simple and has shown great potential for the removal of fluoride ions.

## 2.6 Use of nanostructured materials

Nanomaterials are fast emerging as potent candidates for water treatment in place of conventional technologies because of their low cost and high efficiency. This would be beneficial for developing nations like India and Bangladesh. Nanoparticles can be used as potent sorbents as separation media, as catalysts for photochemical destruction of contaminants; nano-size zerovalent iron used for the removal of metals and organic compounds from water and nanofiltration membranes (Savage and Diallo, 2005).

Adsorption of fluoride on to solid adsorbent usually occurs through three phases (Mohapatra et al., 2009; Fan et al., 2003):

1. Diffusion or transport of fluoride ions to the external surface of the adsorbent from bulk solution across the boundary layer surrounding the adsorbent particle, called external mass transfer;
2. Adsorption of fluoride ions on to particle surfaces;
3. The adsorbed fluoride ions probably exchange with the structural elements inside adsorbent particles depending on the chemistry of solids, or the adsorbed fluoride ions are transferred to the internal surfaces for porous materials (intra particle diffusion).

Many researchers reported successfully fluoride remediation using different metal oxides and hydroxides characterized by high surface area and numerous of them have used iron oxide as an adsorbent to treat heavy metals, anions, and hazardous elements in wastewater (Huang et al., 2011). Hydrous titanium dioxide (TiO<sub>2</sub>) has been found to be a potential selective adsorbent for fluoride ions, as well as halogens and arsenic compounds. Chen et al. (2012) investigated the possibility of fluoride removal using a nano-adsorbent bimetallic oxide adsorbent synthesized by co-precipitation of Fe(II) and Ti(IV) sulfate solution using ammonia titration at room temperature. Goswami and Purkait (2012) applied acidic alumina for adsorbing fluoride from water and found it to be highly pH dependent with 94% fluoride removal efficiency at pH value of 4.4. The defluoridation capacity of alumina with alkoxide origin varied from 3.14 to 0.59 mg/g for dosage varying from 0.5 to 8 g/L (Kamble et al., 2010). A modified immobilized activated alumina (MIAA) using alum through the sol gel process was prepared, which gave a performance 1.35 times better than unmodified immobilized alumina and the removal rate was also comparatively faster (Rafique et al., 2012). Other modified forms of AA used for fluoride removal include modification by using different metals such as magnesia, manganese oxide, manganese dioxide, cerium and titanium. Aluminum–

cerium (Al–Ce) hybrid adsorbent was synthesized through the co-precipitation method, which had high sorption capacity up to 27.5 mg/g for fluoride at equilibrium fluoride concentration of 1 mg/L (Liu et al., 2010). Since, aluminium has the highest affinity for fluoride ions; calcium based adsorbents impregnated or doped with aluminium, aluminum oxide or aluminate is being developed to increase the defluoridation capacity. Aluminium hydroxide impregnated limestone (AILS) was prepared and defluoridation experiments were performed (Jain and Jayaram, 2009). The highest adsorption capacity shown by limestone was 43.10 mg/g; while in case of AILS sorbent it increased to 84.03 mg/g.

Iron and aluminum binary oxide ( $\text{FeAlO}_x\text{Hy}$ ), aluminum oxyhydroxide ( $\text{AlO}_x\text{Hy}$ ) and iron oxyhydroxide ( $\text{FeO}_x\text{Hy}$ ) were investigated with the aim to evaluate their removal efficacy towards arsenate and fluoride, to determine the effects of pH and the ratios of iron to aluminum on the removal of arsenate and fluoride, and finally, to investigate the competitive adsorption between arsenate and fluoride onto  $\text{FeAlO}_x\text{Hy}$  (Liu et al., 2012). Magnesium-doped nano ferrihydrite was used for fluoride removal by Mohapatra et al. (2012). The preliminary test showed that increase of Mg content on nano ferrihydrite from 0.39% to 0.98% increased fluoride removal from 66% to 91%. Poursaberi et al. (2012) synthesized adsorbent for fluoride removal using  $\text{Fe}_3\text{O}_4$  nanoparticles, obtained by co-precipitation of ferrous and ferric ions in a 3-aminopropyl triethoxysilane and additionally functionalized them using a zirconium(IV) porphyrin complex. A granular zirconium-iron oxide composed of amorphous and nano-scale oxide particles were prepared and their adsorption characteristics in fluoride removal were investigated by Dou et al. (2011). Due to the results of batch tests, the authors reported a high adsorption capacity of 9.80 mg/g under an equilibrium concentration of 10 mg/L and at pH = 7.0, and efficient fluoride removal over a wide pH range (3.5–8.0), especially between pH 6.0 and 8.0. Fluoride removal efficiency of  $\text{CeO}_2\text{-ZrO}_2$  nanocages prepared by Kirkendall effect and a study of its structure was conducted by Wang et al. (2013). Due to results of batch adsorption study, the porous  $\text{CeO}_2\text{-ZrO}_2$  nanocages showed the maximum capacity was calculated to be 175 mg/g at pH = 4.0 and isotherm are described well by the Langmuir model. The synthesized Fe–Al–Ce trimetal hydroxide adsorbent (Fe–Al–Ce) obtained by spraying of a Fe–Al–Ce nano-adsorbent suspension onto glass beads with acrylic-styrene copolymer latex used as a binder was used for fluoride removal from drinking water by Chen et al. (2011).

Few carbon based sorbents have also been explored for fluoride removal by some researchers. Carbon nanotubes (CNTs) have huge potential since their discovery. Their small sizes, large surface area, high mechanical strength and remarkable electrical conductivity properties make them useful materials for water remediation. Gupta et al. (2009) developed a micronanohierarchical web (MiNaHiWe) consisting of activated carbon fibers (ACF) and carbon nanofibers (CNF), impregnated with Al for the removal of fluoride from wastewater. Various grades of graphite have also been used as adsorbents and tested for the removal of fluoride from aqueous solution (Karthikeyan and Elango, 2008). Adsorbent exhibited commendable fluoride sorption in wide pH range.

Graphene is a single flat atomic sheet of carbon with the atoms arranged in a two-dimensional (2D) honeycomb configuration (Romero et al., 2009). Graphene has drawn much scientific attention since its discovery and exhibits great promise for potential applications in developing field-effect transistors, solar cells, sensors, and adsorbent for heavy metal removal. The adsorption capacities and rates of fluoride onto graphene at different initial pH, contact time, and temperature were evaluated by Li et al. (2011). The experimental results showed that graphene is an excellent fluoride adsorbent with an adsorption capacity of up to 17.65 mg/g at initial fluoride concentration of 25 mg/L and temperature of 25 °C.

### 3. CONCLUSIONS

Various technologies are currently applied for fluoride removal from groundwater, however, adsorption processes are generally more popular because of their efficiency, convenience,

simplicity of design and for their eco-friendly nature. Performance comparison of different adsorbents is difficult because of the inconsistent data due to different experimental conditions.

The reuse and recycling perspectives are essential in case of developing an efficient adsorbent for defluoridation of drinking water. However, very few researchers have considered these perspectives in their research works. Many natural adsorbents are considered to be inexpensive, but it is difficult to regenerate most of these adsorbents due to complexity in their structures. Presence of residual ions from metal adsorbents used for water treatment is a major area of concern. A particular sorbent which can show high adsorption of fluoride in the laboratory may fail to do so in field conditions. Hence, the selection of the appropriate technology/sorbent media would be essential for remediation purpose.

Adopting a particular method of fluoride remediation depends on the initial fluoride concentration, source and cost effectiveness in an area. Communities should be educated and encouraged to actively participate in the technical and management systems of fluoride remediation. Development of community based defluoridation unit is needed for rural areas with an adsorbent which is cost effective, technologically simple in operation while is able to keep the fluoride level in permissible limit.

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