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Fluoride in Drinking Water and Defluoridation of Water

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1. INTRODUCTION

1.1. Fluoride in Water

Water is an essential natural resource for sustaining life. Water is certainly not free everywhere. However, chemical composition of surface or subsurface is one of the prime factors on which the suitability of water for domestic, industrial, or agricultural purpose depends. Though groundwater contributes only 0.6% of the total water resources on earth, it is the major and preferred source of drinking water in rural as well as urban areas, particularly in developing countries like India. It caters to 80% of the total drinking water requirement and 50% of the agricultural requirement in rural India. However, in the current era of economical growth, groundwater is getting polluted due to urbanization and industrialization in addition to geogenic contamination. Anions are commonly present in water; however, some of the anions including oxy-anions are undesired and often responsible for serious environmental and health problems. Fluoride is one of the most abundant anions present in groundwater worldwide and creates a major problem in safe drinking water supply. Fluorine is the most electronegative and reactive among all the elements in the periodic table. Because of its great reactivity, fluorine cannot be found in nature in its elemental state. It exists either as inorganic fluorides (including the free anion F^-) or as organic fluoride compounds, always exhibiting an oxidation number of -1. In the environment, inorganic fluorides are much more abundant than organic fluoride compounds.

Fluorides in drinking water may be beneficial or detrimental depending on their concentration and total amount ingested. Fluoride is beneficial especially to young children for calcification of dental enamel below eight years of age when present within permissible limits of 1.0−1.5 mg/L. An excess of fluoride in drinking water causes dental fluorosis and/or skeletal fluorosis.[1] Indian standards for drinking water recommend an acceptable fluoride concentration of 1.0 mg/L and an allowable fluoride concentration of 1.5 mg/L in potable waters (BIS 10500, 1991).[2]

The problem of excess fluoride in drinking water is growing day by day, as noted by a growing number of surveys to assess the groundwater quality that have been undertaken. Fluoride in water derives mainly from dissolution of natural minerals in the rocks and soils with which water interacts. Reaction times with aquifer minerals are also important. High fluoride concentrations can be built up in groundwaters, which have long residence times in the host aquifers. Surface waters usually have low concentrations, as do shallow groundwater from hand-dug wells as they represent young, recently infiltrated, rainwater. High fluoride concentrations are also a feature of arid

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Table 1. Districts Showing Fluoride Concentration > 1.5 mg/L in Groundwater in India in 2010

states	districts	range of F (mg/L)
Assam	Goalpara, Kamrup, Karbi Anglong, and Nagaon	1.45−7.8
Andhra Pradesh	Adilabad, Anantpur, Chittoor, Guntur, Hyderabad, Karimnagar, Khammam, Krishna, Kurnool, Mahbubnagar, Medak, and Nalgonda	1.8−8.4
Bihar	Aurangabad, Banka, Buxar, Jamui, Kaimur(Bhabua), Munger, Nawada, Rohtas, and Supaul	1.7−2.85
Chhattisgarh	Bastar, Bilaspur, Dantewada, Janjgir-Champa, Jashpur, Kanker, Korba, Koriya, Mahasamund, Raipur, Rajnandgaon, and Surguja	1.5−2.7
Delhi	East Delhi, North West Delhi, South Delhi, South West Delhi, West Delhi, Kanjhwala, Najafgarh, and Alipur	1.57−6.10
Gujarat	Ahmadabad, Amreli, Anand, Banaskantha, Bharuch, Bhavnagar, Dohad, Junagadh, Kachchh, Mehsana, Narmada, Panchmahals, Patan, Rajkot, Sabarkantha, Surat, Surendranagar, and Vadodara	1.6−6.8
Haryana	Bhiwani, Faridabad, Gurgaon, Hissar, Jhajjar, Jind, Kaithal, Kurushetra, Mahendragarh, Panipat, Rewari, Rohtak, Sirsa, and Sonepat	1.5−17
Jammu and Kashmir	Doda, Rajauri, and Udhampur	2.0−4. 21
Karnataka	Bagalkot, Bangalore, Belgaun, Bellary, Bidar, Bijapur, Chamarajanagar, Chikmagalur, Chitradurga, Davangere, Dharwad, Gadag, Gulburga, Haveri, Kolar, Koppal, Mandya, Mysore, Raichur, and Tumkur	1.5−4.4
Kerala	Palakkad, Palghat, Allepy, Vamanapuram, and Alappuzha	2.5−5.7
Maharashtra	Amravati, Chandrapur, Dhule, Gadchiroli, Gondia, Jalna, Nagpur, and Nanded	1.51−4.01
Madhya Pradesh	Bhind, Chhatarpur, Chhindwara, Datia, Dewas, Dhar, Guna, Gwalior, Harda, Jabalpur, Jhabua, Khargaon, Mandsaur, Rajgarh, Satna, Seoni, Shajapur, Sheopur, and Sidhi	1.5−10.7
Orissa	Angul, Balasore, Bargarh, Bhadrak, Bandh, Cuttack, Deogarh, Dhenkanal, Jajpur, Keonjhar, and Sonapur	1.52−5.2
Punjab	Amritsar, Bhatinda, Faridkot, Fatehgarh Sahib, Firozepur, Gurdaspur, Mansa, Moga, Muktsar, Patiala, and Sangrur	0.44−6.0
Rajasthan	Ajmer, Alwar, Banaswara, Barmer, Bharatpur, Bhilwara, Bikaner, Bundi, Chittaurgarh, Churu, Dausa, Dhaulpur, Dungarpur, Ganganagar, Hanumangarh, Jaipur, Jaisalmer, Jalor, Jhunjhunun, Jodhpur, Karauli, Kota, Nagaur, Pali, Rajsamand, Sirohi, Sikar, SawaiMadhopur, Tonk, and Udaipur	1.54−11.3
Tamilnadu	Coimbatore, Dharmapuri, Dindigul, Erode, Karur, Krishnagiri, Namakkal, Perambalur, Puddukotai, Ramanathapuram, Salem, Sivaganga, Theni, Thiruvannamalai, Tiruchirapally, Vellore, and Virudhunagar	1.5−3.8
Uttar Pradesh	Agra, Aligarh, Etah, Firozabad, Jaunpur, Kannauj, Mahamaya Nagar, Mainpuri, Mathura, and Mau	1.5−3.11
West Bengal	Bankura, Bardhaman, Birbhum, Dakshindinajpur, Malda, Nadia, Purulia, and Uttardinajpur	1.5−9.1

climatic conditions. Here, groundwater flow is slow and reaction times between water and rocks are therefore enhanced. Fluoride buildup is less pronounced in the humid tropics because of high rainfall inputs and their diluting effect on groundwater chemical composition. However, in tropical countries like India, the problem of excessive fluoride is more severe, particularly in arid parts of the country. Beside natural sources, fluoride ions can also be found in effluents from semiconductor, metal processing, fertilizers, and glass-manufacturing industries.[3−7] The discharge of such wastewater into the surface water would lead to increased levels of fluorides in surface and groundwater.

1.2. Global and Indian Scenario

1.2.1. International Status. The problem of excessive fluoride in drinking water has engulfed many parts of the world, and today many millions of people rely on groundwater with concentrations above the World Health Organization (WHO) guideline value.[8] There are >20 developed and developing nations in which fluorosis is endemic.[9] High fluoride concentrations in groundwater are also found in the USA, Africa, and Asia.[10,11] The most severe problem associated with high fluoride waters occurs in China,[12] India,[13] Sri Lanka,[14] and Rift Valley countries in Africa. High fluoride ground waters have been studied in detail in Africa, in particular in Kenya and Tanzania.[15−19] High fluoride groundwater is also found in the East Upper Region of Ghana.[20] In the early 1980s, it was estimated that ∼260 million people worldwide (in 30 countries) were drinking water with >1 mg/L of fluoride.[21]

1.2.2. Current Status in India. In India, fluoride was first detected in drinking water at Nellore district of Andhra Pradesh in 1937.[9] Since then, considerable work has been done in different parts of India to explore the fluoride-laden water sources and their impacts on human as well on animal health. At present, it has been estimated that fluorosis is prevalent in 17 states of India, indicating that endemic fluorosis is one of the most alarming public health problem of the country, especially in Rajasthan, Madhya Pradesh, Andhra Pradesh, Tamil Nadu, Gujarat, and Uttar Pradesh.[9] At present, in India, endemic fluorosis is thought to affect ∼1 million people.[22,23] We have also conducted exhaustive water sampling in Dhar district of Madhya Pradesh, India, to assess the distribution of fluoride in groundwater. Fluoride concentrations in a large number of samples are >1.5 mg/L (WHO prescribed limit for drinking water), and the maximum concentrations found were 12.0 mg/L. The two important issues that need to be addressed immediately include the health effects and bottlenecks or problems associated with existing remediation technologies. Districts known to be endemic for fluoride in various states of India and the ranges of fluoride in drinking water are given in Table 1.[23]

Table 2. Food Containing High Fluoride Concentrations[24]

food items	fluoride conc. (mg/L)
Camella Sinensis (tea dry leaves)	39.8−68.59
Areca Catechu (supari)	3.8−12.0
beetle leaf (pan ka patta)	7.8−12.0
tobacco	3.1−38
cardamom (Ilaichi)	14.4
black and rock salt	14−200
cereals and tubers	
wheat	3.27−14.03
rice	1.72−2.23
maize	5.6
pulses and legumes	
Bengal Gram	3.84−4.84
pulses and legumes	5.6
green gram dal	2.5
red gram dal	3.7
soyabean	4.0
vegetables	
cabbage	1.28−2.29
tomato	3.4
cucumber	4.1
lady finger	4.0
spinach	0.77−4.14
lettuce	5.7
mint	4.8
potato	2.8
carrot	4.1
amaranth leaves	4.91−7.14
bathua leaves	6.3
chowli leaves	1.79−7.33
Brinjal	1.62−2.48
snake guard	2.16−3.44
nuts and oil seeds	
almond	4.0
coconut	4.4
mustard seeds	5.7
groundnut	5.1
beverages	60−112
tea	0.77−1.44
carbonated drinks	
spices and condiments	2.3
coriander leaves	5.0
garlic	3.3
turmeric	1.8
cumin seeds	
food from animal sources	3.0−3.5
mutton	4.0−5.0
beef	3.0−4.5
pork	1.0−6.5
fishes	
fruits	3.7
mango	5.7
apple	5.1
guava	0.84−1.74
grapes	4.5
dates	0.84−1.58
banana	2.9

1.3. Sources of Fluoride and Exposure to Fluoride

1.3.1. Sources of Fluoride in Environment. Fluoride in water derives mainly from dissolution of minerals in the rocks and soils with which water interacts. Usually the surface water is not contaminated with high fluoride, whereas groundwater may be contaminated with high fluoride because the usual source of fluoride is fluoride-rich rocks. When water percolates through rocks, it leaches out the fluoride from these rocks. The rocks rich in fluoride are as follows:

- Fluorospar, CaF_2 (sedimentary rocks, limestones, and sandstones);
- Cryolite, Na_3AlFPO_6 (igneous and granite); and
- Fluorapatite, $Ca_3(PO)_2 \cdot Ca(FCl)_2$

1.3.2. Routes of Fluoride Uptake in Human. Water, air, food, drugs, and cosmetics are the main sources of fluoride for humans. The major sources of ingested fluoride are water and other dietary sources.

1.3.2.1. Water. Although there are several sources of fluoride intake, it is roughly estimated that 60% of the total intake is through drinking water. This is the most accessible form of fluoride and, hence, the most toxic. In groundwater, the natural concentration of fluoride depends on the geological, chemical, and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, the temperature, the action of other chemicals, and the depth of wells.

1.3.2.2. Food. Almost all the food items contain at least traces of fluoride. The fluoride of food items depends upon the fluoride contents of the soil and water used for irrigation; therefore, the fluoride content of the food items may vary from place to place.[24] One potentially dangerous source of fluoride is tea. The details of fluoride-rich food have been given in Table 2.

1.3.2.3. Drugs. Prolonged use of certain drugs has been associated with chronic adverse effects of fluoride, e.g., sodium fluoride for treatment of osteoporosis, Niflumic acid for the treatment of rheumatoid arthritis, and use of fluoride-based mouthwash.

1.3.2.4. Air. The use of fluorides in industry leads to occupational exposure, e.g., inorganic fluoride compounds are used in the production of aluminum. Fluorides are also released during the manufacture and use of phosphate fertilizers.

1.3.2.5. Cosmetics. Estimated fluoride ingestion from toothpaste is significantly high and known to cause fluorosis. The fluoride content arising from the raw materials used for the manufacturing of toothpaste like calcium carbonate, talc, and chalk has a consequent increase in fluoride levels of toothpaste as high as 800−1000 mg/L. In the fluoridated brands, there is a deliberate addition of fluoride, which may range from 1000 to 4000 mg/L.

1.3.2.6. Other. Human activities, such as aluminum smelters, discharges of fluoridated municipal waters, and plants manufacturing brick, ceramics, glass, and fluoride chemicals, may cause a significant increase in the fluoride concentration of surface waters. There are large numbers of industrial sources of fluoride including semiconductor and integrated circuits manufacturing, hydrofluoric acid plants, phosphate fertilizer plants, etc.

1.4. Health Effects

Fluoride, being a highly electronegative ion, has an extraordinary tendency to get attracted by positively charged ions like calcium. Hence, the effect of fluoride on mineralized tissues like bone and teeth leading to developmental alternations is of clinical significance as they have the highest amount of calcium and thus attract the maximum amount of fluoride that gets deposited as calcium−fluorapatite crystals. Tooth enamel is composed principally of crystalline hydroxyapatite. Under normal conditions, when fluoride is present in the water supply, most of the ingested fluoride ions get incorporated into the apatite crystal lattice of calciferous tissue enamel during its formation. The hydroxyl ion gets substituted by fluoride ion because fluorapatite is more stable than hydroxyapatite. Thus, a large amount of fluoride gets bound in these tissues and only a small amount is excreted. The most common health problems associated with excess fluoride in drinking water are dental and skeletal fluorosis. Endemic fluorosis is known to be global in scope, occurring in all continents and affecting many millions of people. Cases of skeletal fluorosis have been reported all over the world.[25,26] Dental fluorosis leads to pitting, perforation, and chipping of the teeth, whereas skeletal fluorosis causes severe pains in joints followed by stiffness, which ultimately leads to paralysis. However, recent studies have proved that the health effects of fluoride are not only restricted to dental or skeletal fluorosis but also cause other ailments like neurological disorders, muscular and allergic manifestations, and gastrointestinal problems and may also cause lethal diseases like cancer.

1.4.1. Dental Fluorosis. In dental fluorosis, enamel loses its luster due to excessive fluoride intake during permanent dentition, and it mostly affects children. The mild form of dental fluorosis is characterized by chalky white teeth, whereas yellowish-brown pigmentation in the middle of the teeth and severe pitting of the teeth is an indication of the severe form. The effect of dental fluorosis may not be apparent if the teeth are already fully grown prior to the fluoride overexposure. Therefore, the fact that an adult shows no signs of dental fluorosis does not necessarily mean that his or her fluoride intake is within the safety limit.

1.4.2. Skeletal Fluorosis. Skeletal fluorosis affects both children and adults. It does not manifest until the disease attains an advanced stage. In the early stages of skeletal fluorosis, patients complain of arthritic symptoms. Fluoride gets deposited in joints of shoulder bones, neck and pelvic, and knees and makes it difficult to move, walk, and bend. In later stages, skeletal fluorosis is marked by restriction of spine movements and, hence, can be easily diagnosed. The advanced stage is osteoporosis.

1.4.3. Nonskeletal Fluorosis/Other Problems. Besides skeletal and dental fluorosis, excessive consumption of fluoride may lead to muscle fiber degeneration, low hemoglobin levels, deformities in RBCs (red blood corpuscles), excessive thirst, headache, skin rashes, nervousness, neurological manifestations (it affects brain tissue similar to the pathological changes found in humans with Alzheimer's disease), depression, gastrointestinal problems, urinary tract disorders, nausea, abdominal pain, tingling sensation in fingers and toes, reduced immunity, repeated miscarriages or still births, male sterility, etc. It is also responsible for alterations in the functional mechanisms of liver, kidney, digestive system, respiratory system, excretory system, and central nervous system.

1.4.4. Role of Nutrition in Fluorosis. Role of diet in fluorosis is a double-edged sword action. Intake of high fluoride in diet increases the toxic manifestations of fluorosis, whereas intake of diet rich in calcium and vitamin C helps in overcoming the toxicity of fluorosis. There is already convincing evidence to justify the important role of malnutrition and dietary habits on the severity of fluorosis. Dietary fluoride is playing a secondary role in causing fluorosis, whereas the primary role is related to the drinking water fluoride concentration and liquid diets. In food, fluoride is present in two forms: (a) organically bound and (b) inorganic form. The chances of toxicity due to the bound form of fluoride are much less than those due to the inorganic form of fluoride. In water, most of the fluoride is present in the inorganic form, thus making it more harmful than dietary fluoride. The liquid form of food is more prone to have a high content of fluoride in the inorganic form. Chinoy and Dipti indicated that protein supplementation has a beneficial effect on reducing the fluoride-induced liver toxicity and is necessary for recovery from fluoride toxicity.[27] Community-based studies strongly suggest that the calcium status modifies the type of bone changes seen in fluorosis. Jolly et al. have highlighted the role of nutritional factors relative to the different clinical patterns of the skeletal fluorosis seen in various endemic regions in India.[28] The observations of wide variations in the prevalence of both dental and skeletal fluorosis at the same fluoride exposure level make it clear that health and nutritional status plays an important role in fluorosis.[9]

1.5. Standards for Fluoride in Drinking Water

WHO standards and Indian standards for fluoride in drinking water are given in Table 3.

1.6. Existing Remediation Options

1.6.1. Precipitation—Coagulation. Precipitation processes involve the addition of chemicals and the formation of fluoride precipitates. These methods coprecipitate fluoride with aluminum sulfate and lime (Nalgonda technique) or precipitate fluoride with calcium and phosphate compounds. 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 of water up to 11−12.[29]

$$\mathrm{Ca(OH)_2 + 2F^- \rightarrow CaF_2 + 2OH^-}$$

As lime leaves a residue of 8.0 mg F^-/L, it is used only in conjunction with alum treatment to ensure proper fluoride removal.[30,31] As a first step, precipitation 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 aluminum hydroxide ($Al(OH)_3$). In the second reaction, alum reacts with fluoride ions present in the water. Optimal fluoride removal is accomplished in the pH range of 5.5 −7.5.[32]

The Nalgonda process developed by NEERI is one of the most widely used defluoridation method in India, particularly at the community level.[33−35] The bucket defluoridation system based on the Nalgonda technique has also been developed for domestic use.[18] This process is suitable for a daily routine, where one bucket of water is treated for one day's water supply of ~20 L. The process produces water with residual fluoride between 1 and 1.5 mg/L.[36] Fill-and-draw type defluoridation systems based on the Nalgonda technique have also been reported.[18] However, coprecipitation methods based on aluminum salts have some advantages and limitations as below:

Advantages:

- Established method;
- Most widely used method, particularly at the community level.

Table 3. Standards for Fluoride in Drinking Water

agency/sources	desired limit/ guideline value (mg/L)
Indian standards drinking water specifications 1992, reaffirmed 1993 IS:10500	1.0 (desired limit) 1.5 (permissible limit in the absence of other source)
WHO guidelines Third edition, vol. 1 recommendations 2004	1.5

Limitations:

- Low treatment efficiency of ~70% (which means the process cannot be used in cases of high fluoride contamination);
- Requirement of large dosage of aluminum sulfate, up to 700−1200 mg/L;
- Adverse health effects of dissolved aluminum species in the treated water;
- Requirement of skilled manpower (hence the technique is not suitable for rural areas where the fluoride problem is more severe).

Precipitation methods based on salts of calcium, aluminum, and iron are also reported in the literature.[37−39] Precipitation processes are governed by the solubility of a forming salt.[40] However, problems associated with lime-based defluoridation processes are low solubility of the calcium hydroxide, which does not allow complete removal of fluoride, and poor settling characteristics of the precipitate.

1.6.2. Membrane Based Processes. Membrane processes such as reverse osmosis (RO), nanofiltration (NF), and electrodialysis have also been used for fluoride removal from water.[41−43] RO is a physical process in which the contaminants are removed by applying pressure on the feedwater to direct it through a semipermeable membrane. The process is the reverse of natural osmosis as a result of the applied pressure to the concentrated side of the membrane, which overcomes the natural osmotic pressure. RO membrane rejects ions based on size and electrical charge. NF is a relatively low-pressure process that removes primarily high concentration of dissolved solids as compared to RO. Conversely, RO operates at higher pressures with greater rejection of all dissolved solids. The factors influencing the membrane selection are cost, recovery, rejection, raw water characteristics, and pretreatment. Efficiency of the process is governed by various factors such as raw water characteristics, pressure, temperature, and regular monitoring and maintenance, among other factors.

However, RO membranes are subject to fouling and can also act as media for microbiological growth.[44] Moreover, RO systems produce concentrated brine discharges that must be disposed off safely. Reverse osmosis systems also results in significant water loss and are not suitable for arid regions where water scarcity is a serious problem. The capital cost implications are not in favor of RO systems. Electrodialysis (ED) is a membrane process similar to RO, except that ED uses an applied dc (direct current) potential electric current, instead of pressure, to separate ionic contaminants from water. Lounici et al. have also studied fluoride removal using electrodialysis.[45] However, the ED process, besides having disadvantages associated with RO processes, is energy-intensive and hence is not suitable for rural applications. The study conducted by Lhassani et al. indicates that fluoride can also be removed using nanofiltration, which is a relatively new technique and needs more research for its practical application for fluoride removal.[42]

Advantages of membrane process:

- Highly effective technique;
- No chemicals are required;
- No interference by other ions;
- Works under a wide pH range.

Limitations:

- Skilled labor required;
- Relatively higher cost;
- May not be suitable for water with high salinity and TDS (total dissolved solids).

1.6.3. Ion-Exchange Method. Ion-exchange resins have also been evaluated for fluoride removal from drinking water. Fluoride can be removed from water with a strongly basic anion-exchange resin containing quaternary ammonium functional groups. The removal takes place according to the following reaction:

$$\text{Matrix-NR}_3{}^+\text{Cl}^- + \text{F}^- \rightarrow \text{Matrix-NR}_3{}^+\text{F}^- + \text{Cl}^-$$

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 backwashed 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 electronegativity of the fluoride ions. Mohan Rao and Bhaskaran[46] have reported the removal of fluoride using ion-exchange materials and their regeneration using aluminum sulfate solution (2−4%). Haron et al.[47] studied the fluoride removal using yttrium-loaded poly(hydroxamic acid) resin. Castel et al.[48] have also studied the removal of fluoride by a two-way ion-exchange cyclic process. This system used two anion-exchange columns. These studies show that the ion-exchange process can be effectively used for removal of fluoride from water. Veressinina et al. studied fluoride removal in the presence of other anions and observed that the sorption capacity is normally <0.5 mg/L.[49] Chubar et al. studied the removal of various anions like fluoride, chloride, bromide, and bromate ions on a newly developed ion exchanger.[50] Zhou et al. reported removal of fluoride from aqueous solution on lanthanum-impregnated cross-linked gelatin.[51]

Advantages:

- Removes fluoride up to 90−95%;
- Retains the taste and color of water intact,

Limitations:

- Presence of sulfate, phosphate, bicarbonate, etc. results in ionic competition;
- Relatively higher cost;
- Treated water sometimes has a low pH and high levels of chloride.

1.6.4. Adsorption. A comprehensive review of the literature reveals that fluoride removal through adsorption onto various materials is most promising in terms of cost of the medium and running costs, ease of operation, adsorption capacity, potential for reuse, number of useful cycles, and possibility of regeneration. Adsorption processes involve the passage of the water through a contact bed where fluoride is removed by ion exchange or surface chemical reaction with the solid bed matrix. In the past few years, surface adsorption is the most interesting area of research for removing fluoride from water. This method is frequently used in large scale by many water treatment plants as it can operate at high flow rates, can produce high quality of water without the generation of sludge, and removes contaminant from water very effectively. Several adsorbent materials have been tried in the past to identify an efficient and economical defluoridating agent. Activated alumina, activated carbon, activated alumina-coated silica gel, calcite, activated saw dust, activated coconut shell carbon-activated fly ash, groundnut shell, coffee husk, rice husk, magnesia, serpentine, tricalcium phosphate, bone charcoal, activated soil sorbent, carbon, defluoron-1, defluoron-2, etc. are different adsorbent materials reported in the literature.[52−60] The most commonly used adsorbents are activated alumina and activated carbon. The fluoride-removing efficiency of activated alumina gets affected by hardness, pH, and surface loading (the ratio of total fluoride concentration to activated alumina dosage). The adsorption process can remove fluoride up to 90%, and the treatment is very cost-effective. Regeneration is required after every 4−5 months as effectiveness of the adsorbent for fluoride removal is reduced after each regeneration cycle.

Advantages:

- Locally available adsorbent materials;
- High efficiency;
- Cost effective.

Limitations:

- Process is dependent on pH;
- Presence of sulfate, phosphate, bicarbonate, etc. results in ionic competition;
- Regeneration is required;
- Disposal of fluoride-laden material.

1.7. Materials for Defluoridation of Water

The different sorbents reported for fluoride removal are reviewed in detail in the following sections.

1.7.1. Activated Alumina. Activated alumina (AA) is the most extensively studied adsorbent for removal of fluoride from drinking water. AA shows high affinity and selectivity for fluoride. Defluoridation process based on AA has been used at both the community and domestic levels. The earliest study conducted by Savinelli and Black has demonstrated the high potential of activated alumina for fluoride uptake.[61] 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. Ghorai and Pant concluded that removal was the result of ion exchange as well as adsorption process, which follows both Freundlich and Langmuir isotherms.[62,63] AA has a great capacity for fluoride adsorption, which is dependent upon the crystalline form, activation process solution pH, and alkalinity. Li et al. reported that γ-alumina is 10 times more efficient for fluoride removal than α-alumina. Interference due to the presence of other anions/cations also affects the fluoride-removal capacities of AA.[64] Johnston and Heijnen studied the sorption of different anions on AA and gave the following selectivity sequence in the pH range 5.5−8.5:[65]

$$\mathrm{OH^-} > \mathrm{AsO_4^-} > \mathrm{Si(OH)_3O^-} > \mathrm{HSeO_3^-} > \mathrm{F^-} > \mathrm{SO_4^{2-}}$$

$$> \mathrm{CrO_4^{2-}} \gg \mathrm{HCO_3^-} > \mathrm{Cl^-} > \mathrm{NO3^-} > \mathrm{Br^-} > \overline{\mathrm{I}}$$

The use of activated alumina in a continuous-flow fluidized system is an economical and efficient method for defluoridating water supplies,[62] and an adsorption capacity of 1.45 mg/g at pH 7 can be achieved. The greatest disadvantage of fluoride removal by activated alumina is that the optimum fluoride-removal capacity occurs only at a pH value of the solution below 6.0, which limits the practical applications of the AA heavily. Moreover, it has been reported that alumina begins to leach below pH 6 and poses severe threats to human health because the aluminum and its fluoride complexes are known to cause Alzheimer's disease and the other health effects are also well-documented.[66−69]

Farrah et al. investigated the interaction of fluoride ion with amorphous aluminum hydroxide ($\mathrm{Al(OH)_3}$), gibbsite (naturally occurring aluminum hydroxide), and aluminum oxide ($\mathrm{Al_2O_3}$) over a range of pH values from 3 to 8 and fluoride concentrations from 0.1 to 1 mM.[70] Hao et al. reported the adsorption characteristics of fluoride onto hydrous alumina.[71] Shimelis et al. also showed the importance of activation, comparing untreated hydrated alumina (UHA) and thermally treated hydrated alumina (THA) obtained from hydrolysis of locally manufactured aluminum sulfate.[72] Schoeman and MacLeod regenerated AA by flushing with a solution of 4% sodium hydroxide, which displaces fluoride from the alumina surface.[73] This procedure is followed by flushing with acid to reestablish a positive charge on the surface of the alumina. A major disadvantage of adsorption on activated alumina is that pH needs to be on the acidic side, i.e., 5−6, and dissolution of some aluminum oxide/hydroxide is inevitable, releasing toxic aluminum ions.[74]

1.7.2. Modified Alumina and Aluminum-Based Adsorbents. Activated alumina is one of the best available and generally used sorbents for defluoridation of drinking water. However, the slow rate of adsorption of commercially available activated alumina limits its use for treating water. In recent years, a considerable amount of work has been done on developing new adsorbents by impregnation of low-cost porous solids with chemicals for better defluoridation performance. Lanthanum(III) and ytterbium(III) impregnated on alumina have shown very promising results for defluoridation of water.[75] The efficacy of alum-impregnated activated alumina (A/AA) in removal of fluoride from water was 92.6% at pH 6.5 with a contact time of 3 h, A/AA dose of 8 g $\mathrm{L^{-1}}$, and initial fluoride concentration of 25 mg $\mathrm{L^{-1}}$.[76]

Maliyekkal et al. reported that a new adsorbent, manganese oxide-coated alumina (MOCA), was able to bring fluoride concentration below the statutory 1.5 mg $\mathrm{L^{-1}}$ for drinking water, was faster-acting than activated alumina, and had a greater fluoride load capacity (2.85 mg/g) compared with 1.08 mg/g for activated alumina.[77] Tripathy and Raichur found that manganese dioxide-coated activated alumina could bring fluoride concentration down to 0.2 mg/L when the initial concentration of fluoride in water is 10 mg/L. The authors concluded that the uptake of fluoride occurred through physical adsorption as well as initial intraparticle diffusion at the porous surface.[78] The adsorption of fluoride was found to decrease in the presence of other ions. Teng et al. prepared and characterized hydrous manganese oxide-coated alumina (HMOCA). Both batch and column adsorption experiments were carried out to evaluate the adsorption behavior. The effect of competing anions was revealed to be an adverse effect of fluoride uptake.[79] The effluent fluoride containing 5.0 mg/L was defluoridated in the column, giving <1 mg/L in the treated solution. Recently, Maliyekkal et al. described a magnesia-amended activated alumina (MAAA) prepared by impregnating alumina with magnesium hydroxide and calcining the product at 450 °C. MAAA adsorbed fluoride from drinking water more effectively than activated alumina.[80]

Biswas et al. coprecipitated aluminum and iron(III) hydroxides from a chloride mixture in equimolar quantities using ammonia; the resulting mixed hydroxide, after aging and drying, is a better adsorbent for fluoride than either aluminum hydroxide or iron(III) hydroxide.[81] The monolayer adsorption capacity of the mixed hydroxide, derived from Langmuir isotherms, was greater than that for the pure hydroxides. Chubar et al. studied the anion-adsorption capacity of an adsorbent precipitated from equimolar aluminum and iron(III) chloride by addition of ammonia.[50] The anions investigated were fluoride, chloride, bromide, and bromate. At pH 4, fluoride was most strongly adsorbed with adsorption capacity of 88 mg/g of adsorbent. Sujana et al. prepared a series of amorphous Fe−Al oxides with different molar ratios and studied the fluoride uptake behavior by varying experimental parameters.[82]

1.7.3. Ion-Exchange Resins. Chikuma and Nishimura studied the fluoride removal by a chloride-loaded anion exchanger, Amberlite IRA-400. The chloride ions held on the surface of this resin were exchanged for fluoride ions in aqueous solution.[83] However, Ku et al. have noted that anion-exchange resins are more vulnerable to interference than cation-exchange resins.[84] Lopez et al. made similar observations, finding that on Amberlite IRA-410 anionic resin the order of selectivity was sulfate > chloride > bicarbonate > hydroxide > fluoride.[85] Ku et al. also studied fluoride adsorption on Amberlite IR-120 resin that had been amended by adsorption of aluminum(III).[84] Luo and Inoue compared the fluoride-adsorbing capacities of Amberlite-type cation-exchange resin Amb200CT bearing a range of trivalent cations.[86] The adsorption capacity of fluoride ion for different metal(III)-loaded Amb200 resin was in the order La(III) ≥ Ce(III) > Y(III) > Fe(III) ≈ Al(III).[86] The use of anion-exchange resins for F removal is not common because of their relatively high costs. Moreover, the competitive sorption of other anions such as chloridem bromide, etc. also presents a major problem. The technique is expensive because of the cost of resin, pretreatment required to maintain the pH, regeneration, and waste disposal.

1.7.4. Carbon. The three best-known allotropes of carbon are diamond, graphite, and fullerene. Diamond is not relevant to adsorption of fluoride, but graphite and fullerene can be good adsorbents when suitably treated and amended.

Abe et al. have reported the fluoride uptake capacity of various carbon-based adsorbents in the order bone char > coal charcoal > wood charcoal > carbon black > petroleum coke.[87] Bhargava and Killedar studied the fluoride adsorption on fishbone charcoal through a moving media adsorber.[88] Daifullah et al. studied fluoride adsorption on activated rice straw, which produced a low-density and highly porous activated product.[89] The activated rice straw carbon was treated with the strong oxidants nitric acid, hydrogen peroxide, and potassium permanganate. The adsorption capacity was greatly increased relative to similarly activated carbon that had not been treated with oxidants. This effect was more marked if activation was carried out at 750 °C than for carbon activated at lower temperatures.[89] The effect of permanganate was greatest, followed by that of nitric acid. Hydrogen peroxide had some effect but much less than the other oxidants. Recently, Gupta et al. applied waste carbon slurries from fuel-oil energy generators for defluoridation down to levels within the WHO guideline of <1.5 mg/L. Solid from the slurry was activated by heating in air at 450 °C, and washed with sodium hydroxide solution to remove ash and then with fluoride-free water. The product was dried at 100 °C. The resulting material contains 92.0% carbon, 0.45% aluminum, and 0.6% iron. Both adsorption of fluoride and regeneration by removing fluoride were strongly pH-dependent with an optimum pH of 7.6.[90] Ramos et al. studied adsorption of fluoride from an aqueous solution on plain and alumina-impregnated activated carbon. It was found that the aluminum impregnation of carbon increase the fluoride uptake capacity by 3−5 times as compared to untreated carbon.[91]

1.7.5. Carbon Nanotubes. The application of carbon nanotubes has been explored to adsorb fluoride. A team led by Li prepared aligned carbon nanotubes (ACNT), by the decomposition of xylene, catalyzed by ferrocene.[92] The ACNT has an adsorption capacity of 4.5 mg/g fluoride at 15 mg L^{-1} of fluoride concentration and at pH 7. The adsorption capacity appears to increase with increasing acidity owing to the increasing positive charge on the surface.[92] Li et al. also investigated adsorption of fluoride on alumina supported on carbon nanotubes. The nanotubes were prepared by pyrolysis of a propylene−hydrogen mixture with Ni particles as the catalyst. The adsorption capacity of the Al_2O_3/carbon nanotubes was found to be 13.5 times higher than that of AIC-300 carbon, four times higher than that of γ-Al_2O_3, and also higher than that of IRA-410 polymeric resin.[64,92]

1.7.6. Zeolites. Very few attempts have been made to evaluate various zeolites for fluoride removal in spite of the fact that zeolite has all the properties necessary for a good adsorbent. Shrivastava and Deshmukh and Xu et al. have studied removal of fluoride using zeolites.[93,94] Mayadevi has also studied the fluoride uptake capacities of various zeolites modified using aluminum salts. These zeolites show adsorption capacities comparable to that of other defluoridation materials.[95] Recently, Onyango et al. reported aluminum- and lanthanum-exchanged zeolite F-9 for fluoride removal. It was observed that aluminum-exchanged zeolites have a higher affinity for fluoride as compared to lanthanum-exchanged zeolite. The author concluded that adsorption on Al^{3+}-exchanged zeolite was by ion exchange whereas that on La^{3+}-exchanged zeolite was by electrostatic attraction.[96] Modified zeolites appear to be potential materials for fluoride removal because they have high surface area, high aqueous and thermal stability, easy regenerability, etc. However, systemic study to develop modified zeolite analogues for removal of fluoride from drinking water has not yet been attempted. Subsequently, Onyango et al. focused on Al^{3+}-loaded low-silica zeolite as adsorbents for fluorides and were able to show that charge-reversed zeolites were able to defluoridate water to below the WHO maximum allowable concentration (MAC) of 1.5 mg L^{-1}.[97,98]

1.7.7. Calcium-Based Materials. Fan et al. studied fluoride adsorption on a wide array of minerals including fluorite, calcite, quartz, and iron-activated quartz and compared their fluoride uptake capacities.[99] Fan et al. used radioisotope ^{18}F (10−13 mg) to understand the deposition of fluoride on calcite, hydroxyapatite, and fluorite along with quartz and iron(III)-activated quartz from very dilute solutions (0.025−6.34 ppb).[99] Badillo Almaraz et al. reported that the best pH range for adsorption on hydroxyapatite is 7.0−7.5, where the mineral adsorbs 19 mg of fluoride/1 g of solid.[100] Larsen and Pearce developed a procedure for defluoridating water that could be used for domestic purposes. It made use of calcite and brushite, a mineral of formula $CaHPO_4 \cdot 2H_2O$, believed to be a precursor of apatite and found in guano-rich caves. Equal charges of 300−500 mg of brushite and calcite were stirred with 1000 mL of the fluoride-contaminated water; the suspensions were boiled in an electric kettle and left to cool, and the calcium salts were allowed to sediment.[101]

1.7.8. Soils/Clays, Minerals, and Other Low-Cost Materials. Extensive work has been reported on usage of locally available soils/clays as low-cost adsorbents for fluoride from drinking water. Omueti and Jones studied the adsorption of fluoride by Illinois soils. They reported that at low concentrations of fluoride both Langmuir and Freundlich isotherms described adsorption onto soils. It was also suggested that fluoride adsorption onto soils was due to the presence of the amorphous aluminum hydroxides.[102] Bjorvatn et al. studied the defluoridation of water using soil samples from Ethopia. It was reported that the soil samples from highland areas around Addis Ababa reduced the fluoride content of the water from ~15 to 1 mg L^{-1}.[103] Zevenbergen et al. studied the defluoridation of water using the Ando soil of Kenya. It was concluded that the use of Ando soils appears to be an economical and efficient method for defluoridation of drinking water.[104] Wang and co-workers studied the adsorption of fluoride on goethite and Illite and reported that thermal and chemical activation of these soils improves the adsorption capacities.[12,57]

Das et al. studied the adsorption of fluoride on thermally activated titanium-rich bauxite (TRB). Thermal activation at moderate temperatures (300−450 °C) greatly increased the adsorption capacity of TRB. Adsorption was rapid, and maximum level was attained within 90 min. The uptake of fluoride increased with increasing pH, reaching a maximum at pH 5.5−6.5, and decreased thereafter. The presence of common interfering ion in drinking water did not affect the uptake of fluoride from aqueous solution, indicating fluoride-specific sorption behavior of TRB.[105]

Several researchers have also studied the removal of fluoride using various clays. Hauge et al. studied the defluoridation of drinking water using pottery. The study investigated the effect of temperature on fluoride adsorption. The results show that clays fired at temperature up to 600 °C gave higher fluoride adsorption.[106] Moges et al. studied the defluoridation of water using fired clay chips. Their findings indicated that fluoride adsorption is affected by factors such as initial concentration, mass of adsorbent, and pH of the solution.[15] The structure of the clay plays a very important role in determining the charge on the clay surface and type of exchange that can occur with ions in solution. In general, the more positive the surface the better the sorption will be for negatively charged ions, such as fluoride. Srimurali et al. reported that chemical pretreatment, which includes the use of 1% Na_2CO_3 and 1% HCl, was reported to improve the adsorption capacity of clays and soils.[107] In general, it was observed by Agarwal et al. and Zhuang and Yu that firing and chemical pretreatment both improve the adsorption capacity of some clays and soils. Studies on the surface coatings of clays and soils were also reported. The coating of clays and soils with aluminum and iron hydroxides improves their adsorption capacity.[13,108]

Srimurali et al. investigated the removal of fluoride using low-cost minerals such as kaolinite, bentonite, charfines, lignitem and nirmali seeds. Their results show that fluoride adsorption using nirmali seeds and lignite is low (6−8%). The removal of fluoride by kaolinite is slightly better, whereas charfines and bentonite give higher fluoride removal capacity of 18.2 and 33%, respectively, at an initial concentration of 5 mg L^{-1} of fluoride and an adsorbent dose of 0.1 g/50 mL.[107] Kau et al. investigated the adsorption of fluoride by kaolinite and bentonite. The results show that bentonite has higher fluoride-adsorption capacity than kaolinite.[109] Chaturvedi et al. studied fluoride removal using china clay and observed that, at low fluoride concentration, high temperature and acidic pH are factors favoring the adsorption of fluoride. It was concluded that the alumina constituent of the china clay is responsible for fluoride adsorption.[5] Chaturvedi et al. also studied the defluoridation of water by adsorption on fly ash.[110]

Recently, rare earth oxides, red mud, bleaching earth, hydrocalcite, hydroxyapatite, fluorspar, calcite and quartz, brick powder, and Gypsum have also been evaluated as low-cost materials for fluoride removal.[111−116] Some of these materials indicate high adsorption capacities for fluoride, but the major limitation is that these materials are local products and cannot be utilized on large scale. Further, most of these studies are limited to only uptake of fluoride from water, and very few attempts have been made to regenerate the used adsorbents. The detailed studies using these materials for fluoride removal under varying conditions of pH, flow, and presence of interfering ions are lacking. Kemer et al. used waste mud from the copper mine industry as adsorbent for fluoride removal and found that the process was feasible, spontaneous, and endothermic. Batch adsorption studies revealed that adsorption was independent of pH and effect of fluoride concentration; coexisting anions were also studied.[117]

1.7.9. Biopolymer-Based Adsorbents. In the past few years, a lot of research work on chitin and chitosan has been reported in the literature for a variety of applications and for fluoride removal; some of these are as follows:

Ma et al. have prepared magnetic chitosan particle using a coprecipitation method and investigated extensively for fluoride removal from drinking water. They found excellent fluoride-removal capacity of 22.49 mg/g for magnetic chitosan particles at pH of 7.0 ± 0.2, and therefore they can be used as a potential adsorbent for defluoridation of water and wastewater.[118] Regeneration studies show that a loaded fluoride magnetic particle was recovered by 0.8−1.0 NaOH media, and a reused sorbents adsorption capacity of 98−99% was achieved. Kamble et al. studied the applicability of chitin, chitosan, and 20% lanthanum-incorporated chitosan (20% La-chitosan) as adsorbents for the removal of excess fluoride from drinking water.[119] Lanthanum chitosan adsorbents show excellent removal of fluoride from water, which is much better than bare chitosan and chitin. It was found that the presence of anions has a deleterious effect on the adsorption of fluoride, particularly carbonate and bicarbonate anions. The fluoride adsorption capacity of 20% La-chitosan was 3.1 mg/g at an acidic pH of 5.0 and was high as compared to alkaline pH. No significant leaching of lanthanum was observed from the adsorbent, and it was also possible to regenerate the material. Menkouchi Sahlia et al. have reported defluoridation of brackish underground water by adsorption on chitosan. The fluoride adsorption is found to be very fast and requires a slightly acid medium.[120] The importance of this operation lies in the valorization of industrial animal waste in the region. However, the efficiency of this support in salt removal remains very weak. Sundaram et al. have prepared and studied a bioinorganic composite, namely, nanohydroxyapatite/chitosan (n-HApC) composite, for defluoridation of water. A slight enhancement in the defluoridation capacity was observed for n-HApC composite (1.560 mg/g) versus nanohydroxyapatite (n-HAp), which has a defluoridation of 1.296 mg/g. Field trial studies indicated n-HApC composite could be used as an effective defluoridation agent.[121]

Viswanathan and co-workers reported that the carboxylated chitosan beads (CCBs), which have a defluoridation capacity of 1.39 mg/g, have been further chemically modified by incorporating La^{3+} ion (La-CCB); its defluoridation capacity was found to be 4.71 mg/g whereas the raw chitosan beads (CB) possess only 0.05 mg/g.[122] La-CCB possesses higher DC (defluoridation capacity) than CCB and chitosan bead. Fluoride removal by La-CCB is influenced by pH of the medium and is slightly affected in the presence of coanions. La-CCB removes fluoride by both adsorption and complexation mechanism. The results of field trial indicate that the La-CCB could be effectively employed as a promising defluoridation agent. Viswanathan et al. have studied chitosan in its more convenient bead form chemically modified by simple protonation and employed as a most promising defluoridation medium. Protonated chitosan beads (PCBs) showed a maximum DC of 1.66 mg/g whereas raw chitosan beads (CBs) possess only 0.05 mg/g.[123] The sorption process was found to be independent of pH and altered in the presence of other coexisting anions. Desorption efficiency of PCB was experimented with using 0.1 M HCl, H_2SO_4, and NaOH as eluents. Among three eluents, HCl had been identified as the best eluent as it has 94.5% desorption whereas H_2SO_4 and NaOH have 89% and 85% desorption efficiencies, respectively.

Viswanathan et al. have chemically modified chitosan beads (CBs), which exhibit negligible defluoridation capacity by introducing multifunctional groups, e.g., NH_3^+ and COOH groups, by means of protonation and carboxylation in order to utilize both amine and hydroxyl groups for fluoride removal.[124] The protonated and carboxylated chitosan beads (PCCBs) showed a maximum DC of 1.8 mg/g whereas raw chitosan beads displayed only 0.05 mg/g. Field trial results indicate that PCCB reduces the fluoride level below the tolerance limit, and it can be effectively used to remove other ions in addition to fluoride. So, PCCB is an effective, inexpensive, and promising defluoridation agent.

Jagtap et al. synthesized a new modified chitosan-based adsorbent for defluoridation of water. The metal-binding property of chitosan is used to incorporate titanium ions and applied as an adsorbent for fluoride adsorption. Titanium macrospheres (TMs) were synthesized by a precipitation method. TMs show an excellent fluoride removal capacity of 7.2 mg/g, which is very high as compared to chitosan.[125] The major advantage of using TMs for removal of fluoride over other adsorbents is that TMs are in the form of beads and have good stability and settling properties so that they can be easily separated from water. Jagtap et al. have observed the regeneration of fluoride-loaded adsorbent by alum solution at pH of 12.0, which desorbs nearly 85% of the adsorbed fluoride.

Davila-Rodriguez et al. obtained a biocomposite based on chitin and a polymeric matrix that is capable of adsorbing fluoride from aqueous solutions. The optimized biocomposite shows a fluoride-removal capacity of 0.29 mg/g at an initial fluoride concentration of 15 mg/L and a pH of 5.0.[126] Finally, according to the physicochemical characteristics of the optimum chitin-based biocomposite (OBACCR), it is a promising adsorbent material that can be used in continuous processes to remove a wide range of contaminants present in the aqueous phase.

1.7.10. Recent Developments. Sivasankar et al. have presented the defluoridation capacities of activated tamarind fruit shell (ATFS) and MnO_2 coated tamarind fruit shell (MTFS), using batch and column sorption techniques. They found that sorption capacities of the ATFS and MTFS adsorbents were 0.2145 and 0.2178 mg/g, respectively, at pH of 6.5 with an initial fluoride concentration of 2 mg/L.[127] Alagumuthu and Rajan 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. The treatment conditions were optimized: pH value of 7.0, room temperature, and particle size of 53 μm. Salt rejection (80.33%) has been identified in 3 mg/L of 100 mL fluoride using 1.5 mg dosage of adsorbent. The adsorption capacity was found to be 1.85 mg/g at pH of 3.0 with an initial fluoride concentration of 10 mg/L. The used adsorbents could be regenerated by 96.2% of 2.5% sodium hydroxide in 180 min.[128] Tchomgui-Kamga et al. have synthesized charcoal adsorbents that contain dispersed aluminum and iron oxides by impregnating wood with salt solutions followed by carbonization at 500, 650, or 900 °C. Substrates prepared at 650 °C with aluminum and iron oxides exhibited the best efficiency with a fluoride sorption capacity of 2.31 mg/g. More than 92% removal of fluoride was achieved within 24 h from a 10 mg/L solution at neutral pH.[129] Bansiwal et al. reported the fluoride-removal performance of activated alumina modified by incorporating copper oxide. They reported the very interesting result that the optimal fluoride adsorption occurs at all pH's ranging from 4.0 to 9.0 with 7.22 mg/g fluoride adsorption capacity. This material overcomes the drawback associated with activated alumina showing optimal fluoride adsorption below pH of 6.0 and low adsorption capacity.[130] A high desorption efficiency of 97% was achieved by treating fluoride-loaded adsorbent with 4 M NaOH solution. Viswanathan and Meenakshi have prepared a new biocomposite by incorporating an inorganic ion exchanger, namely, zirconium(IV) tungstophosphate (ZrWP), into the chitosan biopolymer matrix and investigated it for removal of fluoride ion from water. The sorption behavior of fluoride from aqueous solutions by this ZrWP/chitosan (ZrWPC) composite was found to be 2.03 mg/g at pH of 3.0 with an initial fluoride concentration of 10 mg/L. Viswanathan and Meenakshi also showed that alumina possesses an appreciable defluoridation capacity of 1.57 mg/g.[131,132] To improve its defluoridation capacity, it is aimed to prepare alumina polymeric composites using the chitosan. Alumina/chitosan (AlC) composite was prepared by incorporating alumina particles in the chitosan polymeric matrix, which can be made into any desired form, e.g., beads, candles, and membranes. AlC composite displayed a maximum DC of 3.81 mg/g versus that for the bare alumina and chitosan of 0.052 mg/g at pH of 5.0 to 9.0 with an initial fluoride concentration of 10 mg/L. Jiménez-Reyes abd Solache-Ríos found that hydroxyapatite is a potential material that could be used for the treatment of water contaminated with fluoride ions. The fluoride sorption capacity of the adsorbent was found to be 4.7 mg/g at a pH range of 5.0−7.3 with an initial fluoride concentration of 5 mg/L.[133] Thakre et al. synthesized lanthanum-incorporated chitosan beads (LCBs) using a precipitation method and tested for fluoride removal from drinking water. The fluoride adsorption capacity of LCB-10 was found to be 4.7 mg/g, which is much higher than the commercially used activated alumina, i.e., 1.7 mg/g.[134] The LCB-10 not only has much higher fluoride adsorption capacity but also has numerous advantages, namely, relatively fast kinetics, high chemical and mechanical stability, high resistance to attrition, negligible Lanthanum release, suitability for column applications, etc. LCBs can reduce the fluoride concentration below the permissible level of 1.5 mg/L and, therefore, can be used as an effective adsorbent for defluoridation of drinking water. Swain et al. have developed cerium-impregnated chitosan (CIC) adsorbent and undertaken to evaluate the feasibility for fluoride removal from water. Reusability of the CIC adsorbent was found to be >93% at pH of 12.[135]

Thakre et al. have developed low-cost bentonite clay chemically modified using magnesium chloride for fluoride removal from water. It was observed that magnesium bentonite (MB) works effectively over a wide range of pH and showed a maximum fluoride removal capacity of 2.26 mg/g at an initial fluoride concentration of 5 mg/L, which is much better than the unmodified bentonite.[136] A desorption study of MB suggested that almost all the loaded fluoride was desorbed at 97% using 1 M NaOH solution; however, maximum fluoride removal decreases from 95.47 to 73% after regeneration. Ramdani et al. have studied the elimination of the excess of fluoride from the El Oued Souf City water supply located in the southeast of the Algerian Sahara by retention process onto montmorillonite clay using potentiometric method. Two types of natural clays were tested. The first one contains a higher percentage of calcium (AC) and the second one was without calcium (ANC). These adsorbents were activated chemically and thermally with temperatures ranging between 200 and 500 °C. Experimental results showed that chemical activation proved effective with adsorption reaching up to 88%, whereas the thermal activation is ineffective and reached only ~5%. The fluoride adsorption capacity was calculated to be 1.324 and 1.013 mg/g of ANC and NC, respectively, at pH range of 5.5−6.5 and an initial fluoride concentration of 5 mg/L.[137] Maliyekkal et al. have described a novel combustion synthesis for the preparation of nanomagnesia (NM) and its application in water purification. The synthesis is based on the self-propagated combustion of the magnesium nitrate trapped in cellulose fibers. They found that NM is less sensitive to pH, and the maximum fluoride adsorption capacity was found to be 9.39 mg/g at an initial fluoride concentration of 10 mg/L.[138] Choon-Ki and Hyun-Ju have undertaken to evaluate the feasibility of lanthanum hydroxide for fluoride removal from aqueous solutions. Maximum fluoride adsorption capacity was found to be 242.2 mg/g at pH ≤ 7.5 and 24.8 mg/g at pH >10.0 with an initial fluoride concentration of 10 mg/L.[139] It is noticed that the regeneration of fluoride-loaded adsorbent by using 2 M NaOH solution desorbs nearly 89.6% of adsorbed fluoride. Zhao et al. have investigated a novel magnetic nanoscale adsorbent using hydrous aluminum oxide embedded with Fe_3O_4 nanoparticle (Fe_3O_4 @ $Al(OH)_3$ NPs), which was prepared and applied to remove excessive fluoride from aqueous solution. They found 18.58 mg/g of fluoride adsorption capacity at pH of 6.5 with an initial fluoride concentration of 20 mg/L.[140] The main factors affecting the removal of fluoride, such as solution pH, temperature, adsorption time, initial fluoride concentration, and coexisting anions, were investigated. The fluoride adsorption capacity increased with temperature and follows a pseudosecond-order kinetic rate equation.

Biswas et al. have developed a new material, hydrated iron(III)−aluminum(III)−chromium(III) ternary mixed oxide (HIACMO), for removal of fluoride from water. Regeneration of fluoride adsorbed material could be possible up to 90% with 0.5 M NaOH.[141] Liu et al. have shown a novel Al−Ce hybrid adsorbent prepared through the coprecipitation method with high sorption capacity for fluoride. The sorption capacity of the adsorbent was found to be 27.5 mg/g at a pH of 6.0 with an initial fluoride concentration of 10 mg/L.[142] Chen et al. have developed a ceramic adsorbent and undertaken to evaluate the feasibility for fluoride removal from an aqueous environment. The maximum adsorption capacity of ceramic adsorbent for fluoride removal was 2.16 mg/g at pH of 4.0−11.0 with an initial fluoride concentration of 10 mg/L.[143] They have experimented with 0.1 M HCl and 0.1 M NaOH for desorption of fluoride, which was found to be 80.2% and 34.7%, respectively. Very recently, lanthanum alginate beads (LABs) have been reported to have high efficiency for fluoride by Huo et al. The maximum fluoride adsorption capacity of LABs is 197.2 mg/g. Lanthanum, being highly electropositive, is responsible for high fluoride adsorption capacity.[144] However, swelling of beads and leaching of lanthanum in treated water could be limitations for LCBs to be a potential adsorbent for fluoride removal. Thus, development of new materials for efficient and cost-effective removal of fluoride from drinking water is imperative.

2. CONCLUSION

A brief review of fluoride in drinking water has been presented. Research and development efforts made in the field of fluoride remediation have been reviewed. The primary causative factor in endemic fluorosis has been unequivocally identified as the fluoride intake through drinking water. So, the ever-increasing fluoride levels in drinking water pose the greatest threat to human health as evidenced by the endemic of fluorosis in India. The fluoride-removal methods have been broadly divided into two sections dealing with membrane and adsorption techniques. Reverse osmosis, nanofiltration, dialysis, and electrodialysis have been discussed under membrane techniques. Adsorption, which is a conventional technique, deals with adsorbents such as alumina/aluminum-based materials, clays and soils, calcium-based minerals, synthetic compounds, and carbon-based materials. Studies on fluoride removal from aqueous solutions using various reversed zeolites, modified zeolites, and ion-exchange resins based on cross-linked polystyrene and layered double hydroxides are also reviewed. The literature survey and the laboratory experiments have indicated that each of the discussed techniques can remove fluoride under specific 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 herein. 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.

Adsorption appears to be an attractive method for the removal of fluoride from water. It is an eco-friendly, simple, and cost-effective option for the average person using groundwater as a main source. pH of solution plays a very important role for fluoride removal, wherein most of the adsorbents work effectively in pH range of 3.0−7.0. Various adsorbents under different categories such as carbonaceous, geomaterials, biopolymer, alumina, agriculture and industrial waste, mixed oxide, and other adsorbents have been reviewed.

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