



REVIEW

Occurance, Toxicity, Impacts and Removal Technologies of Fluoride ions in Drinking Water

V. LAXMI¹, S. SINGH², J. HUSSAIN^{3,*}, I. HUSSAIN⁴ and S. KUMAR²

¹Department of Science and Technology, Mewar University, Gangrar, Chittorgarh-312901, India

²Department of Chemistry, Banasthali University, Banasthali-304022, India

³Upper Yamuna River Board, Ministry of Jal Shakti, R.K. Puram, New Delhi-110 066, India

⁴Public Health Engineering Department, Bhilwara-311001, India

*Corresponding author: E-mail: drjakirhussain@gmail.com

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One of the most prevalent pollutants of ground water is fluoride. India is among the 23 nations around the globe where health problems occur due to excess ingestion of fluoride (> 1.5 mg/L) by drinking water. The presence of fluoride in exceeding limits (> 1.5 mg/L) and its related problems of drinking water prevailing in many parts of India is well documented. Consumption of fluoride couldn't be avoided because a large section of groundwater is contaminated from it, which results in fluorosis of all the living forms. A number of defluoridation techniques are prevalent. Some of them could be used in day-to-day life for fluoride removal in drinking water. The review article presents the current information on fluoride in environment and its effects on human health and available methods of defluoridation.

Keywords: Groundwater, Fluoride, Dental fluorosis, Skeletal fluorosis, Defluoridation.

INTRODUCTION

Water is a naturally occurring abundant source of nature and a gift of God to Earth, which is essential for the survival of life and ecosystem [1]. Fresh water occurs naturally in the form of surface and ground waters respectively [2]. Surface water constitutes 0.3% of the total available water resources around the globe and one of the preferable sources for consumption [3] and irrigational purposes especially in countries undergoing development like India. Chemical composition of water is the crucial factor determining the compatibility of consumption [4].

From the past earlier decades, due to the exponential increment in population, industrialization, urbanization and unregulated consumption of water resources [5], surface water has depleted in both quantity and quality. Contamination of various hazardous substances like fluoride, chloride, heavy metals, nitrite and nitrates, sulphates, pesticides, etc. in surface water have been reported from various parts of India [6]. It is proven in many instances that consumption and utilization of contaminated water is not only harmful for human beings but

also unsafe for irrigation and industrial activities. Therefore, it is necessary to concentrate on issues arising in future, related to excute the utilization of water resources by adequate planning and development.

Fluoride is the major inorganic pollutant in India, originated from the nature to surface water [7,8]. The present intention herein is to portray the available concentration of fluoride in Indian riverine streams, sources causing its contamination, to depict trends of fluoride parameter along the main rivers in India and to evaluate novel defluoridation techniques utilized in recent times with reference to drinking water.

Fluorine geochemistry: Fluorine is the supreme reactive element and with the highest electronegativity [9]. It has the potential to react with most of the organic and inorganic substances. Because of its higher electronegativity and reactivity, occurrence of fluoride in elemental form is zero [10]. The fluorine ranks 13th midst the elements present in the crystal plate of earth [11]. Fluorine occurrence has been noted in the different forms [12], for example (i) limestone (calcium carbonate); (ii) tremolite (calcium magnesium silicate); (iii) acetalolite (calcium magnesium iron silicate). Clay material

combined with limestone also constitutes small concentration of fluoride [13]. The most significant fluorine minerals are (i) fluorite (CaF_2); (ii) apatite $\text{Ca}(\text{PO}_4)_3(\text{F}/\text{OH}/\text{Cl})$; and (iii) fluoroapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$.

Fluoride in rocks: Fluorine is the 13th bountiful element on the surface of earth and its abundance constitutes to be 0.06-0.09% [10]. The occurrence is recorded in the form of deposits of phosphate in the nature [14]. Calcium fluoride, fluoroapatite and cryolite are the minerals having fluorine content in abundance [15]. Calcium fluoride (CaF_2) in the form of fluorite or fluorspar is the most substantial source of fluorine for industrial activities having its content up to 49%. Fluorite is a commercial mineral often commonly known by the name “fluorspar”, its occurrence has been recorded as a vein mineral and usually co-occur with quartz and barite. These are typical accessory minerals found in many kinds of rocks. Fluorite contributing considerable amount of fluoride in rocks and water because it contains nearly 50% weight of fluorine [15] even though its occurrence is in low quantity. Upto 3.8% fluorine can be found in pure fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$). Clay minerals are most dominant in soils having high sorption capacity and usually prevent pollutants to reach groundwater by acting as natural geochemical barriers [14]. During the adsorption of fluorides on clay minerals, ion exchange process is taking place where fluoride ions are replaced by hydroxyl functional groups partly. The role of micas and amphiboles in the occurrence and mobility of fluoride in soils is enhanced by their relative readiness to disintegrate in weathering processes. About 80-90% of fluorides in clay minerals are included in minerals related to mica group, muscovite and elite.

Despite the fact that fluorides exist in the form of fluoroapatite [$\text{Ca}_5(\text{OH},\text{F})(\text{PO}_4)_3$], the contents of fluoride are at considerable low level ($\text{F}^- = 4\%$) so the reason for mining of this mineral is mostly for obtaining phosphate contents. Cryolite (Na_3AlF_6) has 54% fluorine content and this is rare, found only in Greenland. Besides, calcium fluoride, cryolite and fluoroapatite, fluorides occur in small quantities with some of the minerals namely, oxides, silicates, carbonates, sellaite (MgF_2), topaz ($\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$), etc. Likewise, some more minerals accounting for inorganic fluorides are (i) chain silicates, (ii) apatite, (iii) tourmaline; and (iv) clays (kaolinite, bentonite, etc.).

The hydroxyl sites present in hydroxyl silicates like micas, amphiboles and apatite occupies by chlorine and fluorine and the fluorine load of these minerals is particularly great when they happen in granitic rocks [16]. Occurrence of fluorine can find in hydroxyl minerals like sedimentary rocks and clays [17]. Inorganic fluoride minerals are showing more stability than chlorine containing minerals because of the approximately similar ionic radius with the hydroxyl ion, thus minimizing distortion in lattice.

Fluoride in soils: Fluoride has a concentration between the ranges of 200-300 ppm across the world [18]. Different soil profiles with different texture differed from trace contents to 7070 ppm in 30 soils. The amounts of fluoride in solutions of soil generally observed less than 1 ppm under normal circumstances, but it may reach upto 100 ppm under extremely fluoride contaminated soils [19]. According to a report by WHO (1984),

the source of inorganic fluorides in soil are the parents rocks [10]. During disintegration process, specifically under acidic environmental conditions minerals having the fluoride content undergo rapid fragmentation e.g. cryolite (Na_3AlF_6). In addition to these minerals, some minerals undergo dissolution at a slow pace, examples are calcium fluoride (CaF_2) and fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3$). Fluorophlogopite is a mineral, which is stable in alkaline and calcareous soils [20]. The solubility depends on pH and activities of silicic acid (H_4SiO_4) and aluminium (Al^{3+}), potassium (K^+) and magnesium (Mg^{2+}) ions, respectively.

Higher fluoride percentage is also found in basic minerals available in soil such as hornblende, biotite and muscovite [21]. As a result of this, minerals seem responsible for fluoride in earth clays. Though, prime sources of fluoride are minerals like micas, apatite and tourmaline which are present in soils, therefore, it is concluded that the fluoride concentration in soils is majorly related with the mineral composition of the inorganic fraction.

Fluoride contents can be quickly depleted from minerals in the acid horizons under humid temperature conditions in soils [18]. Considerable fluoride content is reserved in subsoil horizons, here it composites with Al that is probably grouped with phyllosilicates [22]. The degree of fluoride retention related with pH and amount of clay. Thus, fluoride distribution with depth follows approximately similar pattern with the clay [23].

Fluoride solubility varied with the pH and it will be higher at $\text{pH} < 5$ & $\text{pH} > 6$ in soils further, its solubility is complex and it may be restricted by different solid phases which make it as more insoluble than calcium fluoride [24]. Nevertheless, it is related with the aluminium or other species solubility with which it generates complex molecules. Soils containing higher values of pH and minute amount of powder structured Al species, clay and organic content normally sorb little fluoride. Therefore, it shows that the significant retention pathway *i.e.*, fluoride is substituted with the OH group of Al-hydroxides (amorphous materials). In present instance, fluoride ensuing in an immediate discharge of Al and Fe exchanges with the OH^- in clay mineral crystal lattice. Other mechanism involves the fluoride adherence to cation like Ca^{2+} , Al^{3+} in soil or as calcium fluoride precipitation.

Fluoride from volcanoes: Huge amount of volcanic gas and arid ash enters into the environment and to ground during the volcanic eruptions [25]. This emitted dust and ash cloud carrying out various chemicals adsorbed in it which covers over hundreds of kilometres. Finally these toxins containing ash settles on the ground after sometime and that will dissolve into the environment. The dominant chemical compounds like chlorine, sulphur compounds, sodium, calcium, potassium, magnesium and fluorine may adsorbed on tephra and leaches further. Previous studies [26] revealed that the emitted dust, ash and gas during volcanic eruptions are containing fluorine hence clay-rich volcanic ash beds supports for adsorption and provide exchange sites for F^- ions. Fluorine occurs mainly in the form of HF, H_2F_2 or F_2 as well as SiF_4 .

Fluoride in groundwater: Water is the primary channel for fluoride to enter living forms. Its concentration in ground water is generally responsible with the geological, chemical,

physical properties respectively and area of climate. Because of high reactivity of fluoride it is always available in earth crust (0.06 to 0.09%) as a fluoride in combined mineral. The occurrence of fluoride in ground water could be defined by natural phenomena which are further affected by geological circumstances. Fluorine is available as fluoride ions in groundwater which causes formation of soluble complexes along with various types of inorganic and organic ligands [18]. Fluoride solubility from fluoride rich minerals is comparably less in natural conditions [27], but the slow speed of reaction often improves leaching and fluoride enrichment in groundwater. Little amount of fluorides may be available in the form of fluorite (CaF₂) mineral dissolution in groundwater. The fluorite (K_{fluor}) solubility product can be derived according to the $f_{\text{dissociation}}$ formula as following [22]:

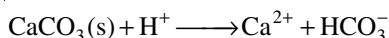


$$K_{\text{fluor}} = \left[a_{\text{Ca}^{2+}} \right] \times \left[a_{\text{F}^-} \right]^2 \times 10^{-9.04} \text{ at } 25^\circ\text{C}$$

where, $[a_{\text{Ca}^{2+}}]$ and $[a_{\text{F}^-}]$ = activities of the concerned ions.

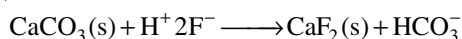
The solubility of fluoride being low, the availability of free Ca²⁺ water regulates the occurrence of aqueous F⁻.

The dissolution constant of calcium carbonate (CaCO₃) is much superior to that of fluorite:



$$K_{\text{Cal}} = a_{\text{Ca}^{2+}} \times \frac{a_{\text{HCO}_3^-}}{a_{\text{H}^+}} = 0.97 \times 10^2$$

Since the solubility product for fluorite is constant, the activity of fluoride is directly proportional to HCO₃⁻, if pH is constant. When computing the thermodynamic equilibrium in the groundwater system in contact with calcite and fluorite, a combined equation is derived:



$$K_{\text{Cal-fluor}} = \frac{a_{\text{HCO}_3^-}}{a_{\text{H}^+}} \times [a_{\text{F}^-}]^2 = 1.06 \times 10^{-11}$$

It can be concluded from the last equation that the aqueous F⁻ concentrations are proportional to HCO₃⁻ concentration and pH values. Therefore, waters which are having higher concentrations of fluorine are generally HCO₃⁻ rich waters, which allow the fluoride dissociation from soils. Thus, fluoride rich waters can form wherever alkaline carbonate containing waters are in contact with fluorine-bearing rocks [28].

Fluoride concentrations are not depending on any other water-soluble components, but notable correlation between fluoride and pH existed. In 5.0-6.5 pH range, lowest fluoride solubility was found in soils. Due to the ionic exchange at higher pH values between fluoride and hydroxyl ions, (illites, chlorites, micas and amphiboles) enhancement in fluoride concentrations occurred in groundwater. Mainly, in pH < 6 *i.e.* acid atmosphere F⁻ and Al³⁺ ions both soak into water and occurred complex formation like [AlF]²⁺ and [AlF₂]⁺ in water. The generation of [MgF]⁺ complexes boosted up when the

calcium concentration and temperature in groundwater increases on the account of fluoride ions.

The reason for high fluoride concentrations apart from mineral occurrence are [29] (i) alkali rocks ; (ii) hydrothermal plants; and (iii) leaching. When the fluoride rich rocks and soils are brought in contact with alkaline water, replace hydroxyl ions through the process of hydrolysis and discharges loads of fluoride in groundwater [30]. The topographical properties also shows significant role in governing the fluoride concentration. The calcium and magnesium carbonate contents appear as abundant sink for fluoride ions, which are usually found in arid and semi-arid areas due to weathering and leaching of rocks. The ability of leaching of fluoride from carbonate concentration will depend on (i) drained solution pH and (ii) CO₂ dissolved and alkalinity in water [31].

Other sources of fluoride for human exposure: Fluoride exposes to human through sources like air, water, solid, by the intake of food and medicament, creams used as cosmetics, *etc.*

Air: The waste produced during the production process from phosphate fertilizers and the dust act as major cause of dispersion of fluorides comprehensively throughout the sky. The ash from the coal industries and volcanic eruptions also constitute to fluorides [32]. The study fluoride concentration of various areas depicted that usually in the non-industrial areas the concentration was limited to 0.05-1.90 μg m⁻³ on the other hand in the industrial areas the concentration went fairly high chiefly due to the coal burning and fertilizer production [33].

China and Morocco encounter enormous content in the atmosphere. In certain areas of China, for the production of food coal is burnt which results in elevating the indoor air fluoride concentration between the ranges of 16-46 μg m⁻³. Greater than 10 million peoples of China are suffering from fluorosis which is relevant to the burning of fluoride rich coal fluoride coal [34].

Drugs: Extended usage of specific drugs having fluoride contents results to toxic affects *e.g.* sodium fluoride for osteoporosis treatment and niflumic acid (rheumatoid arthritis).

Toothpaste's and rinses: Fluoride contamination is caused from the raw materials used in manufacturing of tooth paste such as calcium carbonate, talc and chalk [35]. Contamination appears in higher quantities which ranges from 800-1000 ppm. Fluoride mouth washes are extensively used to render the tooth stronger [36]. Fluoride contents are adding extensively in all the fluoridated brands, it might lies within 1000-4000 mg/L. There is a close relation observed between insertion of fluoride from toothpaste and fluorosis [37].

Food: The concentration of fluorine found in fluorine containing plants especially in cultured plants are very low except for tea plant; it appeared 440 mg/L concentration [38]. Most importantly more amounts of fluorine is found in sea foods rather than fresh water foods. Mainly, maximum amount of fluoride is consumed through drinking water in animals including man. But the polluted environment and certain food products also add up to appreciable concentration of fluoride. The food items cultivated in fluorosis affected regions have high fluorine concentration and consequently, fluoride ingestion through food is certainly large. In some plants, it has been found

that the fluoride concentration in them is directly related to the distribution in their rooting media.

Plants: Although fluoride is not an essential element of plant, but it has its roles in the plant and animal lives. Still consistent consumption of fluoride in the diet or through water ends up in an ailment termed as fluorosis. In this case, the levels of fluoride cross the optimal levels and produces damaging effects on the body. Hence levels of fluoride in plants not only affect plants but also animals [10].

Accumulation and absorption of fluoride in plants is carried out through environment, soils or water [39]. Absorption through root is an important way of entry into the plant, if the soil or water have significant amount of soluble fluoride. The inhalation of fluoride through roots normally goes as a passive mechanism and a concentration gradient always exists between the root and shoot. Plants like *Camellia* sp. however, were able to accumulate fluoride in much higher quantity than the surroundings.

Air borne fluorides are the major sources contributing to their excessive accumulation in plants. Gaseous fluorides introduced into plant mainly through the stomata and enter the inter-cellular spaces. Fluorine is either directly absorbed by the cells in contact or it is transported through vascular tissues and redistributed to the specific sites of accumulation like leaves. Some xerophytes plants exposed to fluoride pollution in the aluminium smelter region and showed that fluoride accumulation was mainly by deposition or adsorption upon external leaf surface followed by a slow diffusion to the inner tissues, regulated by the water potential at the epidermis and cuticle. Absence of fluoride accumulation in substomatic tissues leads to the conclusion that the uptake of gaseous fluoride through stomata may be relatively unimportant for these plants [40].

Once fluoride has passed through the cell walls, it reacts initially with the cytoplasmic membrane where a fraction of it may be retained [41]. Inside the cells, up to 60% of fluoride are found to be associated with the chloroplast and the rest enters the vacuoles. Continued accumulation of fluoride substantially increases its concentrations in the senescent leaves. Rapid growth dilutes fluoride concentration [42,43]. Few plants *viz.* *Dichapetalum*, *Thea*, *Gastrnobiurn*, *camellia*, *Oxylobium*, *Acacia*, *Palicoure* and *Gossypium* sp. can accumulate as much as 4000 ppm concentrations of fluoride without any visible foliar injury and even in an unpolluted environment. According to a case study, trees were more susceptible to fluoride damage followed by shrubs grasses and herbs.

The defluoridation potential of plants that can accumulate fluoride from water has also been studied for *Spirodeta polyrrhiza* and *Eichornia crassipes* under laboratory conditions. Substantial uptake was reported in *Spirodeta* suggesting that this plant could be employed to remove fluoride from polluted waste waters. *Eichornia crassipes* accumulated upto 75 mg fluoride per plant. Since this plant has a high threshold value, it can prove useful for treating industrial effluents containing very high levels of fluoride [44].

Vegetation: Fluoride content of vegetation is indicative of the degree of atmospheric contamination. About 44-281 ppm fluoride in vegetation was found around a phosphorus plant in Finland. Concentrations of fluoride in plant species colonizing

fluorspar mine waste (that contain fluoride levels of the order 22-184 mg/g DW) varied between 0.05-5 mg F/g DW. However individual species from different sites showed consistent concentrations of fluoride indicating interspecific variation in the uptake of soil fluoride. According to the earlier reports fluoride content in plants found upto nearly 4300 ppm, which are growing in the vicinity of phosphate industry in Morocco [45].

Based on the appearance of foliar lesions, it has been generalized that conifers are more sensitive species. Broad leaved species tend to be more tolerant (with exceptions, as some fruit tree are highly sensitive) [39]. Vegetables and field crops are highly resistant. Ornamental plants show variable sensitivity. Gladiolus and tulips are susceptible even to 1 ppb of atmospheric fluoride concentrations. The tolerant plants are able to accumulate higher concentrations of fluoride. Accumulation of fluoride in broad leaved species is more compares with the conifers when they exist together.

Grass: The Italian rye grass (*Lolium multiflorum*) is known to accumulate 189-275 $\mu\text{gF/g}$ dry matter, when exposed to 1.1-1.35 $\mu\text{gF/g HF m}^{-3}$. This grass is used as a standard for fluoride estimation. Appropriate material is available about fluoride effect on agriculturally important plants such as rice, sunflower, soybean, spinach, parsley, cabbage and cauliflower, maize and fruit trees such as apple and grapes [46].

Algae: Limited reports were published on uptake of fluoride by algae [47]. Amongst the marine forms, red algae have been stated to accumulate higher amounts of fluoride. The fluoride concentration in red algae 11.35-20.04 mg/Kg is higher when correlate with the own and green algae *i.e.*, 4.78-17.82 mg/Kg and 3.02-18.86 mg/Kg, respectively. Naturally occurred fluoride concentration in land plants ($< 10 \text{ mg kg}^{-1}$) is less than the concentration available in the algae [39]. An investigation on certain halogens distribution in sea weeds exhibited that the halogen content followed the trend $\text{Cl} > \text{Br} > \text{I} > \text{F}$, but in sea water it followed the order like $\text{Cl} > \text{Br} > \text{F} > \text{I}$. Their concentration factors were in the order $\text{I} > \text{F} > \text{Br} > \text{Cl}$. Iodine enters biological systems quicker than fluoride but the latter's absorption was faster than Br and Cl. Chlorine was not accumulated by weeds but they contain substantial amounts of I, F and Br. It appeared that their uptake and accumulation was mutually independent.

The five freshwater algal forms (*S. oscillatoria iininetica*, *Ankinstrodesmus braunli*, *Scenedesmus cyclotella*, *Neneghiniana* and *Stephanodiscus ininutus*) showed a variable response of fluoride uptake. Fluorine was not spotted in the green even after 50 h exposure to 50 ppm fluoride but found to be associated in the cyanophytes and *C. meneghiniana*. Their fluoride content increased with increasing fluoride concentration in the growth medium. *S. leopoliensis*, *O. limnetica* and *C. meneghiniana* accumulated 54 ± 16 , 71 ± 17 , 116 ± 18 ppm DW of fluoride (control 30 ± 20 , 26 ± 15 , 36 ± 16 ppm DW of fluoride), when exposed to 2.6 mMF. Accumulation of ride appears to be regulated by the differential rates of fluoride absorption and pH of medium. Fluoride sensitive cells of *S. leopoliensis* showed no the other hands showed intracellular increase of 6.1 mMF over control on exposure to 2.6 mMF at pH 6.26. However, uptake decreased with increasing pH values. Fluoride resistant

S. leopoliensis on the other hand showed no measurable increase in cell fluoride. Another green alga (*Chlorella pyrenoidosa*) also showed no detectable increase on addition of 7.9 mM NaF even at a lower pH of 5.9.

Sensitivity and symptoms in plants/leaves/fruits/algae:

The exposed leaves show marginal leaf necrosis followed by light to dark brown rot lesions near or at the leaf tip, mottling and finally chlorosis. In extreme cases over 90% of the affected leaves may become necrotic and over 90% of the leaves of a tree may show injury. Badly injured leaves still remain on the tree. Buildup of intracellular fluoride concentration depends upon the external amount of fluoride [48] and the symptoms appear only when a critical threshold has been reached. Given optimal conditions, sensitive plants may susceptibility even at 1.0 ppb. When injury is severe, growth is suppressed and the tree may ultimately die. In absence necrosis and chlorosis growth generally remains unaffected. It is also known to well-known suture red spot of peach, shrivel tip of cherry and similar of local necrosis on pears and apricots [49].

Severe fluoride toxicity leads to loss in productivity [50]. Impairment of growth of conifers and reduced fruiting in Valencia oranges was observed when fluoride concentrations reached 200 ppm. Yield of tomato fruits was substantially reduced when foliar fluoride content reach 1252 ppm [51]. Development of pollen tube and receptivity has been shown to be impaired. Seed and seedlings appear to be potentially more susceptible to fluorides [52].

Fluoride has various effects on the growth of microalgae, maximum effects were supposed to be at mili molar level and further lower concentrations. Some of the algae of freshwater have been found to show some sensitivity towards fluoride concentration. *Chlorella pyrenoidosa* population was reduced by 37% at 2 ppm fluoride at pH 6.8. 43 ppm fluoride stood toxic at an undetermined pH. Out of six fresh water planktonic microalgae, cyanobacterium *Synechococcus leopoliensis* growth was only inhibited by adding 2.6 mM NaF during mid logarithmic phase. The effect was however transient, showing resumption at reduced fluoride levels. Based on their experience and earlier observations, they suggested that fluoride level found even in fluoride polluted waters should have minimal effects on algal populations.

Guidelines and standards: According to WHO's guidelines for drinking water, a fluoride level of 1.5 mg/L is the desirable upper limit. India reduced the upper limit of fluoride in drinking water from 1.5 to 1.0 mg/L with a rider that "less is better" [53]. Global and Indian standard for fluoride in drinking water is given in Table-1. This is due to the extremes in climatic conditions and the diet being deficient in essential nutrients (calcium, vitamins C, E and antioxidants) in the rural communities of India. So, the Indian standard for the maximum desirable limit of fluoride in drinking water is 1.0 mg/L and the maximum permissible limit is 1.5 mg/L. As the amount of water consumed and consequently the amount of fluoride ingested is influenced primarily by air temperature, USPHS [66] has set a range of concentrations for maximum allowable fluoride in drinking water for communities based on the climatic conditions as shown in Table-2.

TABLE-1
GLOBAL AND INDIAN STANDARD FOR
FLUORIDE IN DRINKING WATER

Type of standards	Description guideline	Guideline value (mg/L)	Ref.
Indian Standards	Allowable limit	1.0	[53]
	Permissible limit in the	1.5	
WHO guideline	Guideline value	1.5	[54]
US EPA	Desired limit	0.7	[55]
	Permissible limit	1.2	
	Max. Contaminant level	4.0	
Canadian guideline	Max. acceptable (MAC)	1.5	[56]
South Korea	Max. permissible limit	0.8	[57]
Japan	Standard value	0.7	[58]
Singapore	Max. prescribed quantity	1.5	[59]
Malaysia	Permissible limit	1.5	[60]
Ireland	Permissible limit	1.5	[61]
UK	Permissible limit	1.5	[62]
Switzerland	Permissible limit	1.5	[63]
Australia	Max. Impurity Conc.	1.5	[64]
New Zealand	Max. acceptable value	1.5	[65]

TABLE-2
USPHS RECOMMENDATION FOR MAXIMUM
ALLOWED FLUORIDE IN DRINKING WATER [66]

Annual average max. daily temp. (°C)	Recommended fluoride concentration (mg/L)			Max. allowable fluoride conc. (mg/L)
	Lower	Optimum	Upper	
10-12	0.9	1.2	1.7	2.4
12.1-14.6	0.8	1.1	1.5	2.2
14.7-17.7	0.8	1.0	1.3	2.0
17.8-21.4	0.7	0.9	1.2	1.8
21.6-26.2	0.7	0.8	1.0	1.6
26.3-32.5	0.6	0.7	0.8	1.4

Fluoride & health effects: Fluoride pollution is causing severe threat to human life around the world. Permissible intake concentration of fluoride lies between 0.5 and 1.5 mg/L beyond this limit it is hazardous for humans [67]. Fluoride restricts tooth decay by reinforcing demineralization of under attacked enamel; in addition, preventing the generation of acid resulting by bacteria which causes impairment in dental plaque [68]. It is worth noting that enamel having fluoride as its one of the general constituent which is fused into growing tooth and protecting it from acid dissolution. Besides, fluoride concentration greater than 1.5 mg/L (with respect WHO 1996, drinking water standards for fluoride) causes dental and skeletal fluorosis, thyroid, kidney changes and cardiovascular, gastrointestinal, endocrine, neurological, reproductive, developmental, molecular level, immunity effects, if concentration is higher than 1.5 mg/L in drinking water [69].

Classification of toxicity: Fluoride toxicity could be classified under two broad headings [70]: (a) acute toxicity: This kind of toxicity is more fatal. It occurs due to accidental consumption of over doses of fluoride; and (b) chronic toxicity: This one is more prevalent of the two. It occurs due to persistent exposure to the toxins or consistent time period.

Dental fluorosis: When the developing tooth is exposed to fluoride, it results in mineralization leading to a state which

is termed as fluorosis. The enamel which is affected by fluorosis has an altered structure, which degrades on further exposure to fluoride [71]. To discuss mineralization, it is essential to go through the process of biomineralization. Biomineralization could be defined as “a process through which the various living organisms undergo production of mineralized tissue”. Some examples of mineralized tissue in vertebrates include tooth enamel, bone, dentin, *etc.* Each mineral tissue is unique in its own kind, the variation depend upon their structure and composition which are also responsible for the mechanical properties.

Dental fluorosis is an unalterable state raised by too much fluoride intake at the growing years and it is primary hint that infants are undergone fluoride exposure. Dental fluorosis is originated by infecting cells involved in enamel formation, known as ameloblasts. Destruction of these cells causes enamel mineralization unevenly, called hypo-mineralization [72,73].

Skeletal fluorosis: Due to the excessive ingestion of fluoride, bone borne diseases like skeletal fluorosis occur [74]. The disease was first discovered in 1920's, among cattle grazing downwind of aluminium and phosphate industries. In human it was first diagnosed in 1932 among a group of Danish cryolite workers. The recommended level of fluoride consumption should be less than 1.5 mg/mL. At this concentration, the consumption of fluoride won't degrade the bones and teeth. The fluoride levels are at a controversial position, for different country the levels of fluoride are different [75]. Due to increment in bone mass and density, skeletal fluorosis arises. Former researchers clearly portrayed that the mechanism involved and the development stages of skeletal.

Alternation in body has been occurred without appearance of any symptoms in patient in first two preclinical stages. Biochemical deformities appeared in compositions of blood and bone in former stage and in later clinical stage, histological irregularities developed like bone and joints, burning sensations, itching and tickling in the limb, proneness in muscles, continuous tiredness and gastrointestinal disorder and reduce appetite. Paining in bones remained steady and few of the ligaments begin to calcify in second clinical stage [76]. In the advance skeletal fluorosis, the tips turn weak and making joints movement difficult. The vertebrate moderately combined together, paralyze the patient hence this stage of fluorosis is also called as crippling skeletal fluorosis.

Abnormalities and crippling fluorosis: The various consequences of the fluoride toxicity appear, when any individual is exposed to 20-80 mg of fluoride on regular basis for a time of more than 10-20 years. The above mentioned substantial exposures are linked to a level of 10 mg/L in the drinking water. The several states India *e.g.* Rajasthan, Punjab and south India are the areas where deformities and fluorosis are in widespread [77]. The usual deformities are kyphosis, flexion, deformity of knees and calcification of cartilages. The quadriplegic patient bent with kyphosis and with markedly-restricted movements of his spine, with contractures of hips and knees.

Cardiovascular effects: The biggest killer of cardiovascular disease worldwide is fluoride. The fluorosilicic acid is the chemical used in the fluoridation of public water supply. This is responsible for the cardiac arrest and ventricular fibril-

lation. Two out of every third family is affected by cardiovascular problem [78]. Due to high concentrations of fluoride, cardiovascular reactions have been ascribed such as hypocalcaemia and hypercalcaemia, which arises by the adequate dose of fluoride binding with calcium in serum. One of the major constituents of calcified deposits in the blood vessel is hydroxyapatite. Gradually over the time the calcification increases and acts as a cause of sudden death. The major cause of arterial calcification is fluorosis. A general observation made in the case of patients affected with fluorosis is that the elasticity of heart decreases over time [78-81].

Gastrointestinal effects: Uninterrupted contact with fluoride causes abdominal defects whose symptoms are nausea, vomiting and gastric pain. The gastric mucosa shows soreness which is attributed to the fluoride exposure which initiates the production of hydrofluoric acid in the stomach's acidic environment, which further penetrates through the cell membranes [70].

Endocrine effects: The endocrine system consists of the synthesis and metabolism of extremely delicate hormones which are associated with enzymatic activity. The interaction with the reaction path would result in chemical clinical changes at an early stage. The fluoride behaviour has received special attention in the hormonal chemistry for clinical variation in the endocrine functioning [82].

Immunological and lymph reticular effects: United States Public Health Services (USPHS) had requested the American Academy of Allergy for a check on the community water supply. The aim of conducting this test was to check the effects of fluoridation occurring from the consumption of water [70]. Suspicious allergic reactions assessment of fluoride is caused by fluoridation, which is used in the community water supplies. A valid proof of the hypersensitivity reaction to fluoride exposure of types I, II, III, or IV were obtained, which are anaphylactic or reaginic, cytotoxic, toxic complex and delayed type reactivity, respectively [83]. The various symptoms spotted are vomiting, gastric pain, headaches, scotomata (blind or partly blind fields in the visual region), personality alteration, lack of strength in muscles, painful deadness in limbs, pain at joints, migraine headaches, mouth dryness, mental degradation, oral ulcers, convulsions, colitis, pelvic haemorrhages, urticaria, nasal congestion, epigastric distress, hematemeses and skin rashes. These signs are not likely to be immunologically mediated reactions of type's I-IV. It is examined that changes in immune response were found due to the exposure of humans to fluoride.

Nervous effects: Fluoride is a powerful central nervous system toxin [84]. The neurological indexes specifically from India have been laid out. Effect of fluoride has also been affecting the glycolysis which further shows direct effect on the central nervous system. The main reason for this direct effect is because glycolysis is the main source of energy. It has been observed that fluoride toxicity not only affected the enzyme involved with glycolysis but was also a cause for hypocalcaemia [85]. Hypocalcaemia is a state of low calcium level in the body and is caused when fluoride binds to calcium [86].

Reproductive effects: An extensive research has been carried out to investigate the interconnection between fluoride

ingestion and reproductive structure or function. NaF has direct effect in the reproductive system. The metabolism and morphology of the sperms of rats was found to be altered and the cause of this alteration was fluorosis. Fluorosis decreased the fertility by 33%. The sodium and potassium ion levels were also decreased because fluoride causes leaking of these ions from the body. In case of female rats, the effect of fluoride was observed in the form of dilated blood vessels, abnormal ovarian follicles and necrotic granulosa cells [87]. Apart from this the results are uncertain for human because the animals were given excess of the fluoride dose regularly. The data for fluoride toxicity is on reproductive health is relatively limited.

A significant report on the relation between fertility and fluorides level was obtained by decreasing the fertility rate and increasing the fluoride levels in municipal water supply. As per the data by NCHS, women living in the high fluoride level areas were compared to those living in the adjacent countries with low fluoride levels. Fluoride levels of more than 3 ppm were reported in one of the system. Another similar study provided with the details that considerably low levels were found in the men who were found affected by skeletal fluorosis. The average level of fluoride consumption varied from 0.11 mg F/kg/day to 0.014 F/kg/days.

Developmental effects: The study of birth defects is termed as teratogenesis. A teratogen is defined as a chemical that increases the occurrence of functional abnormalities in off-spring if consumed by either of the parent before conception, the female during pregnancy or directly to the developing organism [88].

The developing foetus is also prone to the fluoride exposure, but no studies were successful in providing strong argument to defend the study. The fluorides crossed the placenta and assimilated in the developing foetus. Study of people of Africa and India showed elevated levels of fluoride consumed through drinking water. The assimilation of fluoride could be teratogenesis. The body also exhibits natural protective mechanism such as placental barrier and detoxification [88].

Fluoride crosses the placenta in limited amounts and is found in foetal and placental tissue [89]. Fluoride can be toxic at levels which are associated with moderate to severe fluorosis [90]. According to the data of humans and animals, the foetus is not a target of fluorosis [86].

Effect on kidney: The renal framework is in charge of discharging the vast majority of the body's over abundance fluoride and is presented to higher groupings of fluoride than are different organs [91]. This recommends that it may be at higher danger of fluoride harmfulness than most delicate tissues. Nonetheless, at present there are just two distributed investigations which recommend that the chronic consumption of fluoride can have non-cancer causing impacts on the kidney and both relate to the frequency of kidney stones. It was discovered that occupants living in high fluoride locale of Finland [91] (*i.e.*, where groundwater fixations surpass 1.5 mg/L) experienced higher medical clinic affirmation rates for urolithiasis (kidney stones) than did inhabitants living in different regions, in spite of the fact that the rates contrasted distinctly by 16%. A more persuading examination inspected in excess of 18,700 individuals living in a locale of India where fluoride

focuses in the drinking water varies from 3.5 to 4.9 mg/L and found that patients with clear indications of skeletal fluorosis were 4.6 times bound to develop kidney stones. Be that as it may, on the grounds that the subjects of this investigation were most likely at more serious danger of kidney stone development in light of lack of healthy sustenance, it is hard to reach firm inferences [92].

Fluoride as carcinogen: The National Cancer Institute described fluoride as an ambiguous toxin [93]. The young males are found affected by bone cancer. Several studies establish connection between cancer and fluoridated water. Although, all of the research were ecologic studies and the sensitivity limit of even the maximum subtle analysis in these readings appears to be an increase by 10-20%. Fluoride related increase in osteosarcoma of rats was found by a study of NTP. The evidences found were ambiguous. On the other hand a Procter & Gamble sponsored found no evidence of carcinogenic effects by fluoride [94].

The NTP is presently carrying out additional experiments on the relationship, if any, between fluoride and cancer. Osteosarcoma is a kind of cancer responsible for the production of immature bone. Fluoride has been causing aberrations in chromosomes and exchange of sister chromatids and hence acting as a mutagenic agent. Development of osteosarcoma is because of elevated levels of fluoride. High fluoride levels in the bones are suspected to be a major cause of development of osteosarcoma [95].

Fluorosis mitigation: Fluorosis couldn't be eradicated completely. The only measure to deal with it is through prevention and controlled management. Selecting alternative water sources for water consumption could be very helpful in attaining an approach for minimization of fluorosis [96].

Technologies of defluoridation: Variations in the fluoride levels have been observed from different sources in different locations ranging from low to high levels. Normally, the content of fluoride depends upon geological structures of aquifers. The distribution of fluoride is uneven in the groundwater, so every well needs an individual examination of the fluoride distribution in the areas which are endemic for fluorosis. Developing countries are seriously affected by the problem of high fluoride levels in the drinking water [97]. The fluoride dissolved in drinking water is odourless and completely soluble and further producing no turbidity at all. To detect the dissolved fluoride analytical grade chemicals and laboratory methods and skills are desirable. Regulation of fluorosis is a difficult task in absence of proper skill and techniques [98]. A number of defluoridation techniques are said to exist, but only a few of them are effective and efficient simultaneously. It's essential for a technique to be cost effective and efficient in problem solving. Although a variety of procedures are available for defluoridation of water, but they remain ineffective due to absence of optimal conditions. Various kinds of defluoridation methods are available to treat fluoridated water. The fluoride present in water combines with reagents to form an insoluble compound. To treat high fluoridated groundwater *in situ* and *ex situ* methods are available, which reduce down the fluoride levels and makes the water fit for consumption [29].

in situ methods of treatment: This method is applicable to dilute the concentration of fluoride in groundwater. To attain this method, the aquifer needs a recharge which is done artificially by construction of dams. Constructions of rainwater harvesting structures are also examples of this [99].

ex-situ methods of treatment: There are a lot of *ex-situ* methods available for treatment of water both at individual or at large scale.

The processes of defluoridation are categorized into five main groups [100]:

(A) Adsorption methods: Materials with active adsorption sites on the surface are appropriate for this technique of purifying water. The active sites on the surface are ion specific in nature. The ions are adsorbed through a particular physico-chemical process, which is further left for another process leaving them ready to be used after regeneration. Some of the adsorbents showed great resemblance to the sorption media *e.g.* clay, coated silica gel, activated alumina, bone char, *etc.* where the saturated columns could be regenerated. While some economical materials with adsorbent properties are also used for the defluoridation [101] *e.g.* coconut shell, alumina, coffee husk, groundnut shell, activated carbon, magnesia, fly ash, saw dust, *etc.*

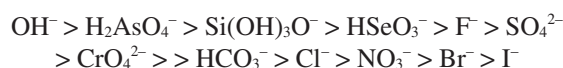
Activated alumina and activated carbon are the adsorbents used mostly. Removal of fluoride is a pH dependent process and the pH limits lie between 5.0-6.0. In acidic medium, the activated alumina gets dissolved which results in loss of adsorption media. The fluoride removal through this process is 90% and it's effective and economical too [101]. However, the disadvantage of this technique is the specific physico-chemical conditions which favour the adsorption or desorption of particular ion/s.

Bone charcoal: Bone charcoal is a widely used adsorbent due to its easy availability, high porosity and low cost [102]. Humic acids are degraded in the process of ozonation where bone charcoal acts as catalyst [103,104]. Earlier methods of defluoridation of water supply suggested uptake of fluoride on the bone surface [38]. It was an ion exchange process where in hydroxy radical of the apatite comprising bone, $\text{Ca}(\text{PO}_4)_6 \cdot \text{OH}_2$, was replaced by fluoride to form an insoluble hydroxyapatite. Carbonizing bone at temperature range of 1100-1600 °C resulted in production of bone char [105]. The carbonized bone char had superior qualities and thus replaced the unprocessed bone as a defluoridating agent [106]. Bone charcoal has the specific ability to take up fluoride from the water. The chemical composition is responsible for efficient fluoride action. As hydroxyapatite, $\text{Ca}(\text{PO}_4)_6 \cdot \text{OH}_2$, one or both the hydroxyl group can be replaced with fluoride [106].

One of the limitations of defluoridation through bone charcoal is associated with the belief of unethical use of bones of animals. In such circumstances, the practise of using bone charcoal must be evaded. However, it has been experienced that many handlers only take repugnance to the use of bone charcoal originating from specific animals [106]. From the scientific perspective all sorts of bones are equally good as raw ingredients from bone charcoal but in such cases the problem would be solved through information and production of the

bone charcoal in accordance with local acceptability. Secondly, medium needs renewal or regeneration when saturated. Thirdly, saturation point difficult to predicts requires monitoring, low removal efficiency if water is withdrawn at high rate and finally the less convenient packing and setting up

Activated alumina: The granular form of aluminium oxide (Al_2O_3) is also known as activated alumina, has a high surface area of the range 200-300 m^2/g^{-1} [107]. The large surface area makes adsorption more efficient by providing greater number of active sites. The fluoride removal mechanism resembles as that of ion exchange resin. The efficiency rate of fluoride removal is 95% and dependent on pH. The optimal pH fluoride removal is typically 5.5-6. The selectivity sequence of activated alumina in the pH range of 5.5-8.5 is:



Regeneration of activated alumina can be done by flushing with a solution of 4% sodium hydroxide [108]. In this fluoride is displaced from the surface and the positive charge is re-established on the surface of alumina. This method is highly effective for the removal of some organic chemicals, selected pesticides and THMs. The main advantages of this method are inexpensive, appropriate to use at home, simple process of filter changing, small production of sludge and negligible maintenance [108]. However, few disadvantages are also persist such as high cost of activated alumina, effectiveness is dependent on contaminant type, concentration and rate of water usage and most likely alumina surface may grow bacteria.

Hydroxyapatite: Hydroxyapatite is an exceptionally crystallized material [109]. The particular surface area of 0.052 m^2/g is exceptionally near that of calcite, quartz and fluorspar. The fluoride uptake in hydroxyapatite is overwhelmed by particle trade. In water defluoridation, the fluoride particles initially adsorb onto hydroxyapatite surfaces and the adsorbed fluoride is exchange with OH^- ions at the closest surface of apatite particles and then exchange with the portable OH^- ions inside the hydroxyapatite particles, bringing about an a lot higher take-up of fluoride by hydroxyapatite [110].

Carbonaceous materials: The treatment of water through carbon based adsorbents is a widely used technique. The surface areas of these adsorbents are quite high, but the affinity towards the ions is low [100]. The internal surface area of these adsorbents is usually high, whereas the carbon affinity to ions is comparatively low. Aluminium impregnated carbon gave 3-5 times higher result of fluoride affinity than carbon. Like other adsorbents, aluminium-impregnated carbon also showed dependence on the pH and temperature [111].

Clay and soil adsorption studies: The comprehensive study of fluoride adsorption onto the minerals and soils was indicated that the adsorption of fluoride onto minerals and soils is accompanied by the release of OH^- ions. It was also found that the fluoride adsorption is concentration dependent and it is described by the Langmuir adsorption isotherm [112]. Several studies on the adsorption of fluoride using clay minerals and soils were undertaken. These studies include the use of Ando soils of Kenya, illinois soils of USA (Alberta

soil), illitegoethite soils in China, clay pottery, fired clay, fired clay chips in Ethiopia, kaolinite, bentonite and kaolinite and fly ash, *etc.*

Fired clays: Removal of F^- using fired clays is studied extensively. The defluoridation of drinking water is done using pottery. The study considered the effect of temperature on adsorption of fluoride. The results demonstrated that clays fired up to 600 °C contributed higher fluoride adsorption [113].

Burnt clay: The burnt clay is obtained from brick Chula. It is prepared by mixing prepared 70% clay and 30% red soil. Both of these constituents were observed to have creditable defluoridation property. Maximum defluoridation efficiency is exhibited by clay with particle size 500 microns. At low pH range, the defluoridation efficiency was more compared to that at high pH range [114].

Activated carbon: Activated carbon can be prepared from different raw materials such as wood, lignite, nutshells, rice, husk, saw dust, coconut shell, *etc.* Process involves heating the material to high temperature, with or without pre-treatment. Untreated powdered activated carbon showed significant fluoride uptake at acidic pH, whereas little or no removal was observed at neutral pH [115]. This is one of the major drawbacks of the process to be applied for the drinking water [116], prepared carbon from saw dust. After pre-treating with alum, the material exhibited fluoride uptake even at neutral pH. Exhausted carbon was regenerated with 2% alum. No large-scale study was undertaken with the material due to its poor hydraulic characteristic. Activated carbon prepared from several materials including cotton waste, coffee waste, coconut waste, *etc.* was tried for defluoridation but all these materials proved to be of academic interest only [116].

Several studies also examined the fluoride adsorption by means of different types of soils [117]. The consequence of variable levels of exchangeable sodium on the adsorption of fluoride onto sodic soils was studied. At equilibrium concentration of fluoride decreased while increase in soil exchangeable sodium percentage was observed [107]. The adsorption of fluoride onto soils was because of presence of amorphous aluminium hydroxides. The highland soil is good for fluoride removal. Using and soils for defluoridation turned out to be economical [107].

The charge on clay surface is dependent upon its structure. If the surface has more positive charge the sorption of negative ions would be better. Adsorption capacity is governed by pH. The pH creates charge modification on the surface and the charges are usually positive in the acidic environment. Adsorption capacity of clay and soil could be improved by pretreating with 1% Na_2CO_3 and 1% HCl [118].

Ion exchange methods: In the water treatment plants generally ion exchange resins are used, herein the hardness is exchanged for sodium ions. The major ions are removed through the ion exchange filters. Strong base exchange resins are required for the fluoride removal. The efficiency of fluoride removal is quite low because the proportion of fluoride to other ions is quite low. Fluoride was also exchanged for chloride by some inorganic exchangers such as complex metal chloride silicates, it is formed from barium chloride along with silicic acid [118].

Cation exchange resins treated with alum were also used for the defluoridation [119]. Some of the commercial ion exchange resins are generally used presently for example:

Defluoron-1: A domestic defluoridation unit was made using Defluoron-1. It is a sulphonated saw-dust, impregnated with alum solution. The capacity of medium was 310 mgF/L. However, this plant has poor hydraulic properties [120].

Carbion: Carbion has hydraulic properties and act as an cation exchanger. Its plant is installed at Rajasthan's Gangapur city. The regenerant was alum and the average removal capacity of carbion was 364 mg/L. The quantity of treated fluoride water was unpredictable and the capacity of defluoridation dropped after 50 cycle.

Defluoron-2: The saw dust carbon and defluoron-1 faced certain difficulties. To overcome the issues, 'defluoron-2' was developed. Around 4% alum solution is used for the media regeneration. The medium had life of 2 years. Performance of plants was observed at Hyderabad and Nalgonda cities of India. The observation continued for 3 years [120].

Magnesia: Magnesium salt reacts with milk of lime to produce crystalline magnesium hydroxide. The precipitate was filtered, washed and dried. Then the calcination was carried out at 100 °C for 3 h to obtain magnesia out of the dried product. Different concentration of magnesia was added to the jars of test sample and then they were stirred. The content of fluoride was checked after 1 h of settlement [121].

Serpentine: Serpentine is a name of mineral, applicable to materials containing either chrysolite or antigorite, or both of them. The chemical formula of mineral is $Mg_6Si_4O_{10}(OH)$ and appears to be green or yellow. Both green and yellow types were studied for defluoridation capacities [100].

Co-precipitation method

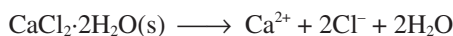
Lime treatment: Lime treatment is used for removal of water hardness. If the water is having high magnesium hardness, then removal of fluoride is possible as a side reaction. The fluoride removal mechanism involves adsorption of fluoride on magnesium hydroxide surface. For removal of 1 mg of fluoride, 45-65 mg/L of magnesium is needed. Limitation of this method is that the treated water has high pH and requirement of high magnesium hardness [122].

Alum coagulation: Fluoride can also be removed through addition of alum. The doses for fluoride removal are higher than that required for turbidity removal. Alum (250 mg/L) was required for reducing groundwater fluoride concentration. The dosage reports from various studies showed the different results. The use of alum for water purification is one of the oldest methods, yet not used in the developed countries. The major limitations accounted for decrease in the pH and generation of sludge [123].

Nalgonda technique: A process where removal of fluoride is ensured by a coagulation-flocculation based sedimentation process is termed as Nalgonda process. The process involves use of aluminium and sulphate. By proper stirring, aluminium sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$ is added to water [124]. The mixture is allowed to settle and the microparticles synthesized are all negatively charged. The water treated through the Nalgonda

technique has high sulphate ion concentration. The maximum permissible sulphate concentration is 400 mg/L.

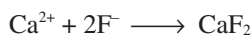
Contact precipitation method: By adding calcium and phosphate compounds respectively, followed by a bone char treatment fluoride is removed through water. This technique of removing fluoride is called contact precipitation. In the reaction mixture, the formation of fluoroapatite is hypothetically possible but practically difficult due to reaction inertness [125]. Using calcium chloride and sodium dihydrogen phosphate, as chemicals the following equations may illustrate the removal. Dissolution of calcium chloride:



Dissolution of sodium dihydrogen phosphate:



Precipitation of calcium fluoride:



Precipitation of fluoroapatite:



It could be inferred from the equations that hydroxyapatite *i.e.* bone char medium doesn't participate in the reactions. Therefore there is no need to for its regeneration, but after a certain time period it could be drained off. The one everyday routine mandatory is to add the two chemicals, preferably in stock solutions, along with the water, either continuously as water flows into the unit or when the water is supplied batch wise for daily consumption. The process seems to be promising, since it implies the relatively low daily working load, high reliability without the need of surveillance of flow or effluent concentration, high removal efficiency, even in case of high raw water concentrations and low operation cost.

Synthetic tricalcium phosphate: The first medium for defluoridation at the Britton defluoridation plant was synthetic tricalcium phosphate. Better results were obtained, but were not of much use at large scale. The reaction of phosphoric acid with lime produced this product. Fluoride removal capacity is 700 mg fluoride/L. The medium is regenerated with 1% NaOH solution followed by a mild acid rinse [126].

Florex: Florex is a combination of tricalcium phosphate and hydroxyapatite. It has a capacity of removing 600 mg fluoride/L. Regeneration is done by 1.5% of NaOH solution [127]. This method is quite expensive.

Membrane process: Separation process involving membranes is more prevalent in the industrial sectors for treatment of wastewaters. The particles are primarily isolated on the basis of their molecular sizes and shape. Most commonly used membrane separation systems are (i) reverse osmosis (RO), (ii) nanofiltration (NF), (iii) electrodialysis (ED) and (iv) ultrafiltration (UF) [128].

Before, the utilization of membrane filtration innovation for water treatment, especially for drinking water, generation had been considered uneconomical in examination with regular methods, yet in the ongoing years the expanded interest and contamination of water ascend in water quality principles and the problems related with different techniques have prompted re-examination of film innovation for water filtration. There

are two sorts of films that can expel fluoride from water are nanofiltration (NF) and reverse osmosis (RO). Nanofiltration (NF) is a generally low weight process evacuates fundamentally the bigger broke down solids when contrasted with RO. On the other hand, RO works at higher weights with more noteworthy dismissal of every single broke up strong. Fluoride evacuation efficiencies up to 98% by layer procedures have been reported by numerous analysts. To separate high molecular weight solute from a solvent nanofiltration is used. It has great efficiency in production of drinking water. Lower retention is observed for monovalent ions if compared to RO. The recent updates show that NF separates same valency ions for selective defluoridation of saline water.

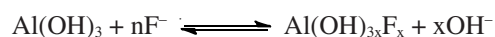
Other methods

KRASS process: KRASS defluoridation process was developed to combat the drawbacks of the pre-existing defluoridation methods. Some key features of this method are (i) low cost, (ii) simpler to use by common people, (iii) harmless and a capable method, (iv) no limit on input quantity of water, (v) independent of temperature, pH, alkalinity and total dissolved solids of input water, (vi) practical approach for rural population, (vii) filters are recharged by alum and (ix) certified by accredited agencies [129].

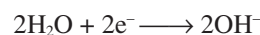
The fluoride tainted water passes across filter through the bed media to yield defluoridated water. A defluoridation study was carried out on a number of columns in a down flow model. The study concluded that at a pH range of 4.3-9.0, the fluoride could be removed for the influent. The treated water contained traces of aluminium. The treated waters concentration was found to be equivalent to that of Nalgonda process [130].

Electrocoagulation/electrochemical methods: Electrochemical strategy (likewise electrocoagulation) is a straightforward and effective technique for the treatment of consumable water. This procedure is portrayed by a quick rate of contaminant evacuation, a reduced size of the hardware, effortless in activity and low capital and working expenses. Also, it is especially progressively viable in treating wastewaters containing little and light suspended particles, for example, slick eatery wastewater, as a result of the going with electro-buoyancy impact [131].

The electrochemical strategy is by and large at a formative stage and in this way isn't a set up innovation for defluoridation. Electrocoagulation (EC) utilizing aluminium anodes are compelling in defluoridation. In the EC cell, the aluminium cathodes first penance themselves to shape aluminium particles. A short time later, the aluminium particles are changed into $\text{Al}(\text{OH})_3$ before being polymerized to $\text{Al}_n(\text{OH})_{3n}$. The $\text{Al}(\text{OH})_3$ floc is accepted to adsorb fluoride unequivocally as appeared by the accompanying response:



At aluminium cathode, hydrogen gas is released according to the following reaction:



Any supporting evidence for adsorption was lacking. The hydrogen produced at the cathode prevented settling of flocs.

To overcome this issue, application of electrofloatation is needed. An innovation of defluoridation through electrochemical course has been created. The essential rule of the procedure is the adsorption of fluoride with newly accelerated aluminium hydroxide, which is created by the anodic disintegration of aluminium or its amalgams, in an electrochemical cell. The procedure uses 0.3 to 0.6 kwh of power per 1000 L of water containing 5-10 mg/L of fluoride. The anode is persistently devoured and should be renewed. The procedure produces ooze at the rate of 80-100 g for each 1000 L (on dry premise).

Rare earth-based materials: The treatment of water from hazardous anions such as fluoride, arsenic, selenium, *etc.* by using rare earth materials have not yet used efficiently by the industries. For removal of hazardous anions solid lanthanum and yttrium ions have been used as adsorbents. To improve the economic and engineering performance either lanthanum or yttrium ions are loaded on porous silica or alumina beads. Cerium iron adsorbent (CFA) is a rare earth metal based inorganic adsorbent developed for the removal of fluoride. The experimental data confirmed that rare earth metals had high capacity of adsorption and good kinetic property for removal of fluoride. At pH 3, the highest capacity was obtained, however at pH 5 the effect become unremarkable [132].

Conclusion

Water contamination from fluoride is widespread problem across the globe. Over consumption of fluoride results in a health condition called fluorosis. The main reason for fluorosis is the contaminated drinking water. Fluoride toxicity could be lethal and it's toxicity could be classified as acute and chronic, depending upon the consumption pattern. To get rid of fluoride in drinking water various steps need to be taken. These involve adsorption, filtration through membrane process, *in situ* defluoridation process, *etc.* in the areas with no alternative to fresh drinking water, defluoridation should be practiced. Efficiency removal of fluoride Selection of process should be done accurately as per the needs.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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