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Removal of fluoride from aqueous solution: status and techniques

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ABSTRACT

Presence of various hazardous contaminants like fluoride, arsenic, nitrate, sulfate, pesticides, heavy metals, and other elements in ground water or surface water make the water unsafe and dangerous for the drinking purpose. The presence of any of these elements in drinking water in excess to the permissible limit is harmful for the human life. Fluoride is one of the elements which is very important for health especially for the children during teeth formation as well as harmful for human health if present in water more than permissible limit. Absence or insufficient amount of fluoride in drinking water causes dental caries during teeth formation of children whereas the presence of excess fluoride in drinking water causes dental and skeletal fluorosis. Therefore, maintaining of fluoride concentration within the safe limits is very important. The presence of excess fluoride in drinking water is a global problem. Excessive fluoride concentrations have been reported in ground waters of more than 27 developed and developing countries including India. In India, about 19 states are facing acute fluorosis problem due to excess fluoride concentration. Fluoride is the major inorganic pollutant of natural origin found in ground water. The excessive fluoride from the drinking water should be reduced to the permissible limit. Various technologies such as coagulation–precipitation, ion exchange, electrocoagulation/electrochemical treatment, membrane processes, nanotechnology, and adsorption are being used to remove fluoride from water. Every method of fluoride removal has its advantages and limitations of operations. The selection of treatment process should be site specific as per local needs and prevailing conditions as each technology has some limitations. The present paper deals with the short review on sources of fluoride, its effects on human health, and the techniques available for removal of fluoride from drinking water.

Keywords: Fluoride; Removal; Wastewater; Treatment; Precipitation; Adsorption; Electrochemical; Membrane

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1. Introduction

Water is one of the basic needs of life on the earth. It is available abundantly covering about 75% of the earth. The chemical nature of water is one of the most important criteria that determine its usefulness for specific need and as such all the waters are not fit for drinking, hence the problem of scarcity of drinking water arises [1]. There are several natural trace elements in drinking water, fluorine is one of those natural trace elements and exists in almost all soils, through which it leaches into the ground water. In elemental form fluorine is flammable, irritating, and toxic halogen gas which is known as one of the most powerful oxidizing agents. It occurs naturally in reduced form (Fluoride, F^-) in combination with other minerals. Fluoride is classified as a binary compound of fluorine with another element. Fluorine compounds make up approximately 0.08% of the earth´s crust [2]. Fluoride is a naturally occurring element in minerals and geochemical deposits and enters food chains through either drinking water or eating plants and cereals. Fluoride is generally released into subsoil water sources by the slow natural degradation of fluorine in rocks. Fluorine and its compounds are valuable and are extensively used in industries such as fertilizer, production of high purity graphite, semi-conductors, electrolysis of alumina, and in nuclear applications [3]. Virtually, all food stuffs contain at least trace amounts of fluoride which enters human in increasing amounts through consumption of fluoride containing foods and beverages [4]. Table 1 [5] lists the various foods containing fluoride.

Fluoride is toxic, but at the same time it is beneficial for calcification of dental enamel and bone formation. Excess intake of fluoride would lead to various diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility in women, male sterility, brain damage, Alzheimer syndrome, and thyroid disorder [6]. According to World Health Organization guidelines (WHO), the fluoride concentration in drinking water should not exceed 1.5 mg/l [7]. However, this limit of fluoride is not universal. Various health impacts with varying concentration of fluoride from long-term use of fluoride-contaminated drinking water are shown in Table 2 [4]. The most common symptoms of chronic fluoride exposure are skeletal fluorosis, which can lead to permanent bone and joint deformation and dental fluorosis. Various symptoms of fluorosis are shown in Table 3 [5]. US Public Health Service (USPHS) Drinking Water Standards has set a range of concentrations for maximum allowable fluoride in drinking water for communities based on the climatic conditions as 1.4–2.4 mg/l for the annual average at maximum daily air temperature from 32.4˚C to 10˚C, respectively [8]. According to National Health and Medical Research Council, fluoride is considered beneficial in drinking water at level of about 0.7 mg/l but is harmful once it exceeds 1.5 mg/l [9]. According to Indian Standards Specifications for drinking water, the desirable and permissible limits for fluoride in drinking water are 1.0 mg/l and 1.5 mg/l, respectively [10].

A study by United Nations International Children's Emergency Fund (UNICEF) shows that fluorosis is endemic in at least 27 countries across the globe. These countries are Algeria, Argentina, Australia, Ban-

Table 1
Food containing higher fluoride contents [5]

Name	Fluoride content (mg/100 g)
Tea	39.8–68.59
Areca nut (supari)	3.8–12.0
Beetle leaves	7.8–12.0
Tobacco	3.1–38.0
Cardamom	14.4
Salt (kala namak)	14.4

Table 2
Health impacts of fluoride [4]

Fluoride concentration (mg/l)	Health effects
<0.5	Dental carries
0.5–1.5	Promotes dental health
1.5–4	Dental fluorosis
>4	Dental and skeletal fluorosis

Table 3
Symptoms of fluorosis [5]

Dental fluorosis	Skeletal fluorosis	Soft tissue fluorosis
Chalky white teeth	Pain in lower limbs	Gas in stomach
Yellow to brown pigmentation	Knock knee	Anemia, tiredness
Teeth becomes brittle	Bow leg	Delayed puberty
Enamel chips off	Stiffness of back and neck	Destruction of thyroid gland
	Unable to stand and bend	Infertility, low IQ

Table 4
Fluoride endemic districts in various states of India [14]

States	Districts	Fluoride concentration (mg/l)
Assam	Karbianglong, Nagaon	0.2–18.1
Andhra Pradesh	All districts except Adilabad, Nizamabad, West Godavari, Visakhapatnam, Vijzianagaram, Srikakulam	0.11–20.0
Bihar	Palamu, Daltonganj, Gridh, Gaya, Rohtas, Gopalganj, Paschim Champaran	0.6–8.0
Delhi	Kanjhwala, Najafgarh, Alipur	0.4–10
Gujarat	All districts except Dang	1.58–31.0
Haryana	Rewari, Faridabad, Karnal, Sonipat, Jjind, Gurgaon, Mohindgarh Rohtak, Kurukshetra, Kaithal, Bhiwani, Sirsa, Hisar	0.17–24.7
Jammu and Kashmir	Doda	0.05–4.21
Karnataka	Dharwad, Gadag, Bellary, Belgam, Raichur Bijapur, Gulbarg, Chitradurga, Tumkur, Chikmgalur, Manya, Banglore, Mysore	0.2–18
Kerala	Palghat, Allepy, Vamanapuram, Alappuzha	0.2–2.5
Maharashtra	Chandrapur, Bhandara, Nagpur, Jalgaon, Bulduna, Amravati, Akola, Yavatmal, Nanded, Sholapur	0.11–10.2
Madhya Pradesh	Shivpuri, Jabua, Mandla, Dindori, Chindwara, Dhar, Vidisha, Seoni, Sehore, Raisen and Bhopal	0.08–4.2
Orrissa	Phulbani, Koraput, Dhenkanal	0.6–5.7
Punjab	Mansa, Faridcot, Bhatinda, Muktsar, Moga, Sangrur, Ferozpur, Ludhiana, Amritsar, Patiala, Ropar, Jallandhar, Fategarh Sahib	0.44–6.0
Rajasthan	All the 32 districts	0.2–37
Tamilnadu	Salem, Periyar, Dharampuri, Coimbatore, Tiruchirapalli, Vellore, Madurai, Virudunagar	1.5–5.0
Uttar Pradesh	Unnao, Agra, Meerut, Mathura, Aligarh, Raibareli, Allahabad	0.12–8.9
West Bengal	Birbhum, Bhardaman, Bankura	1.5–13.0

gladesh, China, Egypt, Ethiopia, India, Iran, Iraq, Japan, Jordan, Kenya, Libya, Mexico, Morocco, New Zealand, Palestine, Pakistan, Senegal, Srilanka, Syria, Tanzania, Thailand, Turkey, Uganda, and United Arab Emirates [11,12]. In India, Fluorosis was first detected in Nellore district of Andhra Pradesh in 1937 [13]. At present more than 17 states Table 4 [14] are affected with fluoride contamination, in the country. Fluoride concentration more than 1.5 mg/l has been reported from the isolated pockets in the state of Andhra Pradesh, Assam, Chattisgarh, Delhi, Gujarat, Haryana, Jharkhand, Karnataka, Kerala, Madhya Pradesh, Maharastra, Orissa, Punjab, Tamil Nadu, Uttar Pradesh, West Bengal, and all 32 districts of Rajasthan [14]. Fluoride contamination above acceptable level has been reported in Chandrapur, Satara, Solapur, Yavatmal, and Nagpur districts of Maharashtra State of India. Extremely high concentration of 14.2 mg/l has been found in Yavatmal district in Maharashtra. The natural water reservoirs in 16 talukas of Yavatmal district are heavily contaminated with fluoride [15]. The fluoride concentration of water collected from borewells at different locations in Yavatmal district has been presented in Table 5 [16]. The problem of

Table 5
Fluoride concentration at different locations in Yavatmal districts of Maharashtra, India [16]

Locations	Concentration (mg/l)
Runjha	4.81
Khatara	3.03
Sonurli	7.22
Karanji	2.45
Wadhana	5.76
Dharna	13.41
Sakhra	11.9
Nilzai	3.50
Ganeshpur	2.84
Wai	3.02
Gevrai munch	4.81
Shushri	5.95
Pendhari	2.88

fluoride is still exists in some of the villages in India which is clear from the news appears in news papers. One report says that about 50 peoples out of 200 residents from 25 families are affected due to excessive fluoride concentration in villages Pindkepar and Kanhartola of Goregaon Tahsil in Gondia district of Maharashtra State of India [17]. In Nanded, a district in Maharashtra State of India, about 11,000 persons from 222 villages are affected by either dental or skeletal fluorosis out of which 437 patients were found in the village Sawarkhed in the district. The concentration of fluoride was found to be in the range of 7–9.5 mg/l [18]. Not only in Maharashtra but there are several villages in many States of India which are still affected by fluoride contamination. The extensive research has been carried out in this field which has brought a wide range of adsorbents in reach of industries. Authors group have widely worked on wastewater treatment and environmental engineering area [19–39].

In view of the health impacts of fluoride, it must be reduced from drinking water up to permissible level. Various methods are available to remove the fluoride from drinking water such as coagulation–precipitation, adsorption, ion exchange, electrochemical process, and membrane process. In present paper, recent advances of these processes are presented in view of their application for the removal of fluoride from drinking water.

2. Methods of treatment

Several methods have been reported in the literature for removal of fluoride from drinking water. The subsequent paragraphs deal with these methods, their applications, advantages, and disadvantages Table 6.

2.1. Coagulation–precipitation

The coagulation–precipitation method involves an addition of aluminum salt, lime, and bleaching powder followed by rapid mixing, flocculation, sedimentation, and filtration. Aluminum salt is responsible for the removal of fluoride from water. The dose of aluminum salt increases with increase in fluoride and alkalinity levels in the raw water. The dose of lime is empirically 1/20th of the dose of alum. Lime facilitates forming of denser flocs for rapid settling. Bleaching powder is added to the raw water at the rate of 3 mg/l for disinfection [40]. Most of coagulation–precipitation processes are not effective for the presence of higher concentration fluoride in drinking water.

A two-column lime stone reactor has been designed to reduce fluoride concentration from wastewater by Reardon and Wang [41]. It is reported in the study that the initial fluoride concentration of 109 mg/l was brought up to less than 4 mg/l by this process. In this method, the fluoride gets precipitated in first column whereas; the calcite dissolved in the first column gets

Table 6
Advantages/disadvantages of various treatment processes

Methods	Advantages	Disadvantages
Precipitation/ coagulation	Established method, widely used method	High chemical dose required, moderate efficiency, aluminum salt produces sludge, health impact due to aluminum solubility
Adsorption	Locally available adsorbent material, high efficiency, cost effective	pH dependent, ionic competition, regeneration required, disposal of fluoride laden sludge
Ion Exchange	Removes fluoride up to 90–95%, retain the taste and color of water intact	Ionic competition, higher cost
Dialysis	Good potential	Membrane fouling, frequent cleaning requires, technology is not mature enough for application on large scale
Electrodialysis	Effective technique, no chemical required, works under wide pH range	Higher power consumption, skilled labors require
Reverse osmosis	Effective technique	Membrane fouling, energy consumption
Electrochemical	Good efficiency	Costly process, higher power consumption, frequent replacement of anode required
Nanotechnology	Effective technique	Costly process
Biotechniques	Economical, high efficiency, environment friendly, regeneration not required	Decomposition/degradation of biosorbents

precipitated in second column. A simple method called the Nalgonda technique was designed to remove fluoride from drinking water by Bulusu et al. [42]. This process involves the addition of alkali, chlorine, and aluminum sulfate or aluminum chloride or both, agitation or mixing and the settlement of precipitation to remove fluoride from drinking water. This technique is effective even when the fluoride concentration is above 20 mg/l. It is possible to lower the concentration of fluoride up to 1 mg/l from 20 mg/l by Nalgonda technique [43]. Banuchandra and Selvapathy [44] have reported that the concentration of fluoride can be reduced to 1 mg/l from 20 mg/l by alum and lime addition. Chang and Liu [45] investigated coagulation–flocculation of calcium fluoride precipitates in combination with polyaluminum chloride and polyacrylic acid at lower dosage. Nath and Dutta [46] showed that a combination of precipitation and adsorption of fluoride can be more effective. The result of study with crushed limestone and fluoride solution acidified with edible acids shows that both citric acid and acetic acid can reduce fluoride concentration from 10 mg/l to 1.5 mg/l. Summary of the work on removal of fluoride by using coagulation–precipitation methods has been presented in Table 7.

2.2. *Ion exchange*

Strong base exchange resins remove the fluoride either on hydroxyl cycle or chloride cycle along with anions. Fluoride can be removed with strongly basic anion exchange resins containing quaternary ammonium functional groups. The removal takes place according to the following reaction:

$$\mathrm{Matrix} - \mathrm{NR}_3^+\mathrm{Cl}^- + \mathrm{F}^- \rightarrow \mathrm{Matrix} - \mathrm{NR}_3^+\mathrm{F}^- + \mathrm{Cl}^- \quad (1)$$

The fluoride ions replace the chloride ions of the resin. The process continues until all the sites on the resin are occupied. The resin is then backwashed with water that is supersaturated with dissolved NaCl. New chloride ions then replace fluoride ions leading to recharge the resin and starting the process again. The driving force for the replacement of chloride ions from the resin is due to the stronger electronegativity of the fluoride ions [47]. In order to improve the ion exchange capacity, mesoporous titanium oxohydroxide had been prepared by using dodecylamine as template by Ho et al. [48]. Zirconia and silica have been introduced in the mesoporous titanium oxohydroxide to enhance the ion exchange capacity. Results showed that mesoporous titanium oxohydroxide-containing zirconia exhibited the highest fluoride ion exchange capacity as it has the smallest particle size with high uniformity among the mesoporous materials prepared. Process is costly and problem of membrane fouling is present in this process. The advantages and disadvantages of ion exchange process are mentioned in Table 6. Jamhour [49] showed that 96% removal of fluoride is possible by using zirconium oxide etanolamine. Decrease in efficiency of fluoride removal is due to presence of other ions and increased pH. The transport of fluoride through Neosepta ACM anion exchange membrane has been studied as a function of feed phase and receiver phase concentration and coexistence anions under Donnan dialysis by Tor [50]. It was observed that the transport of fluoride was maximum at pH 6 of feed phase and at pH 1 of receiver phase. Moreover, transport of fluoride increased with increase in feed and receiver phase concentrations and decreased in the presence of other coexisting anions in the feed phase. The defluoridation capacity (DC) of a chelating resin, namely Indion FR 10 (IND), and Ceralite IRA 400 (CER), are studied by Meenakshi and Viswanathan [51]. An anion exchange resin was compared under various equilibrating conditions for the identification of selective sorbents. The results showed that chelating resin is more selective than an anion exchange resin for fluoride removal. The adsorption mechanism is more selective for fluoride removal than ion exchange process even from the dilute solutions of fluoride ion as the ion exchange mechanism depends on the concen-

Table 7
Summary of few studies on coagulation–precipitation for removal of fluoride

Reference	Result	Remarks
[41]	Initial fluoride of 109 mg/l were brought below the 4 mg/l	Efficiency of process is low. System monitoring is minimal, chemicals are not added permanently
[44]	Remove fluoride concentration above 20 mg/l to 1 mg/l	Formation of large amount of sludge, their disposal problems
[45]	Effective process	Permissible effluent standard is 15 mg/l to discharge to centralized waste water treatment plant
[46]	Reduce fluoride concentration from 10 mg/l to 1.74 mg/l and 0.977 mg/l, respectively	Problem of sludge formation, pH is sometime not in desirable range because of use of acid

Table 8
Summary of few studies on ion-exchange for removal of fluoride

Reference	Result	Remarks
[48]	Ion exchange order TiOx(OH)y < mesoporous TiOx(OH)y containing silica < TiOx(OH)y containing zirconia	Costly process
[49]	96% removal is possible by zirconium oxide ethanolamine	Decrease in efficiency due to presence of other ions and increase in pH
[50]	Neosepta ACM anion exchange is used; transport of fluoride is maximum at pH 6 of feed phase and at pH 1 of receiver phase	Transport of fluoride depends on conc. of feed and receiver phase, pH and presence of other coexisting ions
[51]	Chelating region is more selective than anion exchange	Depends on the concentration of ions

trations of ions which are normally present in water with excess of fluoride. The summary of a few works for the removal of fluoride by using ion exchange method has been presented in Table 8.

2.3. Electrochemical process

In this process when aluminum (Al) electrodes are used, Al dissolves at the anode and hydrogen gas is released at the cathode. During the dissolution of Al at the anode, various aqueous aluminum species are produced, which depends on chemistry of the solution. The Al species act as a coagulant by combining with the pollutants to form large size flocs. The electrolytic dissolution of Al at anode by oxidation in water produces aqueous Al^{3+} species [52]. The electrode reactions are outlined below:

$$\begin{aligned} &\text{Anode:}\quad Al(s) \rightarrow Al^{3} + 3e^{-} \\ &\text{Cathode:}\quad 2H_2O + 2e^{-} \rightarrow H_2(g) + 2OH^{-} \end{aligned} \tag{3}$$

The H_2 bubbles float and hence drive the flotation process. The Al^{3+} ions further react to form solid $Al(OH)_3$ precipitate as follows:

$$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3(s) + OH^{-} \tag{4}$$

Fluoride is adsorbed by the freshly precipitated $Al(OH)_3$.

In its simplest form, an electrocoagulation reactor is made up of an electrolytic cell with one anode and one cathode [53]. Yang and Dluhy [54] studied the fluoride removal by producing aluminum sorbent in electrochemical reactor. Aluminum sorbent was produced in a parallel plate electrochemical reactor by anodic dissolution of aluminum electrodes in a dilute sodium chloride aqueous solution. The NaCl in the solution effectively reduced the power consumption and promoted the sorbent generation by depositing the aluminum water electrochemical system. The freshly generated Al-sorbent is able to reduce fluoride concentration from 16 to 2 mg/l in 2 min. The final concentration was further reduced to 0.1 mg/l by partial neutralization of the mixture to pH 6.3. The sorbent generation and fluoride adsorption was integrated into a single electrochemical reactor. The system was able to reduce the fluoride concentration from 16 to 6 mg/l in 2 min of treatment and to about 2 mg/l in 4 min. The effluents from the electrochemical system needs pH adjustment to bring the fluoride concentration down to less than 1 mg/l. Fluoride ions were removed electrochemically from a solution using a combined electrocoagultion and electroflotation process by Shen et al. [55]. For an influent fluoride concentration of 15 mg/l, a value after lime precipitation, the effluent fluoride concentration can be lower than 2 mg/l when the pH in the coagulation cell is around 6. Even lower effluent concentration can be achieved if 50 mg/l of Fe^{3+} or Mg^{2+} are added into the coagulation unit. The anions generally reduce the fluoride removal efficiency except Cl^{-} whose corrosion pitting of the electrode can result in 130% current efficiency. The composition of the sludge produced from the operation was analyzed by using X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscope system (ToF-SIMS). The characterization results show that the defluoridation is a chemical adsorption process with F^{-} replacing the OH group from the $Al_n(OH)_{3n}$ flocs. Electrocoagulation was investigated for the effective removal of fluoride from drinking water by Ghosh et al. [56]. Different initial concentrations (2–10 mg/l) of fluoride were considered for the experiment. Two different electrode connections (monopolar and bipolar) were examined for choosing the better alternative in order to intensify the performance of the process. It was observed that the removal of fluoride was better for bipolar connection than for monopolar connection. The final recommended limit of fluoride (1 mg/l) was obtained in 30 min at 625 A m^{-2} using bipolar connection. The corrosion of electrodes as well as the sludge formed during the process was estimated for the bipolar connection. Treatment of synthetic fluoride containing solution by electrocoagulation method using aluminum electrode has been studied by Drouiche et al. [57]. Applied potential 10–30 V and supporting electrolyte NaCl (0–100 mg/l) was used. The result showed that with an increase in applied potential and electrolysis time the Al^{3+} dosage increases and there by favouring the fluoride ions removal. Electrocoagulation process using aluminum electrode for removing fluoride from treated industrial waste water from steel industry has been studied by Khatibikamal et al. [58]. The authors have studied the removal of fluoride through electrocoagulation process by using aluminum electrodes. They have studied the effects of various operating conditions such as temperature, pH, voltage, hydraulic retention time (HRT), and number of electrodes between anode and cathode plates on removal of fluoride. It is reported that fluoride concentration can be reduced from 4 to 6 mg/l to lower than 0.5 mg/l with the HRT of 5 min. They also studied the kinetics of fluoride removal, which obeys the second-order kinetic model. The summary of a few works for the removal of fluoride by using electrochemical method has been presented in Table 9.

2.4. Membrane process

The membrane separation processes over past two decades have achieved a lot of industrial importance for wastewater treatment and sea water desalination, their potential for treating ground water to remove fluoride and other undesirable ions remain unexploited [59]. In a membrane separation process, a feed consisting of a mixture of two or more components is partially separated by means of a semi-permeable barrier (the membrane) through which one or more species move faster than another. In most of the general membrane processes, the feed mixture is separated into retentate (the part of feed which does not pass through the membrane, i.e. retained) and permeate (that part of the feed which passes through the membrane). Although the feed, retentate and permeate are usually liquid or gas, they may also be solid. The semi-permeable barrier is most often a thin, nonporous, polymeric film, but may also be porous polymer, ceramic, or metal material or even a liquid or gas. The barrier must not dissolve, disintegrate, or break [60]. The most commonly used membrane separation processes for removal of fluoride are reverse osmosis, Donnan dialysis, and electrodialysis. The summary of few works by using membrane separation processes are mentioned in Table 10.

2.4.1. Reverse osmosis

The phenomenon of movement of solute particles from higher concentration to a lower concentration so as to bring an uniform concentration throughout the bulk solution is known as diffusion. Diffusion of solvent through a semi-permeable membrane from a solution with a lower solute concentration to a solution with higher solute concentration takes place until there is an equal concentration of fluid on both sides of the membrane. The semi-permeable membrane allows free passage to solvent molecules but not to the solute molecules. When a solution is separated from the pure solvent by semi-permeable membrane and the pressure applied on the solution is more than the osmotic pressure, the solvent will start flowing from the solution towards the pure solvent. This phe-

Table 9
Summary of few studies on electrochemical process for removal of fluoride

Reference	Result	Remarks
[54]	Reduces fluoride concentration upto 2 mg/l from 16 mg/l	Effluent from electrochemical system need pH adjustment to bring the fluoride concentration down to less than 1 mg/l
[55]	Fluoride concentration. Can be reduce below 2 mg/l from 15 mg/l	pH adjustment is needed, it should be around 6, presence of other anions decrease fluoride removal efficiency
[56]	Fluoride concentration can be reduced to 1 mg/l from initial 10 mg/l	Costly process
[57]	Electrocoagulation is attractive process as no contaminants are introduced and beneficial contents present in raw water can be remained during defluoridation	Problem of sludge removal
[58]	93% removal is possible	Removal depends on voltage and electric current

Table 10
Summary of few studies on membrane separation process for removal of fluoride

References	Process	Result	Remarks
[61]	Membrane technology and lime stone filtration	Both reverse osmosis and nanofiltration are effective, removal is greater than 95% in RO and 76% in nanofiltration	Higher investment cost of reverse osmosis than nanofiltration, nanofiltration depends on pressure, temperature. Both effective for fluoride removal from soft high fluoride ground water
[64]	Donnan dialysis	Initial fluoride concentration of 9.5 mg/l and 6.1 mg/l was reduced to less than 1.5 mg/l	Mineralization of water increased by 25%
[66]	Donnan dialysis	Modified poly (2-chloroaniline) is most effective than unmodified membrane	Fluoride removal depends upon structure of membrane, pH of solution, different valence anions and fluoride concentration in feed
[55]	Reverse osmosis membrane	80% recovery of fluoride is possible	Problem of fouling, minimization of energy consumption is possible
[63]	Reverse osmosis membrane	Rejection of fluoride is greater than 96%	Problem of scaling (precipitation of salts on membrane)
[65]	Adsorption and Donnan dialysis	Removes fluoride concentration below acceptable values	Costly presses

nomenon is known as reverse osmosis. Combination of membrane technology and limestone filtration to control fluoride and aluminum concentration in drinking water was studied by Kettunen and Keskitalo [61]. A plant including reverse osmosis and nanofiltration techniques was constructed in 1999 in the city of Laitila of Finland to control fluoride and aluminum concentration in drinking water. It is reported that both reverse osmosis and nanofiltration were effective to remove fluoride around 95% and 76%, respectively. A posttreatment step with lime stone filtration was implemented for control of alkalinity. Sehn et al. [62] reported about 80% of fluoride removal by using reverse osmosis membranes in Finland. Dolar et al. [63] investigated the removal efficiency of reverse osmosis and nanofiltration membrane to reduce the fluoride and phosphate load from fertilizer industry. Six membranes were chosen for fluoride and phosphate removal. Artificial model waters similar to those from the fertilizer industry were prepared. It is reported that fluoride removal with reverse osmosis membranes was higher than 80% for model water and higher than 96% for real wastewater. In case of nanofiltration membrane, fluoride removal was higher than 40%. The reverse osmosis membrane XLE and nanofiltration membrane NF90 was found effective for removal of fluoride.

2.4.2. Donnan dialysis

Donnan dialysis is also known as diffusion dialysis, is similar to ion exchange membrane but different from electromembrane process in which the driving force is not an electrical current, but simply a difference in chemical potential. Concentration difference is the most obvious driving force for ion transport in Donnan dialysis. A negative ion can be driven out of a feed solution through Donnan dialysis equipped with anion exchange membrane by utilizing a second alkaline stream. The concentration difference of hydroxide ion between the two solutions compels the hydroxide ions to diffuse into feed solution. This creates an oppositely directed electrical field driving an extraction of negative ions from the feed solution. Hichour et al. [64] used synthetic waters and treated it with Donnan dialysis. The technique is more adopted for the treatment of low concentration water. The Donnan dialysis process was studied under two circulating modes of the receiver solution, single pass, and batch, while the feed solution flowed continuously as a single pass to maintain fluoride concentration below acceptable values. At the outlets, the feed compartment the extracted fluoride ions complexed by Al^{3+} ions which were added in the receiver solution. Nevertheless, this technique seems more adopted for the treatment of low concentration waters. However, mineralization of water increases by 25%. Garmes et al. [65] applied a hybrid process combined with the adsorption on aluminum and zirconium oxide along and Donnan dialysis to treat the groundwater with an excessive fluoride concentration of 4 mg/l resulting from phosphate mining in Morocco. The Donnan dialysis unit consisted of 11 cells (5 feed and 6 receiver cells) separated by anion exchange membrane. The commercially available anion exchange membrane used was Neosepta-ACS. The Donnan dialysis process was studied under two circulating modes of receiver solution, single pass, and batch, where as the feed solution flowed continuously as a single pass to maintain the fluoride concentration below acceptable values at the outlet of the feed compartment, the extracted fluoride ions are adsorbed by Al_2O_3 and ZrO_2. The removal of fluoride from aqueous solution with plasma-modified and unmodified poly (2-chloroaniline) (P2ClAn) anion exchange membranes were studied by Kir and Alkan [66]. The effects of concentration, pH, and different valence anions on feed phase were investigated. The surfaces of P2C1An membranes were modified by electron cyclotron resonance plasma (ECR) to increase the performance. The flux values of fluoride before and after the modification were obtained. An increase in fluoride flux has been observed with increasing concentration of the feed phase. Also, the flux value for the plasma-modified P2C1An membrane was found to be higher than that of the unmodified membrane due to wider and increased number of pores in the plasma-modified membrane. In addition, effects of different valence anions on flux of fluoride were studied and found as $Cl^- > SO_4^{2-}$. pH values of NaF solution were changed between 3 and 9 in the feed phase to see the effect of pH on fluoride removal. It was observed that removal of fluoride increased with increasing the pH value to 5.5. At a pH above 5.5, fluoride removal decreases as a result of stronger competition from hydroxide ions on the membrane surface. The highest fluoride removal was found at pH of 5.5.

2.4.3. Electrodialysis

Electrodialysis refers to an electrolytic process for separating an aqueous, electrolytic feed solution into a concentrate or brine and a dilute or desalted water by means of an electric field and ion selective membrane. In electrodialysis process, multiple electrodialysis cells are arranged into a configuration called an electrodialysis stack, with alternating anion and cation exchange membrane forming the multiple electrodialysis [67]. Zeni et al. [68] examined two ion exchange membranes for electrodialysis process. The selenium anion membrane and photo polymeric anionic membrane were tested in an experimental apparatus of a mini-electrodialysis cell having two acrylic compartments. The selenium anionic membrane removed fluoride from 69% to 97% depending on current density. The removal of fluoride from water by using electrodialysis with SB-6407 anion exchange membrane was tested at different current densities by Ergan et al. [69]. After the determination of the optimum pH of feed phase under Donnan dialysis condition which gave the maximum transporty of fluoride, the effect of mono and bivalent ions such as chloride and sulfate ions, in the feed phase on the removal was also correlated with the flux data and explained according to structure of membrane. It was found that the removal of fluoride was higher in the absence of mono and bivalent ions. The reducing effect of sulfate ions on the transport of fluoride was higher than that of chloride ions. Moreover transport of fluoride increases with current density and feed phase concentration. Despite the presence of chloride and sulfate in real water samples, fluoride concentration could be reached to 0.8 mg/l (96% removal).

2.5. Nanotechnology

"Nanotechnology" is the study of controlling of matter on an atomic and molecular scale. Generally, nanotechnology deals with structures sized between 1 and 100 nanometer in at least one dimension, and involves developing materials or devices within that size. Surface fluoride adsorption potential of novel nanohydroxyapatite/chitin (n-HApCh) composite was explored by Sundram et al. [70]. Kinetic studies indicate that the rate of sorption of fluoride on n-HApCh composite follows pseudo-second-order and pore diffusion patterns. n-HApCh composite possesses higher defluoridation capacity of 2.84 mg/g than nanohydroxyapatite (n-HAp) which showed a defluoridation capacity of 1.296 mg/g.

A technology for the granulation of Fe–Al–Ce nano-adsorbent (Fe–Al–Ce) in a fluidized bed was developed by Chen et al. [71]. The coating reagent, a mixture of Fe–Al–Ce and a polymer latex, was sprayed onto sand in a fluidized bed. The coating amount was from 3% to 36%. With increasing coating amount, granule stability decreased and adsorption capacity increased. FTIR analysis showed that the latex can react with active hydroxyl on the Fe–Al–Ce adsorbent, which led to a decrease of the adsorption capacity. Coated granules with a coating amount of 27.5% had a fluoride adsorption capacity of 2.22 mg/g (coated granules) at pH 7 and initial fluoride concentration of 0.001 M. A column test showed that 300 bed volumes can be treated with the effluent under 1.0 mg/L at an initial fluoride concentration of 5.5 mg/l. A novel combustion synthesis for the preparation of Nanomagnesia and its application in water purification studied by Maliyekkal et al. [72]. The fluoride scavenging potential of this material was tested as a function of pH, contact time, and adsorbent dose. The result showed that fluoride adsorption by Nanomagnesia is highly favorable and the capacity does not vary in the pH range usually encountered in groundwater. The effects of various coexisting ions usually found in drinking water on fluoride removal were also investigated. Phosphate was the greatest competitor for fluoride followed by bicarbonate. The presence of other ions studied did not affect the fluoride adsorption capacity of Nanomagnesia significantly. A batch household defluoridation unit was developed using precipitation–sedimentation–filtration techniques, addressing the problems of high fluoride concentration as well as the problem of alkaline pH of the magnesia treated water. The method of synthesis reported here is advantageous from the perspectives of small size of the nanoparticle, cost-effective recovery of the material, and improvement in the fluoride adsorption capacity. Fe_3O_4/polypyrrole magnetic nano composite was used as a novel adsorbent by Bhaumik et al. [73]. Results showed that the adsorption is rapid and that the adsorbent has high affinity for fluoride which depends on temperature, solution pH, and adsorbent dose. Extremely small size and high surface area to volume ratio of nanoparticles provide adsorption of target contaminants. The magnetic-nanosized adsorbent using hydrous aluminum oxide embedded with Fe_3O_4 nanoparticle was applied to remove excess fluoride from aqueous solution by Zhao et al. [74]. The residual concentration of fluoride by using this adsorbent could reach 0.3 mg/l with an initial concentration of 20 mg/l. Due to competition from coexisting anions adsorption capacity of fluoride decreases. Due to nanosizes such adsorbents have higher surface area and shorter diffusion route. In this case, less amount of adsorbent required and defluoridation is rapid. Super magnetic and strong magnetization properties are favorable. Removal of nitrate and fluoride by using nanofiltration has been used by Hoinkis et al. [75]. Two commercial NF membranes were chosen based on tightness of membrane. NF 90 was regarded as a “dense” membrane and NF 270 as a “loose” NF membrane. Fluoride-spiked model water and tap water was used for study. They found that the NF 270 can keep the fluoride level below the maximum contaminant level (MCL) i.e. 1.5 mg/l for 10 mg/l feed concentration whereas, the NF 90 has the ability to keep fluoride permeate concentration below MCL for 20 mg/l feed concentration. The effect of pH on removal rate is low. The above works are summarized in Table 11.

2.6. Adsorption

The phenomenon of accumulation of any molecular species at the surface of a solid from the bulk solution is known as adsorption. Adsorption technique has been quite popular due to its simplicity as well as availability of wide range of adsorbents. Adsorption onto solid surface is a simple, versatile, and appropriate process for treating drinking water systems, especially for small communities. Adsorption technique is considered as economical and can remove ions over a wide range of pH to a lower residual concentration than precipitation [76,77]. The process become even

Table 11
Summary of few Studies on nanofiltration process for removal of fluoride

References	Result	Remark
[70]	Nano hydroxide chitin composite posses higher defluoridation capacity of 2840 mg/F/kg than nanohydroxyapatite which showed defluoridation capacity of 296 mg/F/kg	Presence of co-anion effects fluoride removal
[71]	Coated granules with a coating amount of 27.5% had a fluoride adsorption capacity of 2.22/g at pH 7	It works at neutral pH, no need of pH adjustment
[72]	Fluoride removal effected by phosphate ion. Fluoride removal happened through isomorphic substitution of fluoride in brucite	Cost effective recovery of material Improvement in the fluoride adsorption capacity
[73]	Adsorbent has high affinity for fluoride and adsorption is rapid	Adsorption depends upon temperature pH, adsorbent dose
[74]	Effective in fluoride removal, removal capacity is 68 mg/g	Due to super magnetic and magnetization property removal of adsorbent after treatment is easy
[75]	Tightness of membrane plays a major role in removal efficiency	The effect of pH on removal rate is low. Promising technique, based on results technical devise can be designed

economical if the adsorbent used is a low-cost adsorbent, which can be used as an alternative to the activated carbon. There is no need to regenerate the low-cost adsorbents. It is more economical to dispose the low-cost adsorbents rather than to regenerate them. A large number of materials have been tested as adsorbents for the removal of fluoride, such as activated alumina [78], zeolite, charcoal [79], activated carbon [80], calcite [81], clay, bleaching earth [82], and red mud [83]. The fluoride removal capacity of adsorbents is depend upon the concentration of fluoride in water. The fluoride removal capacity of some of the adsorbents reduces with the reducing initial concentration of fluoride in aqueous solution [84]. This may be due to the decreasing solid-to-liquid ratio of the solution at that concentration. The lowest limit upto which fluoride can be removed is greater than 2 mg/l [85], therefore, such adsorbents are not suitable for drinking water, especially as some of them can only work at an extreme pH values, such as activated carbon which is only effective for fluoride removal at pH less than 3 [86]. The high cost and irreversible nature of adsorption make its use limited. Fluoride removal by rare earth oxides was studied by Raichur and Basu [87]. The authors have used mixed rare earth oxides for the removal of fluoride from synthetic solution. They have studied effect of various parameters on the removal of fluoride. It is reported that the adsorption process is fast and more 90% of fluoride can be removed by using these low-cost adsorbents at the optimum pH of 6.5.

Low-cost adsorbents like hydroxyapatite, fluorspar, calcite, quartz, and quartz activated by ferric ions studied by Fan et al. [88]. The adsorption capacity was found in the order hydroxyapatite > fluorspar > quartz activated by ferric ion. Acid treated spent bleaching earth was studied by Mahramanlioglu et al. [82] to access its capacity for the adsorption of fluoride from aqueous solution. The removal of fluoride from aqueous solution depends on the contact time, pH of solution, and adsorbent concentration. The ability of alum-impregnated alumina for the removal of fluoride from water through adsorption has been investigated by Tripathy et al. [89]. The efficiency of alum-impregnated alumina to remove fluoride from water was found to be 99% at pH 6.5. Feasibility of using alumina cement granules as an adsorbent in removing fluoride from water was studied by Ayoob and Gupta [90]. It was observed that a dose of 2 mg/l of alumina cement granules could bring down fluoride concentration in water from 8.65 mg/l to below the permissible level of 1 mg/l at optimum conditions. Mohan et al. [91] studied nonviable algal spirogyra as biosorbent for adsorption of fluoride. Fluoride adsorption by spirogyra found to be effective at low pH. Adsorption potential of manganese-oxide-coated alumina was investigated by Maliyekkal et al. [92]. Results indicated that fluoride adsorption rate and adsorption capacity are far superior to that of activated alumina. Iron containing laterite ores—both low and high iron containing and chromite overburden—were used as effective adsorbents for fluoride removal from aqueous solution by Sujana et al. [93]. Results indicated that removal of fluoride is dependent on initial concentration, pH, adsorbent dose, and temperature. Mise and Kumar [94] used activated carbon derived from royal gulmohar fruit shell for the removal of fluoride from aqueous solution. Adsorption behavior of fluoride ions from aqueous solution by hydroxyapatite (HAP) was studied by Jimenez-Reyes and Solache-Rios [95]. They found that the adsorption depends on pH, contact time, initial fluoride concentration, and adsorbent dose. Maximum sorption of fluoride ion was in the pH range between 5 and 7.3. With adsorbent dose of 0.1 g of HAP and 25 ml of solution 96% of fluoride was removed. Fluoride removal capacity is 1.53 mg/g by using HAP as adsorbents. Adsorption potential of alkoxide origin alumina for defluoridation of drinking water was studied by Kamble et al. [96]. The removal of fluoride from aqueous solution depends on initial fluoride concentration, adsorbent dose, pH of solution, and contact time. Carbonates, bicarbonates, and sulfate reduce the fluoride sorption capacity because of competition of these ions for active sorption sites and change in pH. The maximum removal occurs in pH range 5–7. Fluoride removal capacity is 2.27 mg/g. Calcite-packed columns were investigated for their performance in treating two types of fluoric acid waste waters from a semiconductor industry by Choi et al. [97]. They found that in case of relatively pure hydrofluoric acid wastewater, the calcite column were capable of reducing the fluoride concentrations from 860 mg/l to 7.7 mg/l. Whereas the fluoride in the mixed fluoric acid wastewater was removed to remarkably low levels (lower than 0.1 mg/l) because it was additionally adsorbed onto a calcium phosphate solid after precipitated as fluorite at the elevated concentration of calcium. The summary of work for the removal of fluoride by using adsorption method has been presented in Table 12. There is lot of scope to study the low-cost adsorbents from agriculture wastes and other sources e.g. rice husk, bagasse fly ash, almond shell, etc.

2.7. Biotechniques

According to United Nations Convention on Biological Diversity, Biotechniques involve technological

Table 12
Summary of few studies on adsorption for removal of fluoride

References	Result	Remarks
[82]	Maximum adsorption takes place at pH 3.5	Fluoride removal depends on pH, initial fluoride conc. dose of adsorbent, presence of co-anions
[88]	Adsorption capacity follow the order hydroxyapatite > fluorspar > quartz > activated using ferric ions > calcite > quartz	Radioactive method used is very effective and further study needed in this field
[89]	Removal efficiency is 99%	Better efficiency, regenerated adsorbent is needed for further defluoridation
[91]	Experiment shows its ability to remove fluoride from aqueous phase	Fluoride effective at lower pH only
[92]	Magnesia amended activated alumina has high fluoride sorption than activated alumina, more than 95% removal	Depend on pH, higher concentration of bicarbonate and sulfate reduced the fluoride sorption capacity
[90]	Fluoride concentration can be reduced to less than 1 mg/l from 8.65 mg/l	Fluoride removal depend on bed depth Flow rate, initial concentration
[93]	Fluoride concentration can be reduced to less than 1 mg/l from 10.25 mg/l	Fluoride removal depends on pH, initial fluoride concentration, dose of adsorbent, reaction time
[95]	96% removal is possible	Fluoride removal depends on pH, initial fluoride concentration, dose of adsorbent, reaction time
[96]	Improvement in removal capacity than alumina	pH dependent, effect of co-ions present in aqueous solution
[97]	In case of pure hydrofluoric acid wastewater fluoride concentration was reduced to 7.7 mg/l from 860 mg/l and in case of mixed hydrofluoric acid wastewater removal was less than 0.1 mg/l	The effluent produced in calcite columns during operation has higher alkalinity, which is beneficial for water reuse

applications that use biological systems, living organisms, or derivatives thereof to make or modify products or processes for specific use.

Removal of fluoride from aqueous solution using protonated chitosan-beads is reported by Viswanathan et al. [98]. Chitosan is a linear polysaccharide of β-1,4-O-glycosol-linked glucosamine residue, derived from deacetylation of chitin which is a major component of crustacean shells and fungal biomass [99]. Cross-linked chitosan beads were developed by protonation. Protonated chitson beads (PCB) have higher sorption ability for uptake of fluoride than the raw chitosan beads (CB). The PCB posses the defluoridation capacity of 1,664 mg fluoride/kg. Maximum defluoridation was found at pH 7. Nature of fluoride sorption process is spontaneous and endothermic. PCB is an effective, inexpensive, and replicable material. Ramanaiah et al. [100] used waste fungal biomass (*Pleurotus Ostreatus* 1804) derived from laccase fermentation process. The fungi were maintained on potato dextrose agar (PDA) plates and stored at 4˚C with periodic (30 days) subculturing. *P. Ostreatus* 1804, subcultured and grown in PDA (8 days old) submerged medium. The collected fungal biomass was dried under oven at 100˚C (diffused heat) for a period of 24 h and crushed to particle size of 1–2 mm. and used as adsorbent for fluoride removal. The sorption process obeyed the pseudo-first-order rate equation and found to be pH dependent. Fluoride removal was found to be greater at lower pH.

3. Conclusion

A short review on fluoride removal techniques has been presented. Various methods have been used for the removal of fluoride from aqueous solutions. In coagulation precipitation method aluminum salts, lime, and bleaching powder are used as the precipitating agents. This method is established and widely used but high chemical dosage are required therefore it is not economical. The sludge formation is another problem posed in this method and it produces health impacts due to addition of aluminum. Ion exchange treatment method has been used for the removal of fluoride from aqueous solutions. This method is efficient to remove fluoride upto 90–95%, and retains the taste and color of water intact. The regeneration of ion exchange beds is required in case of this method therefore it is not cost-effective method. Membrane separation methods are also used for the removal of fluoride from aqueous solutions. The membrane techniques like reverse osmosis, electrodialysis, and

Donnan dialysis are used for the removal of fluoride from aqueous solutions. These methods are efficient to remove fluoride upto 90–95%. High power consumption is the main disadvantage of these methods. Nanotechnology is being used for the removal of fluoride. The nanomaterials are very efficient in removal of fluoride due to larger surface area but it is not economical. Electrochemical treatment is an efficient method of treatment of fluoride but high power consumption and replacement of anode are the major drawbacks of this method. The most promising method used for the removal of fluoride is adsorption and biosorption. This method is simple to operate and as well as economical. The regeneration of adsorbents is not required if the materials used are low-cost adsorbents. The disposal of adsorbents is also very easy and sludge formation in adsorption/biosorption process is not the problem. There are lots of agricultural materials which can be either used directly as adsorbents or they can be used as raw materials for the preparation of activated carbons for the removal of fluoride.

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