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A review on fluoride: treatment strategies and scope for further research

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ABSTRACT

The past decades showed much research interest in lowering the fluoride ion content in water due to its hazardous nature. Fluoride present in water is likely to have favorable and unfavorable consequences to human life. It depends upon the permissible limits prescribed by the agencies, which paves the way to opt for fluoridation or defluoridation techniques. The excess intake of fluoride by human beings provides many issues that include deformities in skeletal structure, dental fluorosis, weakening of the nervous system, and severe damage to the kidney and liver. This review paper addresses the issues caused due to the over-dosage of fluoride and by compiling the recognized treatment techniques adopted to eliminate it from aqueous solution. The current study also figures out the versatility of every technique by revealing its pros and cons and bridges the gap between the emerging advancements to the practical mode of application. Several pieces of literature have been taken into consideration to withdraw the limitations of the key issues. This review paper suggests that adsorption technology can be adopted due to its simplicity and flexibility to overcome the technological issues. It is one such technique which enhances the defluoridation in trace amount and can be easily implemented in the rural areas.

Keywords: Fluoride; Effects; Toxicity; Removal; Treatment; Adsorption

1. Introduction

The necessity of freshwater has become a high scarcity due to the contamination of underground and surface water by various contaminants constituted by human and industrial activities. Thus, the need for treating the polluted water comes into the frame, which attracts the researchers to address the issue. This paper concentrates on one such toxic element, fluoride. Fluorine, chlorine, and bromine are some of the halogen elements present in the drinking water and they are providing major issues in recent decades. Fluorine is considered an extremely required mineral by our human body but the excessive level of fluorine has affected more than 200 million people around the world [1]. Fluoride bearing minerals are the major cause of fluoride ions (F^-) in the groundwater. The alteration in the composition of the rocks due to fluoride ions, the minerals get dissociated, deposited, and weathered due to the variation in climatic factors [2].

Hydroxyapatite is the main constituent found in teeth and bones. Fluorine helps in the prevention of tooth decay by displacing the hydroxide ions from hydroxyapatite. Thus, forming fluorapatite, this acts as a barrier and protects the teeth from acid attack. Further, excessive fluoride was ingested over a desired period, the teeth become denser and brittleness happens, this is termed as fluorosis [3]. Fluorosis is considered as a public social health problem that can negatively affect the physical and mental health of patients and their families. Fluorosis is an incurable disease,

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so that suitable treatment techniques must be adopted for eliminating the excessive fluoride in contaminated water. Fluoride is non-carcinogenic. The occurrence of fluoride has been taken place all around the world and few have brought into notice [4]. Fluoride contaminated areas are analyzed and potential health risks are brought into the picture. Mainly semi-arid regions have a huge impact because of the ill effects of the fluorides [5]. In Ghana, nearly 20% of the wells which are used for drinking are prone to fluoride. The survey engaged various age groups associated with exposure of fluoride [6]. Another study was assessed in the district of Telangana, India were major causes of fluoride due to the presence of granite rocks in Telangana [7]. Countries like Central Mongolia [8] Afghanistan, Australia, Algeria, Andes, Brazil, Egypt, Indonesia, Japan, Jordan, Kenya, Libya, Morocco, Peru, Saudi Arabia, Turkey, and Syria are some of the countries identified with fluoride. A detailed study has been done on a global basis by dividing into five fluoride zones associated with tectonic zones. The outcomes of the work produced the factors that cause excessive fluoride. The main contributions were the tectonic zones, properties of the water, rock types, and the composition of the soil in that particular region, climate, and weather [9]. Table 1 elucidates the various regions in which fluoride levels are above the permissible limits and the significant outcomes observed were at the time of the study [10–30]. The people residing in the fluoride prone areas are likely to have the illness caused due to excessive fluoride when they ingest it unknowingly. The lowering of fluoride ion content in the fluoride spiked water is coined as defluoridation. There have been numerous researches on defluoridation of the F^- contaminated water.

The occurrence of fluoride in the groundwater may be contributed by natural processes or human activity. Volcanic eruptions and geothermal water increase fluoride levels and cause contamination naturally [31]. Some of the rocks contain fluoride bearing minerals, namely fluorite, fluorapatite, micas, amphiboles, cryolite, villiaumite, topaz, bastnaesite, and sellaite. These minerals react with water, get dissolved, and contaminate the underground water with excess fluoride concentration. The geothermal water contains fluoride as there is a close association between the spring from which it originates and the nearby existing rocks [32]. This usually depends on the temperature of the fluid and the solubility of the fluorite. Contamination by manmade activities includes effluent discharged from industries and agricultural practices. Industries involved in synthesizing of artificial manure, manufacturing of plastics, ceramic and glass industries, chlorinated products, television picture tubes, pest control solutions, electroplating works, fabrication of semiconductors, coal-fired power stations, extraction of beryllium expel fluoride contaminated discharge [33–35]. Application of phosphorus fertilizer and pesticides are the major causes of the elevated level of fluoride in soil and water. These fertilizers percolate through underground water and reach the zone of saturation [36]. As there is a very acute level of precipitation prevailing, the groundwater table reduced drastically when a huge load of water has been utilized for irrigating purposes, it pivots the way for exceeding fluoride concentration in the water. Thus, there is a remarkable increase in the fluoride content and degrades the environment to a greater extent.

Plant uptakes fluoride contaminated water by the absorption mechanism from the soil. The study reported that the species like *Tutcheria championi* and *Camellia oleifera* have good resistance against fluoride contamination [37]. Commonly, several symptoms were analyzed in plants like irregular growth deformities, degenerates the leaf margins, and discoloration in the green pigment [38–40]. The animals and insects which fed on the plants for the nourishment are also adopted to the harmful hazardous of fluoride. Nearly ¾th of death was caused due to the ill effects of fluoride in larva when the level of F^- reached above 365 mg/L [41]. The silk-producing worms are affected due to the fluoride ion content which results in the symptoms of fewer intakes of food, lighter pigment formation, and malfunctioning in their body system. It also hindrances the production of silk where it degrades the quality of the product as these worms fed on the leaves of mulberry that has the influence of fluoride in it [42].

As primitive lives are affected easily, humans and domestic animals have a wide impact when the concentration exceeds the tolerance limit. The persistent exposure to fluoride creates an incurable; but preventable disorder, namely fluorosis, which is characterized by discoloration followed by irregularities in the enamel [43]. Several pieces of literature have reported with dental fluorosis and chronic exposure led to skeletal fluorosis [44]. Ethiopian communities recorded with 7.8 to 18 mg/L of fluoride concentration, where the prevalence of dental fluorosis was 100% among the children and adults [45]. The formation of cracks and fissures was observed on the enamel of the people, residing in Bahabad, Central Iran [46]. The non-carcinogenic risk of infants was high while comparing with other age group people. It was indicated by the Hazard quotient, which was greater than 1 [47]. Fluoride penetrates the nervous system by making an interlocking between brain and brain connectivity. Past reports make the note of reduced intelligent quotient of the children who dwell in the high fluoride prone zone areas [46,48,49]. Long term exposure of fluoride tends to induce changes in the thyroid levels, related to brain development [50]. Nearly 2,000 children from China were taken into the study between the age groups of 7 to 13 years, resulted in the decrement of intelligent quotient [44]. Other study reports about the overweight and obesity caused in the children of China, due to the harmful impacts caused by the fluoride levels. These models were examined with the urinary fluoride concentration [51].

Fluoride can cause occupational disorders, by affecting the labors working in the aluminum industries. It creates breathing disruptions with other breathing-related issues [20,52]. Few studies have assessed the problem of fluoride, as it is the precursors for hindering the energy and carbohydrate metabolism that may affect effectively inhibit diabetes mellitus in humans [53]. Some researchers have reported that fluoride may affect the hereditary genome sequence simulating mutation. On the bird's eye view of the toxicity of fluoride on a living organism, it significantly damages the cellular structure, provoking disturbance to the lung, kidney, and reproductive systems [41]. Thus, the ill effects of the fluoride have been discussed, which initiates the treatment of fluoride contaminated water which reduces the

Table 1
Fluoride prone regions with a prevailing range of fluoride and the outcomes of the study [10–30]

S. No.	Regions		Nature of samples analyzed	F^- range (mg/L)	Outcomes	References
1	India	Agra	Groundwater samples	0.90–4.12	71% of the people have the risk of non-carcinogenic disorders	[10]
2		Semi-arid India	Groundwater samples	0.3–11	64% of the groundwater sample had more than 1.5 mg/L, due to the presence of granite gneiss	[11]
3		Gharwar village, Dhanbad	Well water	0.3–12.5	Fluoride related health problems were established by a fuzzy-analytical hierarchical process	[12]
4		Semi-arid region of Panipat	Groundwater samples	0.2–6.9	Children were easily prone to non-carcinogenic health risk than adults	[13]
5		Siwani Block, Western Haryana	Groundwater samples	0.4–18.5	Groundwater was not suitable for irrigation purpose	[14]
6		Birbhum, West Bengal	Groundwater samples were collected from tube wells and dug wells	0.11–20.9	Elevated fluoride was due to input of phosphorus fertilizers in fields	[15]
7		Birbhum, West Bengal	Groundwater samples	0.3–9.36	Non-carcinogenic health problem existed in infants than children and adults	[16]
8		Alleppey Kerala	Open wells and tube wells	0.68–2.88	62% of the water quality was poor and does not prescribe for domestic purposes	[17]
9		Villages of Shanmuganadhi River Bank	Groundwater samples	0.1–2.5	23% of water is fluoride prone making it unsuitable for consumption	[18]
10	Tanzania	Northern zone of Tanzania	Groundwater samples	>1.5	96% of the samples were unfit for drinking	[19]
11	Argentina	Northeastern La Pampa Province in Argentina	Groundwater samples	0.5–14.2	Long term exposure leads to health-related problems to the local communities	[20]
12	Ethiopia	Lake Hawassa catchment	Well water	0.65–11	Skeletal and tooth decay	[21]
13		Middle Awash basin	Volcanic aquifers	0.1–72.5	High levels of fluoride cause serious health problems	[22]
14		Jimma Zone of Oromia	Groundwater samples	0.15–11.78	12.5% of groundwater was not unsuitable for drinking and irrigation	[23]

(continued)

Table 1 Continued

S. No.	Regions		Nature of samples analyzed	F^- range (mg/L)	Outcomes	References
15	Iran	South of Fars Province, Iran	Surface, ground, and rain water	0.06–4.95	36 inhabitants are susceptible to fluorosis	[24]
16		Ardakan City of Yazd Province	Wells and aqueducts	0.9–6	46.4% of the groundwater resources had excessive fluoride	[25]
17		Iranshahr	Groundwater samples	0.25–1.72	6% of the samples were unfit for the domestic usage	[26]
18	Thailand	Buak Khang Subdistrict	Groundwater samples	>5 mg/L	Bottled water systems are one of the ways to eliminate consumption of fluoridated water	[27]
		San Kamphaeng		0.75–7.46		
19	Suluku Hills, Tororo District, Uganda		Groundwater	0.4–3	Using a modified Galagan equation and considering 31 as average temperature, 0.4 mg/L is the upper tolerance limit	[28]
20	Dargai Region, Khyber Pakhtunkhwa Province Pakistan		Groundwater from the industrial and mining areas	2.3	Dental fluorosis is very prevalent	[29]
21	Shanxi Province, Loess Plateau, North China		Tap water/pine water/well water/spring water	0.03–9.42	More than 10% of the children are affected by dental decay and fluorosis	[30]

effects caused due to it. The existing treatment methods are discussed and based on the necessity it can be selected.

To overcome these ill effects and malfunctioning caused by the elevated fluoride levels, the drinking water regulatory agencies have prescribed the limits (Table 2) which depends on the climatic condition in a particular region [54–63]. The present work aims to capture the idea of choosing suitable and sustainable treatment methods according to the characteristics of F^- spiked water by reviewing areas where real-time fluoride contamination has been treated and the economic aspects of each technique.

2. Treatment methods

2.1. Adsorption

2.1.1. Biosorbents

Adsorption is the most commonly used conventional technique. It primarily modifies the natural materials into treated adsorbents which makes eco-friendly composites as defluoridation agents and produces fewer biodegradable wastes. Water hyacinth petioles, when subjected to alkali-stream treatment improves the efficiency of F^- removal. By chemically characterizing the aquatic plants, 85% of removal was achieved on adding a dosage of about 1 g in 5 mg/L of F^- spiked distilled water. The superiority of the process is cost-effective and less sludge production [64]. Later years, Manna et al. [65] investigated on biosorbents like neem oil phenolic resin treated with lignocelluloses. The study was initiated by varying the height of the bed, the diameter of the column, and adjusting the concentration of fluoride. The regeneration was possible up to five cycles. Optimum results were reached by having a thickest bed of adsorbent with a low concentration of F^- and less flow rate. Results showed that the fluoride can be removed both from synthetic and groundwater. Bio-sorbent used in this research was reusable and recyclable with the cycles of more than five with a continuous decrease in the efficiency of removal. The results proved that the studied biosorbent was more sustainable and inexpensive. From the results, it was observed that breakthrough was achieved quicker for untreated bio-matters than treated bio-matters.

The crystalline zeolite NaA was derived from rice husk for the removal of fluoride ion content from aqueous solution. The influencing parameters such as pH, initial fluoride ions concentration, temperature, adsorbent dosage, and contact time on adsorption have been studied. With a slightly acidic pH of 5 and 4 h of contact time, 90% of removal efficiency was attained. Silica used in this process was derived from rice husks. The maximum adsorption capacity was observed to be 22.83 mg/g with an adsorbent dosage of 105 mg and a fluoride concentration of 10 mg/L. The results indicated that the studied adsorbent was cost and energy-efficient [66]. The potential adsorbent was made from aluminum iron amended activated bamboo charcoal (ABC). To achieve a higher degree of fluoride uptake capacity, the ABC is coated with aluminum chloride ($AlCl_3$) and iron trichloride ($FeCl_3$) solutions and heated at 400°C. When the ABC was coated with aluminum hydroxide, the surface area was decreased due to blockage of the active sites. The working range pH was noted as 5–9, with a good amount of regenerative capacity by 0.1% of sodium hydroxide. The maximum amount of fluoride uptake capacity was found within 3 h. The efficiency will be better if the activation temperature and acid to bamboo ratio were optimized [67].

Li et al. [68] developed an adsorbent by the process of in situ chemical oxidative polymerization. Granular peanut shell biological carbon was deposited with polypyrrole (PPy), which was the candidate for reducing the fluoride content. Even in the presence of other competing ions, PPy-grafted biological carbon showed the maximum adsorption capacity of 17.15 mg/g. The defluoridation was performed using living cyanobacteria, namely *Starria zimbabweensis*, which was set up for the remedy of fluoride contaminated water. The highest removal efficiency (66.6%) was achieved for an initial concentration of fluoride of 10 mg/L. Twice the increase of biomass was observed in fluoride stress conditions. This indicates the richness of biofuel that can be extracted from the fluoridated bacterial strain [69]. This research envisages the development of new bio-sorbent from *Ficus benghalensis* leaf. With this bio-sorbent, the efficacy of fluoride removal was about 92.2% and the concentration of fluoride in treated water is within the permissible limit. During this test, the dosage of bio-sorbent is 8 g/L with a contact time of 90 min and pH ranging about 7.4–8.2 [70]. Here, the extract of *Catla catla* (fish scale powder) was used as a potential adsorbent for fluoride removal. It was found that the efficiency of 98.9% and adsorption capacity of 4.9 mg/g have been achieved at 60 min of contact time. The optimum pH for this adsorption process was estimated at 6.0. When compared to other de-fluoridation capacities of biomass, the uptake capacity was much higher [71]. Table 3 discloses the various bio-sorbents used for the studies and their removal efficiencies.

2.1.2. Activated carbon

One of the very important properties that affect the treatment efficiency of the activated carbon (AC) is the structure and distribution of the surface pores [72]. On passing ultrasonic waves on AC, its adsorption capacity was increased and which makes it more sustainable [73]. These adsorbents are generally thermal stable and yield good efficiency in the removal of pollutants which was likely to be performed in industrial scale [74]. A novel adsorbent was synthesized by Araga et al. [75] from *Syzygium cumini* seeds through the pyrolysis process and then it was used for defluoridation. The real-time water samples are collected from fluoride affected areas and were treated using this adsorbent material.

La/Mg/Si-loaded activated carbon-based palm shell-based was used as an effective adsorbent for the removal of fluoride and aluminum from aqueous solution. It exhibited good selectivity in targeting the contaminants at pH 7 [76]. Another study has been investigated on treating phosphoric acid over the thermally treated AC. Activated carbon derived from biomass of *Manihot esculenta* acts as a defluoridation agent under acidic pH. It showed monolayer formation with a chemisorptive rate-controlling mechanism. It was well described by the Elovich kinetic model, which symbolize the pore diffusions mechanism for sorption [77]. Mullick and Neogi [78] studied that the ultrasonication was used to impregnate the zirconium on AC. This AC has an additional benefit of consuming less energy. The point of zero charges of the adsorbent was likely to be 5.03, where the optimum pH was found to be 4 for better removal. Later new composites were developed using magnesium, manganese, and zirconium for increasing the fluoride adsorption capacity. Satisfactory results were obtained in terms of energy-efficient of 96% [79]. AC obtained from the coconut husk had a higher surface area. The laboratory experiments were conducted in column mode by varying the operational parameters. Thomas and Yoon–Nelson models are applied and the breakthrough curves were described [80].

Roy et al. [81] used calcium impregnated AC for achieving the greater fluoride adsorption capacity. Anions do not make a significant change in adsorption of fluoride ions. 1% of sodium hydroxide solution was used for regeneration where better results were achieved for 5 cycles. A comparative study on removal of fluoride was done through pyrolyzed palm shell activated carbon powder treated with

Table 2
Some of the regulatory agencies and their permissible limits recommended for fluoride [54–63]

Organizations	Permissible limits (mg/L)	References
World Health Organization	1.5	[54]
Environmental Protection Agency	2.0	[55]
Indian Council of Medical Research	1.5	[9]
Bureau of Indian Standards	1.2	[56]
American Public Health Association	10	[57]
United States Department of Health and Human Services	1.2	[9]
Ministry of Health of the People's Republic of China	1.2	[58]
Council of the European Union	1.5	[59]
Health Canada	1.5	[60]
Public Health England	1.0	[61]
Australian Government, National Health and Medical Research Council	1.1	[62]
Ethiopian Federal Ministry of Water Resources	2	[63]

Table 3
Removal efficiency for various bio-sorbents with the influencing parameters and their removal mechanism [64–71]

S. No.	Adsorbents	Adsorption capacity (mg/g)	Time of exposure (min)	Dose (mg)	pH	Temperature (°C)	Mechanism	References
1	Alkali treated water hyacinth petioles	5	210	1,000	6	25–30	Chemical adsorption, C–F and H–F bond formation	[64]
	Alkali treated elephant grass	7	210	1,500	4	25–30		
2	Crystalline zeolite NaA synthesized from rice husk	10	240	105	5	45	–	[66]
3	Aluminum iron amended activated bamboo charcoal	21.1	180	0.8	9	–	Complex process and intraparticle diffusion are not only rate-controlling step	[67]
4	Polypyrrole on granular peanut shell biological carbon	17.15	360	6	2–10	–	Surface adsorption and intraparticle diffusion	[68]
5	*Ficus benghalensis* leaf biosorbent	2.183	120	10,000	7	30	–	[70]
6	Scale of Carp Catla	4.89	179.92	2,260	9.93	–	–	[71]

and without magnesia silica. The adsorption capacity was found to be high for the impregnated adsorbent. Freundlich isotherm model gets fitted well for the data and explains the concept of multilayer adsorption [82]. *Azadirachta indica* bark has been carbonized by microwave and utilized for defluoridation. The adsorption was exothermic and spontaneous according to the values derived from thermodynamic studies [83]. Calcination of *Camellia oleifera* seed shell at 400°C was done to reduce the fluoride ion content level in the water. The mechanism was studied using various characterization procedures, which indicates that defluoridation was due to the ion exchange of hydroxyl and fluoride on zirconium particles [84]. The iron particles are coated over the *Citrus limetta* peels waste and it was employed for the fluoride removal. The adsorption was more vigorous when the temperature shoots up. The Langmuir isotherm fitted well, indicating the monolayer formation of fluoride ions onto the surface of the adsorbent [85]. Activated carbons prepared from a variety of raw materials are briefed in Table 4. Eventually, the activated carbon is an excellent defluoridation agent, in terms of energy consumption, easily available in bulks, less process, more flexible with increased removal efficiency.

2.1.3. Ceramic species

To get rid of the worst effects due to the fluoride loaded water, the cerium loaded materials showed good defluoridation properties at lower adsorbent dosage. A low-cost sorbent has been prepared from the ceramic module which is easily available in the state of Assam, India. The study was aimed at sorbents which are manufactured at affordable prices. The results showed a deep decrease in the sorption rate when the pH moves out of range (4–10). By substituting the kaolin with locally available clay, approximately 56% of the cost was lowered with shooting up of the defluoridation efficiency. It was cheap and easy to handle. The adsorption results are favorable within the pH range of 4–10 [86]. The investigation of the modified surface of bone char by using ceramic species has been discussed in the work. The cerium doped bone char revealed its adsorption capacity as 13.6 mg/g at working pH 7 and 30°C. Potential to resist bacteria was one of the additional merits seen in the adsorbent. Modifying with Ce^{4+} showed good properties related to adsorption of fluoride removal than Ce^{3+} [87]. A novel adsorbent was identified in the study where it predicted to have a high capacity for defluoridation with an amorphous structure. The removal depends on the pH of the medium. It is considered to be a good agent for F^- removal due to quick adsorption [88].

2.1.4. Nanomaterials

The study emphasized nanomaterials manufactured using the sol–gel technique. The maximum adsorption capacity of 2.55 and 5.66 mg/g were found for pure and modified nano-alumina, respectively. The desired removal was possible in neutral pH, a contact time of 2 h, and adsorbent dosage of 10 mg/L [89]. Hybrid anion exchange resin embedded with zirconium oxide nanoparticles (HAIX-Zr) and activated alumina are the adsorbents used in this article to eliminate the excess fluoride content in the drinking water by column studies. The treatment cost of HAIX-Zr was found to be relatively high while this was compared with activated alumina [90]. The study renovated the use of adsorbents in a new fashion by using a flake-ball-like magnetic Fe_3O_4/γ–MnO_2 mesoporous nano-composite. The film diffusion and the intraparticle diffusion were the controlling

Tables 4
Removal efficiency with influencing parameters for activated carbon [75–85]

Adsorbent	Adsorption capacity (mg/g)	Mechanism	References
KOH-treated Jamun (*Syzygium cumini*) seed	3.65	Ligand exchange	[75]
Mesoporous La/Mg/Si-incorporated palm shell activated carbon	285.7	Electrostatic interaction and ligand exchange	[76]
Activated carbon synthesized from *Manihot esculenta* biomass	1.568	Chemisorption involving exchange of electrons	[77]
Acoustic cavitation induced synthesis of zirconium impregnated activated carbon	5.4	Slicing of hydroxyl bond takes places in creation of porous structure	[78]
Ultrasound assisted synthesis of Mg–Mn–Zr impregnated activated carbon	26.27	Film diffusion and intraparticle diffusion	[79]
Coconut husk activated carbon	6.5	Ion exchange	[80]
Calcium impregnated activated charcoal	46.23	Chemisorption	[81]
Limonia acidissima (wood apple) shell activated carbon electrode	2.7554	Physisorption	[82]
Modified *Azadirachta indica* bark	0.923	Monolayer adsorption with chemisorption	[83]
Zirconium dioxide-biochar derived from *Camellia oleifera* seed shell	–	No electrostatic attraction, ion exchange of hydroxyl and fluoride	[84]
$FeCl_3$-activated carbon derived from waste *Citrus limetta* peels	9.79	External boundary layer diffusion or by intraparticle diffusion	[85]

factors in this adsorption process. The adsorption mechanism was found to be enhanced by the bond formation of O–Mn–F on the surface of Fe_3O_4/γ–MnO_2 [91]. The ability of defluoridation using the chitosan template-assisted the synthesis of nanocrystalline aluminum oxyhydroxide at 30°C. The results showed that the affinity of composite towards the fluoride ions persists. Bicarbonates and sulfates are competing for ions that influence fluoride removal. The simplicity and eco-friendly nature of the material make it more suitable [92]. Another material was simulated by the deposition of humic acid on the nano magnesium oxide, as an agent for defluoridation. The treated groundwater samples reported that there was a reduction in fluoride ions and total organic carbon when humic acid was lowered [93]. The synthesized product promoted in this study is magnesium oxide (MgO) nanoparticle loaded on mesoporous alumina. The results inferred with a mechanism of chemisorption with a pseudo-second-order model. The rate of fluoride removal was observed with the initial concentrations of fluoridated water as 5 and 10 mg/L and finally reduced to less than 1 mg/L. The faster rate of adsorption and the higher capacity of adsorption made mesoporous magnesium oxide loaded on aluminum oxide ($MgO@Al_2O_3$) as a suitable and promising adsorbent [94].

One of the promising technologies evolving in the current era is the carbon nanotubes and its modified form of it. These nanotubes have a wide range of applications. In the removal of contaminants from water and wastewater, it plays a vital role. This section reviews the earlier work done using nanotubes in different environments. To set back the conventional treatments, a novel adsorbent has been developed, called trititanate nanotubes (TNT) for an elevated rate of removal. On comparing with the previous studies, TNT showed good efficiency than titanium dioxide (TiO_2). The optimum efficiency was significantly noted at pH 2 to 12. The maximum adsorption capacity of 58 mg/g was obtained in the study. The report highlighted the maximum removal efficiency of 95% due to the synergetic effect of hydroxyl groups and the attraction due to electrostatic forces [95]. The study was demonstrated using multi-walled carbon nanotubes (MWCNT) and single-walled carbon nanotubes (SWCNT) as adsorbent, where the adsorbent capacity of MWCNT was more than that of SWCNT. The equilibrium time was recorded as 30 min and high removal was predicted at the beginning stage [96]. Effluent from the fertilizer industry has been treated using the chitosan sponge with carbon nanotubes. The highest adsorption capacity of 975.4 mg/g has been attained with showing good regenerative results. The characterization results showed that the hydroxyl and the amine groups were the reason for the adhering of fluoride ions [97]. The adsorption capacity of 3 mg/g has been obtained which may be varied due to the input pH value. The maximum fluoride adsorption capacity of 4 mg/g has been increased from 3 mg/g when the pH was adjusted to neutral. The removal was probably due to the inner cavities, inters nano spaces, and active sites on the surfaces of the adsorbent [98].

2.1.5. Fibers and graphene oxides

Mesoporous fibers were synthesized by electrospinning equipped with a soft-template method. One dimensional ZrO_2 mesoporous fiber served as the best fluoride adsorbent with a removal efficiency of 95.3% and with an adsorption capacity of 297.70 mg/g. The fiber was durable and could regenerate. Arsenic- prepared zirconium oxide showed a higher rate of fluoride removal in organic dyes and widely helps in catalysis products. The removal rate efficiency can be up to 95.3%. It was noted that the fibers can be reusable. From the results, it was clear that the equilibrium concentration of fluoride after adsorption was about 1.41 mg/L, which was below the permissible limit of fluoride in the drinking water [99]. Surface modified cellulose fibers are used in the generation of anion adsorbent. No effective change in the adsorption capacity has been noted even though there is a change in variation of adsorption dosage. Fluoride removal was not merely easier when compared to the removal of arsenic. The time consumed for the defluoridation was pretty amazing, that it took less than 1 min [100].

The batch study indicated that the defluorination efficiency was nearly 87.4% and 94.22% for chemically and biologically reduced graphene oxide, respectively. These adsorbents were manufactured from hydrazine hydrate solution and tea solution for treating the fluoride contaminated water. The regeneration was achieved by adding 1% sodium hydroxide to the exhausted adsorbents. The optimization of the study was performed by an artificial neural network and response surface methodology. The optimum removal was achieved at 333 K with 100 min of contact time and 10 g/L dosage of adsorbent [101]. Incorporation of nano-hydroxide on graphene oxide produced a better outcome in defluoridation. The detailed description of the mechanism has been studied, where hydrogen and oxygen bonding helped in the removal of fluoride ions from the water. The calcium present in the composite was used to enhance the removal of fluoride from aqueous solution [102].

2.1.6. Miscellaneous

Some of the materials are modified into adsorbents which showed how the adsorption process is flexible and retrofit. Tons of marble waste powder is synthesized and reused as marble apatite. A conventional and ultrasonic approach (USM) was made feasible by impregnation of waste marble powder treating it with potassium dihydrogen phosphate at 80°C under alkaline conditions. The efficiency of USM was more than the conventional treatment process by 11.1%. The solution pH ranged from 6–8 was well suited for defluoridation of the contaminated water [103]. The adsorbent was prepared from cow dung and it was impregnated with calcium and iron salt solutions. It was found that the most efficient carbon was cow dung carbon which was prepared at 500°C, without any chemical activation, and exists within the pH range of 7–8. This adsorbent showed good efficiency in fluoride removal [104].

Another study was examined using a continuous fixed-bed column by the application of magnesia pullulan composite (MgOP) at a larger scale. The influencing parameters such as bed mass, inlet concentration of fluoride, temperature, flow rate, and pH were analyzed in the experimental work. The adsorption process was analyzed using Thomas and Yan's model where the latter one showed the most accurate results in breakthrough curve analysis. This study concluded that the MgOP was a promising agent in defluoridation. The material loaded with fluoride was again enhanced by calcinating it [105]. In this work, acid-base titration was performed to investigate the properties of the MgOP surface. The effective removal of fluoride can be achieved within the pH range of 3–12. Compared to other adsorbents, it is said to be cost-effective, highly stable, and simple in design and operation. Moreover, the pullulan (bio-composite) tends to increase the accessibility of the adsorbate-binding sites. The major disadvantage is the need for greater backpressure for fine porosity [106].

2.2. Coagulation and precipitation

Coagulation followed by precipitation decreases the excessive fluoride contents from the drinking water. Coagulants (natural or synthetic) are used in the previous works of literature, which provides better results at low-cost. The study was performed to find out the amount of dosage to be added, in lowering the fluoride content in the contaminated water by the coagulation property. Aluminum sulfate and polyaluminum were used in the experimentation study. The result was found to have a decrement in F^- level enhanced with a residual deposit of Al which was lesser in the case of polyaluminum when compared with alum. The main concern for the process is the removal of the secondary components which was a collected residue [107]. A pilot-scale experiment was conducted to compare the removal efficiency using two processes, namely coagulation, and adsorption. The results inferred that coagulation was superior to that of adsorption. In coagulation, the fluoride easily transforms the Al^{3+} ions to aluminum-fluoride precipitation which is more viable [108].

The study suggested that the influence of fluoride on the removal of cadmium and phosphorous by aluminum by the coagulation process [109]. The low residual metal formation on 4–10 working pH added a benefit to the zirconium (IV) chloride when compared to the coagulation by aluminum sulfate, which induced the adsorption capacity of 260 mg/g in acidic pH. The hybrid mechanism (coagulation – adsorption – ion exchange) was probed in the study [110]. Another study has reported that fluoride content removal was analyzed using pre-polymerized Al-based coagulants and its performance was compared with aluminum trichloroalumane (Al_3Cl_3). It was determined that this coagulant showed better efficiency above pH 7 [111]. Another work was based on a product actifluo in defluoridation of the synthetic wastewater and industrial wastewater produced from the industries of Italy. Actifluo is mainly comprised of aluminum polychloride (PAC) and inorganic acid. The dosage of the coagulant was increased according to the requirement of the fluoride concentration of the effluent. For the synthetic waters, the dosage added was about 600 mg/L. The removal of fluoride was achieved by the mechanism of precipitation and coagulation which depends on the pH of the solution [112]. The effect of fluoride removal by aluminum salts as a coagulant was carried out. The experiment was investigated at different pH and concentrations on free fluoride and total fluoride removal. From the result, it can be seen that the aluminum fluoride complexes dominated at low pH.

The comparison between coagulation with complexation and adsorption by aluminum hydroxide flocs were studied and coagulation showed higher fluoride removal efficiency than adsorption in the pH range of 6–9. The removal of fluoride in coagulation, the Al–F–OH co-precipitate formed with Al–F complexes as precursor and co-precipitation with complexation benefitted the process [113]. The removal of fluoride from drinking water using a membrane coagulation system was studied, where aluminum sulfate was used as a major chemical. The optimized pH seems to be from 6 to 6.7. From the result, it can be inferred that the concentration of fluoride was reduced from 4.0 mg/L to less than 1.0 mg/L from raw wastewater to clarified effluent [114].

2.3. Electrocoagulation

Though there exist several conventional defluoridation techniques, electrocoagulation (EC) is one such upcoming technology that has reached to the next successive levels. Electrocoagulation is the process of passing electricity in the aqueous medium through immersed electrodes. The dependent parameters for the electrocoagulation processes are the count of electrodes, the distance between the electrodes, working pH, current density, conductivity, and initial fluoride concentration. Photovoltaic wastewater treatment was remediated using EC by Al electrodes with a purity of 99.7%. Optimization of the experiment resulted in higher defluoridation efficiency, proving it to be an excellent technique [115]. Another study was also induced on the photovoltaic wastewater where iron electrodes are introduced with stipulated reactor dimensions. The work also confirmed that the EC process was influenced by the applied potential and working pH [116]. Synthetic water was created and the removal mechanism of fluoride was made possible through dissolving Al^{3+} in lower pH. The formation of cryolite in pH 5–8 enhanced the defluoridation process [117]. Simultaneous removal of Fe(II) and fluoride ions were carried out by the aluminum electrode. Maximum efficiency of 96% was reached when the initial concentration of 10 mg/L at 1 h of equilibrium time and at neutral pH. The increment in the removal percentage was due to the high electro-dissolution. The lowering of fluoride is directly proportional to the consumption of energy, while total dissolved solids were also eliminated. Eventually, it produces satisfactory results in the removal of fluoride ions [118].

A comparative study was done using deionized water and tap water, in preparing the simulated water for defluoridation. Slight changes have been noted in the pH, where the pH with 6 needed trice of less trivalent Al than the basic pH [119]. Three pollutants namely fluoride, iron, arsenic were removed in this study by the process of EC. Iron removal has an impact on defluoridation, while there was no impact on arsenic. The duration for the removal was found to be lesser than 60 min and arsenic was found to be more feasible in the removal of the three [120]. Another study investigated using response surface methodology, where it indicated no abrupt change in the operational cost even the initial concentration of fluoride changes. The results found were close to the predicted one [121]. The electrochemical reactor was a peculiar model in defluoridation studies. Aluminum and iron are used as the electrodes in this study, where calcium and magnesium uplifted the fluoride removal whereas the sulfates and phosphate ions decrease the removal percentage [122]. Simultaneous removal of arsenic and fluoride from Durango State, Mexico was practiced. The study brought out satisfactory results regarding the decrement of fluoride level which could be an excellent solution to the local issues [123]. Rosales et al. [124] have used aluminum plates coupled to a jar test apparatus to remove hydrated silica, fluoride, and arsenic. Here, the depletion of fluoride was made possible by the substitution of fluoride by hydroxyl ions. Electro-generated adsorbents were made to achieve electrocoagulation through adsorbents. The maximum adsorption capacity was 16.27 mg/g, which proved to the best treatment as it reduces the generation of waste [125]. Thakur et al. [126] studied the sludge utilization which is the waste produced from EC was a good alternative source for the production of bricks. The determination of bricks suggested the sludge produced in of inert form and can be used to substitute the conventional procedure. In this manner, the waste generated can be controlled and recycled without affecting the environment. Several literature works by previous researchers have been displayed

Tables 5
Removal efficiency with influencing parameters for process of electrocoagulation [115–124]

pH	Current density (mA/cm^2)	Other operational parameters	Removal efficiency %	References
7	1.851	T = 30 min	95	[115]
6	–	T = 40 min	–	[116]
7	4.31	T = 60 min	96	[118]
4–8.5	5	I.C = 5–50 mg/L, Cond. = 1–6 ms/cm, Temp. = 25°C–55°C	–	[119]
–	1.25	T < 60 min	–	[120]
7	16.7	I.C = 25 mg/L, T = 25 min	94.5	[121]
6	2	I.C = 5–0.12 mg/L, T = 30 min	97.6	[122]
5	4.5	I.C = 5 mg/L, T = 15 min	85.68	[123]
–	8	–	95.68	[124]

I.C = Initial concentration; T = Time; Cond. = Conductivity; Temp. = Temperature in Table 5. Though the operational cost for electrocoagulation may be high, the removal efficiency obtained by this process overwhelms all the disadvantages.

2.4. Ion exchange process

Ion exchange is one compatible technique which can be operated efficiently with the concern of removing one or more pollutants using a different resin. The transport of ions between the electrodes promotes the desired contaminant to be removed in the process. The report presents the comparison of zirconium (IV)-hexamethylenediamine (ZrHMDA) and amorphous zirconium phosphate (AZrP) in removing F^-. These materials were processed by the ion-exchange technique. The work was experimented by varying the operational parameters at different conditions. Equilibrium was achieved at a faster rate with more than 99% efficiency of removal. The regeneration of adsorbent was used at 10 cycles consecutively without interruption [127]. To increase the uptake of fluoride ions, ion exchange treatment was done by calcium before subjecting ammonia in pure stilbite. Double exchange treated was the remarkable mechanism that performed the defluoridation. Even it was in the groundwater sample from Ethiopia, the increase in removal percentage was observed, while the initial concentration was low [128].

Synthesis of microcubes and manganese carbonate is prepared by ethylene glycol solution methodology. Nanowires showed more fluoride removal than the microtube. Hydroxyl and the carbonate groups contribute to the removal efficiency in this study. The result was made promising by Fourier transform absorption spectroscopy and X-ray photoelectron spectroscopy [129]. Phosphoric-sulfonic acid bifunctional group chelating resin removes fluoride in the mechanism of coordination and electrostatic force or both. It produced considerable results while compared to conventional resins. The kinetic results revealed that the intraparticle diffusion and chemisorption was the reason for the defluoridation [130]. Simultaneous removal of As(III), As(V), F^- was done from the drinking water plant installed in West Bengal, India. Two resin beads like Hiax-Fe-Zr and Hiax-Zr are used in the study. The presence of Fe in the Hiax-Fe-Zr tends was used to lower the fluoride content below the permissible limits. It took less than 30 min of contact time, which makes this can be a good carrier of fluoride [131].

Modified amberlite was introduced in the removal of fluoride from aqueous solution. Separation of fluoride from the aqueous medium was done possibly in the working condition of pH 9. The mechanism inferred is the ion exchange adsorption, where regeneration of the resin was also favorable when treated with an acid medium. Drinking water sample from the Thar Desert was treated with amberlite resin, which proved this work can be used in the real-time study [132]. Next step ahead, imino-diacetate ion exchange resins were selected for the removal of excessive fluoride from aqueous solution. No anion was added in the solution after the treatment, which is an added advantage. Removal of fluoride and chloride was possible at the time of treatment. At the enriched amount of fluoride, the chance of absorption also takes place. There were multiple pathways in removing fluoride content in water, which creates interest to focus on the imino-diacetate resins [133]. Thus, on a concluding note, the ion exchange is said to be a good water treatment process in terms of regeneration, no sludge generation, less cost, no membranes, avoids backwashing and wastage of chemicals.

2.5. Membrane technology

Membrane technology is one of the most superior processes among the conventional treatments, which gets updated in upcoming years. It is a recent innovation in conventional treatments and well-known technology in industrial operations. It comprises of different subclasses based on the pores and nature of purification like nanofiltration (NF), reverse osmosis (RO), dialysis and electro-dialysis.

2.5.1. Nanofiltration (NF)/reverse osmosis (RO)

NF uses membranes to filter the contaminant through its membrane pore sizes whereas the RO treats the fluoride loaded water by passing it through the semi-permeable membrane using physical stimulus. Pores in both processes vary like NF adopts larger pores as compared with RO. In NF, the pressure and energy prerequisites are less as compared with RO [134]. The highest rejection rate was achieved in NF/RO membranes due to the various separation mechanisms which include solution diffusion, size exclusion, charge repulsion, and adsorption. In a study, it was found that the fluoride content was removed well in NF [135]. RO membrane removes the pollutants from water based on the size and electric charge of the pollutants. Nearly 98% of removal efficiencies can be achieved by NF and RO which have been reported by many researchers [134]. A study by Hu et al. [136] revealed that the performance of NF was affected by membrane parameters like water permeability, pore radius, constant surface electrical potential. Experimentation results revealed that the removal of fluoride ions was increased with applied pressure. A research finding by Kettunen and Keskitalo [137] shows that the fluoride removal was >95% for NF and 76% for RO at 0.73 MPa and 0.57 MPa, respectively. Additionally, it was found that the temperature affected the conductivities in NF. The RO process required high pressure and permeability to separate the solute from water. It can able to completely demineralize the water for monovalent ions but it suffers from drawbacks like low permeate flux, high energy requirement, and high operating pressure [138].

Without using scaling prevention, merely 80% of the fluoride removal was achieved. The operation had control over the working condition of the plant by maintaining the pressure as 0.8 MPa in the temperature of 8°C [139]. Membrane process provides more advantages like contaminants removal, good quality water, and being effective in wider pH, it involves only one step and fewer chemicals in removing pollutants. Fluoride removal can also be achieved using forward osmosis technology in which semi-permeable membrane was placed between the concentrated solution and diluted solution so that the water molecules permeate through the membrane using osmotic pressure as a driving force. This kind of removal is called a concentration gradient process with low hydraulic pressure. The main mechanism in forwarding osmosis is the normal solute-diffusion mechanism through composite polyamide membranes. There are a few factors that affect the performance of this process. They are membrane properties, draw solution properties, feed solution properties, hydraulic trans-membrane pressure, flow rate, and operating parameters. The main draws in this process are low flux and performance of high draw solution [135]. Hybrid systems coupling membrane filtration and nano techniques are used in the removal of contaminants and dyes, which serves as the best technology for water treatment [140]. Other study fabricated a novel composite membrane with increased pore size using polymer-based composites like zeolite, alumina. The influencing parameters like pH, the concentration of ions, reaction time, and temperature affects the fluoride removal. It was found that nearly 68% of removal efficiency was achieved in such types of membranes. These membranes are homogenously pored structured [141].

The challenge lies in fabricating a membrane with uniform pore size in order to remove fluoride ion from water. Fabrication mainly depends on the type of procedure adopted like phase inversion, air drying, and material used for casting. Though membrane filtration gives 98% efficiency in removing fluoride ions, concepts like membrane fouling and degradation are the major backs of it. In order to overcome that other technologies like capacitive desalination where membranes fabricated acted as an ion-selective transport barrier through which migration of target pollutants takes place in order to reach the electrodes for further process. Altering the material of membranes may increase its thermal, chemical, and mechanical resistivities over other materials. Ceramic material is one inorganic material which may show the increased application in membrane filtration. These materials reduce the cost for the preparation of membrane as polymeric membrane requires high temperature for sintering which demands more cost than ceramic material. These types of the membrane can be used in hybrid techniques like in combination with electrocoagulation followed by filtration [142]. Among the various types of the membrane process, the most commonly employed are direct membrane distillation, electrodialysis, and Donna dialysis [143].

2.5.2. Electrodialysis

Electrodialysis is one of the best techniques in treating the contaminated water in less time with minimal waste generation. Electrodialysis is a process of ions mobilization governed by the electric potential using selective membranes. This method is highly influenced by the parameters like consumption of energy, feed flow rate, the concentration of the feed solution. It is a nutrient recovery technology that proves to be stable in terms of twinning renewable resources and promotes from lab-scale experiments to higher applications [144]. In a short period of 6 min, fluoride and nitrate ions are removed using electrodialysis techniques in industrial wastewater produced from photovoltaic silicon wafers. Nitrate ion in the solution caused a hindrance in defluoridation, which prolonged the time from 7 to 20 min. This technique was very adaptive to the terminology "zero liquid discharge", where no water is left behind untreated instead of wastewater is recycled and reused [145]. The time of operation of the process was shortened with the greater applied potential was induced. On the other hand, the work established a relation between initial feed concentration and removal efficiency. Feed concentration was increased to increase the separation, whereas the feed flowrate does not influence it [146].

A batch study based on using cation accompanied anions exchange membranes, which dealt good defluoridation capacities at the low estimated time. The removal efficiency was gradually decreased due to the low applied current to lower the chlorine ions. The removal of chlorine was a tedious issue than defluoridation of similar quality [147]. Artesian wells that are spiked in fluoride are taken in to study, where the permeable selective anionic membrane is used to decrease the operational cost. In a short duration, a good degree of defluoridation took place, resulting in 97% efficiency. Indirectly the study interprets the characteristics of water which is influenced by the type of soil and rock present in that particular locality [148]. A comparative study was made with adsorption on the chitosan and electrodialysis process. The adsorption technique grasped the fluoride quickly but was inefficient to work in the brackish water due to the existence of the co-ion environment, whereas electrodialysis broke the obstacle, which provided good removal efficiency. But the later technique is expensive. Thus, a conclusion was made to treat the fluoridated water with electrodialysis and then by adsorption [149]. 91.5% efficiency was attained in treating brackish water by electrodialysis. The study has been discussed with and without pretreatment of raw water. Precipitation technique was done to eliminate calcium from the aqueous solution before electrodialysis. The initial concentration of fluoride is 3 mg/L were few ions where adsorbed on the magnesia during pretreatment. Eventually, satisfactory results were obtained after half an hour [150]. As membranes are used in the process, it adds up the cost and skilled labor which are some of the inabilities to use in rural areas.

2.5.3. Electrodialysis reversal

Electrodialysis reversal (EDR) is an electrodialysis reversal water desalination membrane process. The anionic and cationic ion exchange membranes have been alternatively placed in an electrodialysis stack. An electric current transfers the dissolved salts through this EDR. Once in a while, the route of an ion movement was reversed by reversing the polarity of the applied electric current. It has the ability in removing a wider range of pollutants from water and wastewater. To abolish the ineffectiveness in cost, electrodialysis reversal technique was cast-off in the synthetic water and the real-time groundwater samples taken from Cachoeira, Santana. The removal efficiency obtained was about 80%, as the flow rate increased linearly with the separation performance. This technique has brought down the cost nearly by 90% making it a feasible process [151]. The mini-plant was set up in China to treat the effluent from the steel industry. The treatment process was affordable and fluoride ion in water was reduced to less than 1 from 15 mg/L. It was successful even in lowering chlorine, calcium, and sulfate levels [152]. EDR is also used in eliminating total dissolved salts from the municipal wastewater. It also lowers the fluoride level by 59 %, with less consumption of energy [153]. In this study, EDR is used as tertiary treatment. The raw water was treated with a tannic based coagulant. After the 54th day of operation, the fluoride was reduced to 0.01 mg/L, indicating the process to be well suited for defluoridation. The work also highlighted the reduced consumption of energy when appropriate coagulants are used [154].

2.5.4. Donnan dialysis

Dialysis is a process of separation of solutes using a membrane. Donnan dialysis which is also called diffusion dialysis is primarily applied in the removal of fluoride ion from water. The major force involved in Donnan dialysis is the concentration difference. It is used in combination with an anion exchange membrane to remove negative ions like fluoride with the help of the alkaline system. Hydroxide ion in the alkaline system varies in concentration between two solutions that compel the migration of OH ions in to feed solution. While the diffusion of OH ions in to feed solution induces migration of fluoride ion [155]. One of the most common factors that affect the transport of solutes in Donnan dialysis is pH. It was predicted that the transport of fluoride was maximum at pH 6 in the feed phase and pH 1 at the receiver phase. The most commonly employed receiver phase is 0.1 M NaCl. There are lots of anion exchange membrane DSV, AFX, ACS that are used in common [156]. Other factors like feed concentration, fluoride flux, feed flow rate, temperature, and agitation speed affect fluoride removal efficiency. This process does not need regeneration of anion exchange membrane [157].

2.5.5. Direct contact membrane distillation

Membrane distillation is defined as a thermally driven membrane separation process. The mechanism is completely accompanied by the vapor pressure difference across the hydrophobic membrane. During this process only water vapor can pass through hence it leads to the production of highly pure water. Among membrane distillation techniques, direct contact membrane distillation is a well-known technology in which feed and distillate are separated from membrane. It was studied that feed concentration had no effect on permeate flux and removal. But the presence of carbonate content may increase the fouling behavior of membrane thereby declining the removal efficiency. This can be controlled by the acidification process in the feed. One of the drawbacks in this process is when feed concentration is increased accumulation of fluoride is increased thereby affecting the membrane pores. Apart from the drawback, the studies achieved less detection of fluoride ion in permeate even after increasing the concentration in the feed as 5,000 mg/L [158]. Further study revealed the mass transfer and heat transfer mechanism in the direct distillation process. Heat transfer analysis revealed the presence of conduction through the membrane as major energy. It was found that increasing feed temperature increased thermal efficiency whereas decreased temperature leads to polarization. Mass transfer analysis showed that the Knudsen mechanism is the major diffusion process to describe the transport of water vapor through pores of the membrane. The complete mechanism was studied using micro-porous membranes. It was found that the hydrophobic membrane acts as a barrier for the liquid–vapor interface. The main advantages of this process are low hydrostatic pressure, less fouling, and low feed temperature [159]. The study showed that direct membrane distillation removed 99% of fluoride ion. The study portrayed the run performance that it consumes very less heat to meet energy requirements (2 kWh/m^3) [160].

On viewing the treatment processes, their usage in treating the different drinking and wastewater may provide a better idea in choosing an appropriate technique for defluoridation. Adding up to this, the pros and cons of each technique have been discussed in Table 6.

3. Practical implementations

Some of the studies have reported by demonstrating with the real-time water samples that are produced from the industries which are said to be the foremost cause for fluoride contamination. While using industrial samples, the defluoridation capacity alters due to the presence of other co-ions and various contaminants that makes the study still more tedious. In this study, industrial wastewater has been investigated in reducing fluoride concentration levels. Hybrid crystallization-reverse osmosis technique has been found more suitable for the contaminated water than the other techniques like standalone reverse osmosis (SRO), nanofiltration, and membrane distillation. The SRO process needs pretreatment and fails to lower the fluoride contamination when the initial concentration was greater than 614 mg/L. The working pH was about 9, which showed a good amount of removal [136]. Other studies were performed with the wastewater from the electroplating industry at a range of pH 2–12. Carbon hydroxide nanorods of 2 g/L were implemented in 550 mg/L of the fluoride-containing aqueous solution, with a removal efficiency of 99%. The material developed was found to be applied for two or three cycles with deduction in the adsorption capacity by 10% in subsequent cycles. The mechanism of fluoride lowering was mainly dependent on the co-precipitation along with adsorption [171]. The industrial wastewater from the steel industry is treated using the aluminum electrodes by the method of electrocoagulation. The result showed predictable changes for the initial 5 min and thus it is estimated as the total hydraulic retention time. The aluminum plates placed between the cathode and the anode did not show significant changes in the efficiency of the fluoride removal. To have a steady voltage and a controlled condition in the system, more energy is been spent on this process [172]. The basic science behind the defluoridation process was found to be ionic bonding, electrostatic interactions, and ion exchange. The removal was made possible through Gastropod shells, calcinated at 1,000°C [173]. As per the previous study, a similar fluoride spiked sample was taken, where anionic clay was used as a defluoridation carrier [174]. Some of the real-time implementations are summarized in Table 7.

Table 6
Pros and cons of the various conventional methods for defluoridation in practice [152,153,159,161–170]

Defluoridation processes	Pros	Cons
Adsorption	• Flexible in modification • Simple in construction and efficient • Low-cost operation and reusing ability • Lower sludge production	• Regeneration up to certain cycles • Specifically works in conditional pH
Coagulation	• Traditional technique • Easily adopted in small dwellings	• Concentration of sulphates and traces of aluminum is higher • Taste of the water changes after treatment • Results in high sludge production
Electro-coagulation	• No further treatment for maintaining colour and odour is required • Simple in design and flexible • Less generation of sludge	• Consumes energy in numerous quantities • Merely dependent on characteristics of wastewater
Ion exchange reins	• High defluoridation efficiency • Taste and colour of the treated water are suitable for drinking	• Not economical • Generates large amount of residue • Complexity in resins • Difficulty in regeneration of resins • Expensive • Interfering ions influences the efficiency of the removal
Nano filtration/ reverse osmosis	• Property of the treated water is unchanged • Nearly 95% of removal efficiency is achieved • Less usage of chemicals	• More concern on disposal of fluoride rich waste in huge qualities • Membrane fouling with microbial actions • Operated under controlled total dissolved solids
Electrodialysis	• Less usage of chemicals • Retrofittable • Low cost at post and pre treatments	• Produces reject concentrate • Treatment of reject • Only ionic contaminants can be removed
Electrodialysis reversal	• Reduced surface fouling due to self-cleaning mechanisms • Physically durable membranes • Treats irrespective of the characteristics of raw water	• High working cost • Efficiency decreases on heavy loading
Direct membrane distillation	• Highly pure form of water is extracted • Good performance at low temperature and low pressure	• As concentration increased, leads to blockage of porous resulting damage to the membranes • Cost of the operation is higher

4. Economic aspects of various treatment methods

For the removal of fluoride from aqueous solution and gas sensor, lanthanum – iron binary oxide nanoparticles (LIBONs) are used. They were synthesized using the co-precipitation method and sintered at desired temperatures and the experimental data were analyzed using isotherm and regeneration studies. From the result, the removal of fluoride was seen to be exceptional showing an adsorption capacity of about 14.49 mg/g with a pH of 6.5. By its good sensitivity, reproducibility, ease of availability it can be inferred that the LIBONs were cost-effective and efficient adsorbent for fluoride removal [182]. The hybrid technique (Electrocoagulation followed by microfiltration) coupled with cost estimation was carried out for the removal of fluoride in drinking water. The effect of different operational parameters was carried out in the electrocoagulation chamber. The uptake of fluoride seemed to be highest at pH 7.9 with the final removal concentration of about 0.43 mg/L. It was seen that with the increased current density, the energy cost increases due to the higher energy consumptions. And also, the electrode cost increased with increased current density due to the increased dissolution of the electrode in the solution. Though the cost increases but the hybrid technique was able to lower the fluoride concentration within the permissible limit as prescribed by the World Health Organization [183].

The simultaneous removal of fluoride and arsenic was done through continuous coagulation process using aluminum electrodes and the operating cost was also estimated. The concentrations of two components were found to be within the permissible limit as per the World Health Organization. The major contributing factor to operating cost estimation is the cost of the electrode. From the result, it

Table 7
Practical implementation of defluoridation in fluoride contaminated groundwater and industrial wastewater

Sample source	Region of study	Treatment method	Initial F^- conc. (mg/L)	Removal efficiency (%)	References
Wastewater, China Steel Corporation	China	Electrodialysis Reversal	15	<1 mg/L	[152]
Municipal wastewater	Werribee, Victoria	Electrodialysis Reversal	–	59	[153]
Acidic electroplating industry	Uttarakhand, India	Adsorption	–	91.7	[171]
Basic electroplating industry	Uttarakhand, India	Adsorption	–	70.3	[171]
Mobarakeh Steel Complex	Esfahan, Iran	Electrocoagulation	5–35	93	[172]
Groundwater	Chandrapur District	Adsorption	2.73	97.80	[175]
Groundwater	Medawachchiya area, Sri Lanka	Electrolysis	2.4	57	[176]
Groundwater	Ethiopian Rift Valley	Cation exchange process	8.2	82.92	[177]
Glass factory waste water	Shiraz city, Iran	Adsorption	23	91.30	[178]
Volcanic under groundwater	Island of Tenerife Spain	Electrocoagulation	6.02	92	[179]
Groundwater	Settat and Bejjaad	Adsorption	2 and 3	Below permissible limits	[180]
University sewage	Tramandaí, Rio Grande do Sul, Southern Brazil	Conventional processes and electrodialysis	–	Can be used agricultural use	[181]

can be said that the operating cost reduces with the increase in a flow rate of 0.88 L/h is found as 0.358 USD/m^3 with the run time of 95 min. So, overall, the continuous electrocoagulation process can be effectively used for the removal of fluoride and arsenic in contaminated water [184]. The study emphasized the biosorption of arsenite and fluoride from aqueous solution using activated carbon with SnO_2 nanocomposites. In this study, isotherm, kinetics, thermodynamics along with cost estimation and regeneration were made. The percentage removal of fluoride was about 82%–85% with a pH of 6. While coming to the adsorbent, the total cost for 1 kg of the adsorbent was estimated to be 354.54 INR which is lower than that of commercially activated carbon 600 INR per kg, thereby suggesting the economic feasibility of the material. Furthermore, the recycling studies showed that the adsorbent can be used easily after regeneration with NaOH. Overall, good adsorption capacity, fast removal rate, ability to operate at very low concentrations, and low production cost have made the adsorbent as an effective one to be adopted in the removal of fluoride in drinking water [185].

The economic study was done for fluoride removal by the electrodialysis process. The investment and operating costs were evaluated for an industrial plant with a capacity of 2,200 m^3/d water consumption for 50,000 per capita for rural areas. From the study, it is seen that the parameters are determined from the membrane surface, flow rate, the recovery rate, the velocity in cells, and the outlet concentrations. From the economic data provided it can be said that the capital and operating costs of an ED plant depends strongly on the quality of feed and product water, the total membrane area, the plant capacity, the site characteristics, the prices for membranes and other plant components and their useful life under operating conditions. So, it is difficult to analyze and to compare the costs of different electrodialysis plants [186]. This study emphasizes the implementation of a small photovoltaic powered nanofiltration pilot plant for the removal of fluoride in groundwater. From the analysis, it was said that the fluoride removal was about 98.8% where the concentrate has been reused for washing and flushing of the toilet. And also, the use of solar photovoltaic power (2.25 KWP) for approximately 2.5 h/d allowed producing of 236 L/h permeate on average. However, the high capital costs remain to be the most limiting factor in the African state and it has been proved that the use of locally available material significantly reduces the cost of the unit further [187].

5. Scope for future research

This review elucidates the sources of fluoride that contaminate the drinking water and the industries discharging it. Though there are enormous researches done on removal of fluoride from the drinking water and industrial water, a sustainable and household level treatment solution must be effectively implemented in all working conditions with desirable efficiency and a good rate of regeneration.

The defluoridation process must be easily accessed, simple, and economic in use so that even the common men may initiate the usage of it. This eventually contributes to a pollution-free environment. To achieve this target, there must be an awareness of existing and emerging technologies. The drawbacks in the existing technology must be eradicated or a hybrid system can be suggested to improve the removal efficiency of fluoride. With this effort, the efficiency of the innovated method may uplift its efficiency approximate to the ideal state on a larger scale.

6. Conclusions

The outcomes of the review are

- To create awareness about the toxic, xenobiotic, non-biodegradable fluoride, its causes, effects, F^-prone countries and the permissible limits prescribed by the regulatory agencies, various techniques that lower the elevated fluoride, its benefits and detriment, economic aspects of each technique and eventually, directs further researches must in this field.
- It is better to control the contaminant in the source region because it reduces the cost and the time in treating the contaminant. This work identifies the sources where the fluoride is created, naturally, and anthropogenically.
- The problem statement arises when the fluoride entered into the environment causes destructive effects on the biotic and abiotic components, multiple malfunctioning, and disorders on humans, especially dental and skeletal fluorosis.
- The work spots out the fluoride regions around the world with the prevailing fluoride content, nature of the sample, outcomes of the study. This interprets the reason for excessive fluorides due to climatic condition, soil and rock type and their agricultural practices.
- On discussing the toxicity of fluoride, it is our responsibility to diminish it in an eco-friendly way using cost-effective techniques. In need, this brings out the methods practiced in the current scenario and the selectivity of each process by clustering the pros and cons of various reviews.
- Cost is an important parameter in deciding the process to be implemented. The survey done in this work fills the loopholes in bringing the experimental concepts to the commercial scale. Few real-time data are incorporated to strengthen the selection of the treatment process.
- Thus, the work put forth the emerging ideas by various experts in the field, in parting defluoridation. Selective treatment technology can be chosen to treat the contaminated water based on influencing parameters like pH, temperature, co-existing ions, etc. It stretches the recent updation in the current techniques to increase the success rate. Adsorption is one best method which is liked to be highlighted through this study because of its flexibility, energy-efficient, low operational and capital cost and abundant availability of materials. The above-suggested techniques can be implemented in a coupled way to further increase the removal efficiency.

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