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Chapter

Water Defluoridation Methods Applied in Rural Areas over the World

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Abstract

Overexposure to fluoride (F) through drinking water is the most widespread water problem in the world, but it has now exacerbated due to rapid population growth rates, adverse climatic changes, and increasing levels of water scarcity. Thus, despite the large amounts of data, which has accrued on mitigation methods of high F is still the primary impediment to drinking water programs among many developing nations. The current review chapter on F mitigation techniques applied world-over is aimed at providing a succinct overview of water defluoridation techniques and strategies being used to combat the impact of human F overexposure. It represents a starting point to understand the prospects of reducing the global F impact. It is anticipated that this work will lay a strong foundation for this and also inform strategies for safeguarding public health and the environment from F pollution.

Keywords: defluoridation technologies, drinking water, fluoride, fluorosis, literature review

1. Introduction

The beneficial and detrimental effects of fluoride (F) were established in the early 1940s. Low levels of drinking water F (< 0.1 mg/L) were linked to the occurrence of dental caries, whereas elevated levels of F in water were associated with incidences of dental fluorosis among the communities [1]. Then some countries began artificial fluoridation of drinking water to control teeth decay [2]. Soon the widespread use of F in drinking water and oral products to control teeth decay resulted in a drastic decline in incidences of dental caries with a concomitant rise in dental fluorosis among the communities [3]. The severity of fluorosis increases with increasing F concentrations greater than 1.5 mg/L in drinking water [4] and data over the last few decades indicate trends toward more fluorosis around the world [5].

The new surge in the prevalence of fluorosis around the world has been attributed to, among other the rise in water fluoridation programs [5]; indiscriminate use of fluoridated products [6]; inadequate F legislation in the affected countries [7]; lack of technology and capacity for sustainable F surveillance [2] and widespread water

security problems [8]. The WHO's "guidelines" of 1.5 mg/L as the allowable standards of drinking water F have also come under scrutiny in regard to its success in controlling the adverse F effects among the communities [9]. Severe fluorosis has been recorded among communities using household waters with F levels well within these guidelines [10]. So, there have been efforts to control the adverse F effects in the communities. The strategies that are employed include instituting community health risk assessments and management programs [11]; high water F surveillance [12]; prospecting for safer water [13]; development of water defluoridation strategies; F awareness creation and behavior change campaigns [14]; developing water policies and legislation for F mitigation [9].

It is apparent, however, that there is an urgent need to reconsider the current approaches. The desired approaches for effective control of F impact among the communities should not only be effective but also be affordable, holistic, and comprehensive. In the current work, a review of the previous strategies and methodologies that have been applied in water defluoridation is presented [15]. The chapter aims to provide an update on F mitigation technologies being deployed worldwide and it is expected that this will enhance scientific understanding of the available technologies and the prospect of reducing the global F impact.

Defluoridation of existing waters is the main option where alternate safe water in high F areas is not available. However, the available water defluoridation approaches differ in scale, efficacy, sustainability, affordability, and acceptability. Therefore, the security of supply is heterogeneous. In general, the available options for water defluoridation can be classified as chemical, membrane-based, physical, or adsorption-based.

2. Chemical methods for water defluoridation

Chemical methods of water defluoridation involve the addition of reactive species, which can react with and facilitate water F removal through phase separation steps [16]. Here, five methods of which two are based on precipitation, two on coagulation, and one on electrocoagulation processes will be explained in further detail.
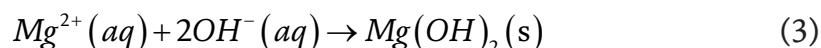
2.1 Precipitation processes

They basically include lime-softening and contact precipitation. The former is a precipitation chemical method of water defluoridation used to remove calcium and magnesium ions from hard water and it is also used to reduce F levels in potable waters [17]. In the traditional "lime-softening" technique, lime ($Ca(OH)_2$) reacts with soluble $Ca(HCO_3)_2$ to precipitate insoluble $CaCO_3$ [18] according to Eq. (1) as follows:

$$Ca(HCO_3)_2(aq) + Ca(OH)_2(aq) \rightarrow 2CaCO_3(s) + 2H_2O(l) \qquad (1)$$
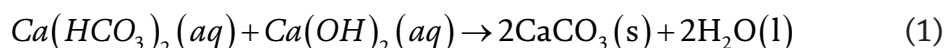
In presence of water F, however, part of $Ca(OH)_2$ precipitates and removes insoluble fluorite, CaF_2, according to Eq. (2) as:

$$Ca(OH)_2(aq) + 2F^-(aq) \rightarrow CaF_2(s) + OH^-(aq) \qquad (2)$$
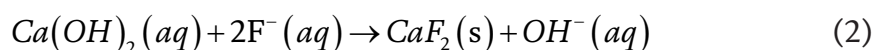
The removal of F by lime-softening is enhanced in presence of dissolved magnesium salts, which precipitate as $Mg(OH)_2$ according to Eq. (3) below [19].

$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s) \qquad (3)$$

This also helps to eliminate excess alkalinity in treated water [20]. Defluoridation by lime is achieved by surface precipitation of fluoride onto the $Mg(OH)_2$ formed but the process is temperature dependent and the F adsorption onto $Mg(OH)_2$ increases at high temperatures.

Lime softening is the most common water defluoridation method in developing countries [21]. Based on this technique, the Indian Institute of Science in Bangalore, developed a simple defluoridation technique, which uses magnesium oxide, lime, and sodium bisulphate [22]. Due to the presence of MgO, the pH of treated water has to be adjusted to desirable levels (6.5 to 8.5) by adding 0.15 to 0.2 g per liter of sodium bisulphate. Even so, water defluoridation based on lime softening is inefficient and the technique requires large amounts of reagents leading to high volumes of F-laden sludge.

2.2 Contact precipitation

Contact precipitation employs the simultaneous addition of soluble calcium and phosphate compounds to brackish water. These react with F ions to precipitate CaF_2 and fluorapatite ($Ca_5(PO_4)_3F_2$) [23] catalyzed by a saturated bone char medium. The process has been applied in Tanzania on raw water with 13 mg/L F resulting in F removal efficiency of 97.9% [24]. Contact precipitation has been floated as being more efficient and reliable than lime-softening, but it also generates large volumes of F-enriched sludge [25] and it can impart bad taste and smell to the treated water compromising its palatability.

2.3 Coagulation techniques

Coagulation is a procedure in which soluble metal cations [26] or commercial polyelectrolytes [27] with a large charge-to-volume ratio are added to water to attract and react with organics and other insoluble aggregates to flocculate and sediment and phase them out of the water. The flocculates formed to provide high sorbent surfaces for F ions. Alum ($Al_2(SO_4)_3.18H_2O$) is the usual flocculant in cases where F removal is also desired [26]. The salt reacts with OH^- ions to form $Al(OH)_3$ flocs according to Eq. (4) as:

$$Al_2(SO_4)_3 \cdot 14H_2O + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3 + 3CaSO_4 + 14H_2O + 6CO_2 \quad (4)$$
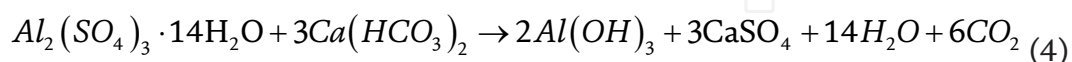
The flocs sorb F from the water. A little lime is added controllably to replenish the OH^- ions. The amount of alum is controlled to prevent the initiation of complexation of Al^{3+} with F. Also, coagulation is not efficient and complete F removal is not achieved. Large amounts of coagulants are used leading to large volumes of sludge [25] and the residual coagulants in the water must be monitored to meet the drinking water standards.

Nonetheless, several authors have reported the application of this method with varying degrees of success [28, 29]. On the other hand, some authors have reported investigations aimed at improving upon the technique. Atia et al. [30], for example, compared the coagulants and demonstrated that the use of $Al_2(SO_4)_3.18H_2O$ as

flocculants was superior to $Fe_2(SO_4)_3.H_2O$. However, F removal by coagulation using poly-aluminum chloride (PAC) has also been reported [31] and compared with other polyelectrolyte coagulants [32]. Most recently some workers have utilized inorganic polymeric coagulant and indicated that 80% defluoridation of 6 mg/L F polluted water [33]. An alternate precipitation technique based on induced crystallization under extreme pH levels and carbonate/bicarbonate equilibriums has recently been applied with high F removal efficiencies [30]. Also, a facile approach to calcium co-precipitation has been reported [34].

2.4 Nalgonda technique

The Nalgonda technique is a modified coagulation protocol, which was developed by National Environmental Engineering Research Institute, Nagpur, India [35]. It takes advantage of the synergy between precipitation using lime and alum flocculation to facilitate F adsorption on $Al(OH)_3$ flocs formed in the solution [36]. The F adsorbed is removed with the flocs by sedimentation. The Nalgonda technique has now been introduced in many countries but it requires high doses of flocculants leading to large sludge transfers and it may release excess Al^{3+} into the treated water [37].

2.5 Electrocoagulation

Electrocoagulation (EC) uses an electrolytic cell (**Figure 1**) [38] to supplies coagulant Al^{3+} ions in a controlled manner [26].

As the electric current passes through the cell, the Al anode gets oxidized to Al^{3+} ions, which are transformed into polymeric species and reacted with hydroxyl ions in solution to form the $Al(OH)_3$ flocs, facilitate F removal from water as in the other coagulation techniques [39].
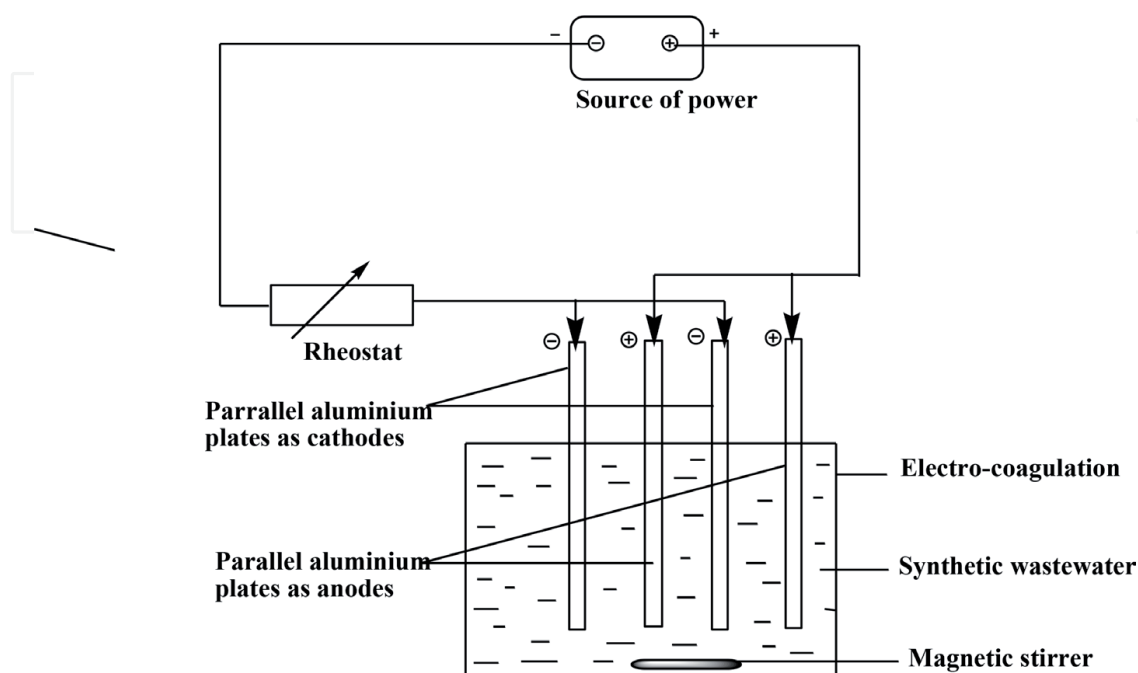

Figure 1.
Schematic representation of an electrocoagulation cell (adapted from Ref. [38]).

Even though the EC technique has been associated with demerits including high running costs, need for reliable electric power, and for specialized personnel to operate [25], the technique is efficient, reliable, and produces high-quality water. The sludge generation is low, and the method is used in different water conditions. In Algeria [40], for example, EC was applied as an efficient affordable water defluoridation technique, and, elsewhere, it has been used to reduce borehole F level from 3.5–4.8 to 0.8–1.0 mg/L [41]. Also, Khatibikamala et al. [42] reported that F concentration was reduced, based on an EC cell, from 4.0–6.0 mg/L in raw water to lower than 0.5 mg/L. Further, EC was applied to treat groundwater from Shivdaspura (Rajasthan): Sinha et al. [43], reported initial F levels of 5.0 mg/L were reduced to 0.2 mg/L plus. Then, Emamjomeh and Sivakumar [40] confirmed the technique as an effective electro protocol for domestic and industrial water defluoridation.

On their part, Vasudevan et al. [44] compared the performance of different electrodes in an EC protocol and found that F removal efficiency reached 96% with a magnesium alloy anode and a stainless steel cathode at a current density of 0.2 A/dm^2 and pH of 7.0 more recently Khan et al. [45], confirmed earlier findings by Takdastan et al. [46] that aluminum electrodes were more efficient and economical in F removal than iron electrodes. In related analyzes, Hu et al. [47] showed that the efficacy of an EC system in water defluoridation was controlled by the molar ratio of hydroxide and F to Al(III) and related that optimum activity coefficients for defluoridation in coagulation and electrocoagulation are both close to 3.

3. Membrane methods

Membrane methods are those that employ the use of a casing that selectively separates a component in water. They include electrodialysis, reverse osmosis, and nanofiltration [48].
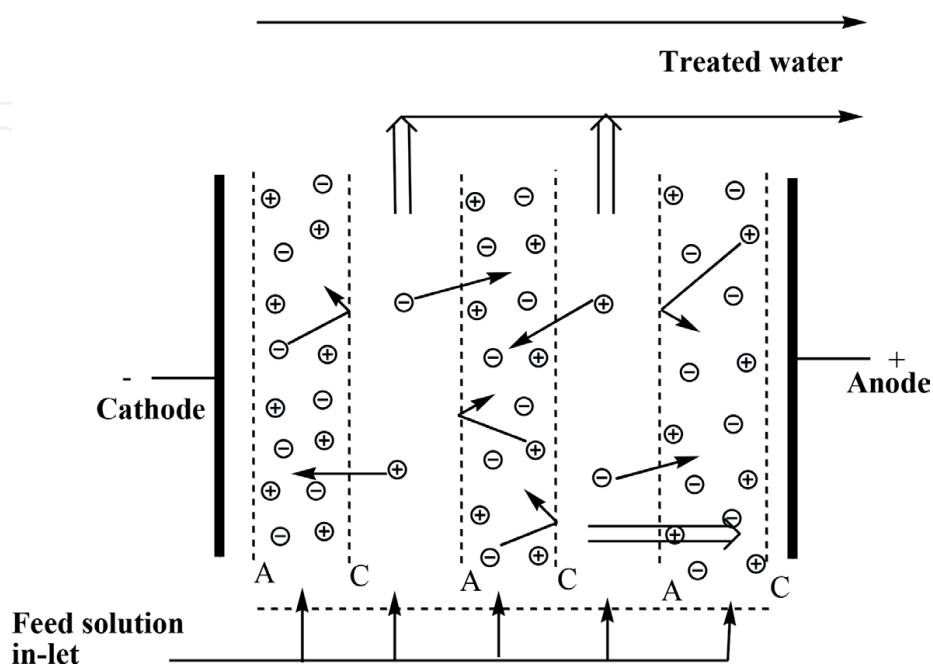

Figure 2.
Schematic representation of an electrodialysis unit.

3.1 Electrodialysis

Electrodialysis (ED) technique uses an electric field to separate ions of one charge from the counter ions [49]. A typical ED unit (**Figure 2**) consists of about 400 alternating cation- and anion-exchange membranes, which are 0.5–2.0 mm wide, sandwiched between an anode and a cathode in a cell [25].

The membranes have charged groups bound into polymeric substrates which attract and adsorb mobile counter ions. The anionic-exchange membranes permeate cations only, while the cation-exchange membranes permeate anions but trap the cations. Under an electric field, cations and anions move in opposite directions and the membranes capture respective ions resulting in alternating cells of ion-concentrated solutions called concentrates and ion-depleted solutions referred to as dilutes [50]. ED is an efficient defluoridation protocol and the sludge volume generated is low. However, the overall protocol is costly, complex, and requires reliable source power and specialized personnel to operate. The process is also non-selective and removes essential ions required for quality drinking water [51].

The technique has been applied to defluoridation of saline water with 3000 mg/L total dissolved salts (TDS) and 3.0 mg/L F [52]. Elazhar et al. [53] compared the performance of ED and nanofiltration (NF). Kabay et al. [54], on the other hand, was able to optimize a water defluoridation process and evaluated its mass transfer and energy use efficiency. ED was applied in Brazil with 97% defluoridation efficiency [49]. In India, ED was applied to saline water with high TDS of 5000 mg/L and 10 mg/L F levels [51] and it has been reported that ED was used to treat brackish water with 2.9 mg/L to just 0.4 mg/L [F] [55].

3.2 Reverse osmosis

Reverse osmosis (RO) is a membrane process in which dissolved pollutants are removed by applying pressure on raw water to force it through a semi-permeable membrane against the osmotic pressure (**Figure 3**) [56].

The level and rate of contaminants removal depend on the sizes and electrical charge of the polluting ions [57]. It is found that RO is efficient and generates little sludge, but it is expensive to install and to run—it requires specialized personnel and reliable electric power to generate necessary pressures [48]. Some of these limitations of RO can, however, be bypassed. A study in Tanzania [58], for example, applied nanofiltration (NF) and reverse osmosis (RO), with an autonomous membrane system, which was powered by solar energy and the tested membranes could achieve the WHO drinking water standards [59]. The process reached 1000–2500 L daily total permeate volume of portable water with an additional 3500–5000 L of non-potable water fit irrigation and washing. However, the integration of such advanced
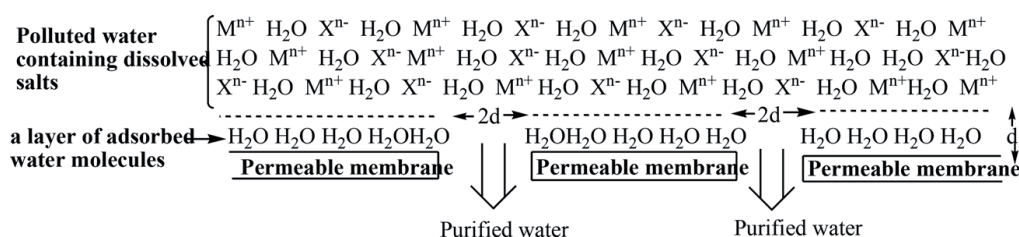

Figure 3.
Schematic representation of reverse osmosis.

technologies has not proven successful in many rural areas of developing nations where the necessary power is always available.

3.3 Nanofiltration

Nanofiltration (NF) operates on the same principle as reverse osmosis but the membranes have larger pores [48] offering less resistance to the flow of solvent and solute particles. The procedure is, therefore, able to operate at much lower pressures reducing energy costs. The retention of solutes is ascribed to steric and charge effects and the procedure is selective and considered to be suited to defluoridation of brackish waters. RO/NF has been applied to the treatment of various groundwater contaminants in India [60] and in the efficient removal of F and salinity from high-F brackish water at a village scale in Senegal [61]. In Finland, Kymenlaakso Water Limited, which is a public company, has operated a 6000 m^3/day water RO plant with a permeate [F] of <0.03 mg/L since 2003 [62]. Richards et al. [63] evaluated the effect of speciation on the retention of F by NF and RO and found that F retention was independent of pH. In a study realized in Tunisia, F removal from water and from wastewater by NF was found to be controlled by trans-membrane pressure, feed water concentration, ionic strength, type of counter-ions, and pH and higher retentions were linked to pH values and vice versa [64]. Some researchers have reported F retention efficiencies of an NF process of 70% [65] mark above pH 7 but another team of researchers in France reported an RO F rejection efficiency greater than 98% [66].

Nonetheless, the protocol continues to attract the interest of researchers from around the globe [67]. Furthermore, hybrid treatments with sequential use of two or more simple techniques have become common in the recent past. For instance, filtration and ultrafiltration as subsequent treatment of coagulation have been recently tested for water defluoridation by a team of workers in India [68].

4. Distillation

4.1 Solar distillation

Distillation is a physical procedure in which water is converted to steam, and then the steam is condensed back into liquid water. The dissolved salts remain in the brackish water that is left behind. Solar distillation takes advantage of abundant sun rays and is the most applicable technique to circumvent the high costs of electricity. The method is simple, clean, and effective but the resulting wastewater must be removed to prevent encrustation of the vessels and be disposed of with care due to their high salinity. Solar distillation can be used from household scale to large industrial scale. Otherwise, it is inexpensive to run but the initial installation costs are big.

Solar distillation units have been used world-over to treat brackish water [69]. A pilot project of Solar driven membrane distillation has been operated on a small village level at Robanda in Tanzania [70]. Also, a similar solar water defluoridation unit has been built using local materials and successfully operated in Bongo District, Ghana, [71].

4.2 Membrane distillation

Membrane distillation uses a hydrophobic membrane with air-filled pores. The surface tension of the feed water and distillate prevents the water from entering the

membrane pores keeping it out of the membrane. Water vapor pressure difference is then generated by applying sufficient temperature difference across the membrane. This is accomplished by heating the feed water and cooling the distillate at the other side of the membrane to cause a flow of water vapor through the membrane and result in distillate condensation [70].

Naidu et al. [71] evaluated the applicability of a modified design vacuum enhanced-multi-effect membrane distillation for drinking water and projected a 70% recovery ratio for a scaled-up unit. The feasibility of a direct contact membrane distillation (DCMD) process to recover F contaminated waters was also tested and up to 99% rejection of F was reported [72]. Boubakri et al. [73], using a similar DCMD process based on polyvinylidene F membrane, observed high thermal efficiency and high permeate flux favored by elevated temperatures.

5. Adsorption

In adsorption, raw water is passed through a bed containing a material that is able to retain F by physical, chemical, or ion exchange mechanisms. Adsorption of F onto solid adsorbents occurs through [74]: external mass transfer; surface adsorption; and, intra-particle diffusion processes. The technique has gained popularity in water defluoridation because it offers satisfactory results; it is simple, affordable, and eco-friendly. Many adsorbents, including alumina, clays, polymeric ion-exchange resin, activated carbons, biosorbents, and layered double hydroxides have been studied for water defluoridation [48].

5.1 Activated alumina

Activated alumina, Al_2O_3, is dehydrated $Al(OH)_3$, which is prepared by heating $Al(OH)_3$ at 300–600°C. It was first used in water defluoridation in the US in 1952, later in many other countries including China, Thailand, India [75], South Africa, and Ethiopia [76] by the 1980s. It is now widely used in many other countries of the world [77]. Alumina has one of the highest water defluoridation efficacies. In one study, aluminum hydroxide, which is a form of hydrated alumina was reported with an exceptional F adsorption capacity of 116.75 mg/g [78]. Recently hydrated alumina modified NaA zeolite was reported to have high F adsorption capacities of 104 mg/g [79]. The use of alumina in water defluoridation is, thus, widespread [39] but it is costly, requires frequent adsorbent regeneration, and the adsorbent gets fouled easily from the dissolved solids in the water [25].

5.2 Clay adsorbents

Soils and clays present high prospects of application in water defluoridation. This is mainly because they are almost always: (1) available in natural abundance; (2) stable and usable in different water conditions; (3) have high adsorption capacities; (4) easy to prepare; and, (5) are eco-friendly [80]. The specific reactions F adsorptions at the soil surfaces are heterogeneous and the particular choice of soil adsorbent for water defluoridation is controlled by its known adsorption capacities, availability, and the desired physicochemical properties. Consequently, soils are among the most studied matrices for water defluoridation.

Nonetheless, minerals, which have attracted the highest attention for water defluoridation research include: apatite, calcareous minerals, diatomite, attapulgites, and ferric minerals. The apatite minerals because are known to control the natural exchange of F in soil-water solutions in the environment [81]. Fan et al. [82] evaluated the capacity of hydroxyapatite, fluorspar, calcite, and quartz for water defluoridation. They found that F adsorption capacities for the minerals decreased from the apatite to quartz thus: hydroxyapatite > fluorspar > quartz activated using ferric ions > calcite > quartz. o, many workers have studied the capacity of apatite to enhance limestone, for example, and reported a maximum F adsorption capacity of 3.83 mg/g [83]. Else, it is often found that many calcareous minerals exhibit limited adsorption capacities for F [84]. In a study conducted by Kumar and Gupta [85], the authors investigated fluoride adsorption onto activated diatomite and found that the maximum defluoridation capacity of the mineral was 71.97 mg/kg. Other researchers have, however, reported a more enhanced defluoridation capacity of 51.1 mg/g for the [86]. These have also been collaborated most recently by Taabu et al. [87].

The adsorption of F onto modified attapulgite has been studied widely [88, 89]. The F adsorption capacity for the mineral approximates 24.55 mg/g. Hamdi and Srasra [90] found that water defluoridation capacities for some Tunisian soils was 55.8071.94 mg/g. However, other soils including ferrihydrite and kaolinite-ferrihydrite associate [91], ferric polymineral [92], lateritic minerals [93], clays [94], zeolites [95] and siliceous minerals [96] have been evaluated. Clearly, the capacity of clays to sorb F is greatly varied between the minerals and it is controlled mainly by their mineralogy and the operative conditions [80].

5.3 Ion-exchange resins

Defluoridation protocols based on the ion-exchange technique use charged anion resins that substitute anions in the substrate structure (normally chlorides) for F ions in the water [97]. The resin exchange sites are made of adsorbed cations (usually calcium) [98]. The natural polymeric organic resins, chitin/cellulose composites, are among the adsorbents with the greatest potential for water defluoridation. The use of natural polymeric materials has additional advantages because they are readily available in nature. Subsequently, natural polymers have been studied with varying adsorption efficiencies such as for chitosan (8.10 mg/g) [99], nanocellulose/polyvinyl alcohol composite, agglutinin derived from *Strychnos potatorum L.* seed (11.363 mg/g) [100] and chitosan-zirconia-ferrosoferric oxide composites (17.81 mg/g) [101]. Much higher adsorption capacities of 45.45 mg/g and 52.63 mg/g have, however, been reported for gamma degraded chitosan-Fe(III) beads [102] and for zirconia modified chitosan beads [103], respectively. Furthermore, a sorption potential of 48.78 mg/g has been reported for β-cyclodextrin grafted upon nanoscale titania surfaces [104].

The main challenge of the use of natural polymers in water purification is their liability to chemical and biological degradation. Also, the F ions tend to bind irreversibly into the exchange sites of the resins degrading the membranes. Then it is found that F removal using ion-exchange resins is often limited by low ionic selectivity [105]. Plus, commercial resins are expensive and require continuous regeneration and the spent adsorbents are non-biodegradable, they persist in the environment and must be disposed of very carefully.

5.4 Metal: organic frameworks

There is an emerging class of F adsorbents in fabricated metal–organic frameworks. This are basically multivalent metal ions intercalated in large organic molecules to enhance the synergic F uptake by the metal ions and the organic substrates. Jeyaseelan et al. [106] investigated defluoridation capacities of three MOF's including fumaric acid–based metal–organic frameworks (MOFs) using Zr^{4+}, La^{3+}, and Fe^{3+} metal ions and found that they had comparable defluoridation capacities of 4.920, 4.925, and 4.845 mg/g, respectively.

5.5 Carbonaceous adsorbents

Carbonaceous F adsorbents include activated carbons from plants and animal biomasses, carbonaceous mineral adsorbents, and graphene.

5.5.1 Plant biomass-derived carbonaceous F adsorbents

Many activated carbons have been studied for water defluoridation. Hanumantharao et al. [107], for example, evaluated *Acacia farnesiana* carbon and reported a low defluoridation capacity of 0.268 mg/g. Similar limited water defluoridation capacities (< 1.5 mg/g) have also been reported for carbons of: *Neem* [108], *Tamarindus indica* fruit shells [109], family fruit [110], zirconium-impregnated coconut shell [111], rice straw [112], zirconium impregnated cashew nutshell [113], pine cone [114], and zirconium impregnated coconut fiber [115]. In contrast, studies by Mondal et al. [116] using sugarcane charcoal revealed F uptake capacities of 7.33 mg/g. Similarly, investigations using *Pithacelobium dulce*, *Ipomoea batatas,* and *Peltophorum ferrugineum* carbons showed defluoridation capacities of 78.96, 76.62, and 74.48, respectively [117] but much higher defluoridation capacities of 142.86 mg/g and 230.61 meq/g have been reported for *Delonix regia* pod carbon [118], certain carbon nanostructures [119] and for activated coffee husks carbons [55], respectively. In general water defluoridation using activated carbons has been shown to be pH-dependent and most carbon adsorbents have the highest F removal at acidic pH < 3 values [80]. Plus, the adsorbent particle appears to play a leading role in controlling the adsorption efficiency – high sorption occurs for the lowest size.

5.5.2 Borne char and activated animal charcoal

Bone char is the oldest known water defluoridation agent, and it was first used in USA from 1940s to the 1960s. The technique was later introduced into other countries and it is now among the most used methods in the developing countries of the world. The method involves the use of animal charcoal which is packed into columns and water percolated through the charcoal media [120]. Mutheki et al. [121] compared to the field and laboratory performance of bone char filters and other filters based on a combination of bone char and calcium-phosphate pellets. They found average uptake F capacities to be 1.2 ± 0.3 mg/g and 3.0 ± 1.0 mg/g, respectively. A study to explore activated carbon from fish bladder showed a maximum F removal of 1.43 mg/g [122]. In related work, Kawasaki et al. [123] who investigated four types of animal biomass and Singanan [124] who studied certain bone char adsorbents for F removal, reported more or less similar defluoridation potential. However, some authors reported 99% F removal from borehole water containing 11 mg/L F based on a cartridge bone char

affixed onto a domestic faucet as a flow-through defluoridizer [125]. Therefore, some authors contend that F removal bone char is an efficient protocol for defluoridation of brackish water [22]. However, care must be taken about the preparation of the bone char, related to the taste and odor released into the treated water [126]. Besides, large amounts of organic materials are needed for gasification by expensive treatment at 800–1400 K in an inert atmosphere to obtain the adsorbents.

5.5.3 Graphene

Graphene is an emerging carbon material with sp^2-hybridized single-carbon atom-layer structure [127] that is also a promising adsorbent for water defluoridation [128]. Some workers have studied amine grafted graphene oxide encapsulated chitosan hybrid beads for water defluoridation and found a defluoridation capacity of 4.65 mg/g [129]. However, Li et al. [127], while studying graphene samples obtained from exfoliating graphite materials, reported high F adsorption capacities of 17.65 mg/g. Also, a team investigating the F adsorption by graphene-aluminum-silver-carbon quantum dots reported an adsorption capacity of 12.04 mg/g [130]. Nonetheless, some workers have shown that enhancing graphene oxide using cupric oxide, improved its F uptake capacity to 34 mg/g [131]. The results collaborate with those of a team of researchers, which used aluminum modified graphene oxide (GO) and showed it to have superior F removal efficacies of 38.31 mg/g [132]. This shows the high potential use of graphene in F water remediation.

Besides activated carbons and graphene, the application of carbonaceous minerals to water defluoridation has been reviewed elsewhere [80]. However, Abe et al. [133] reported that the water defluoridation capacities of various carbons follow the order: bone char > coal charcoal > wood charcoal > carbon black > petroleum coke.

5.6 Biosorption

Biosorption utilizes animal and plant remains in the pulverized form "as is" without prior gasification or charring. A study realized in Tanzania, reported F removal efficiencies, which was 4.1–47.3%, for several biosorbents [134]. In a particular defluoridation study, which was conducted by Yadav et al. [135] using three agricultural-based biomasses as adsorbents tested on groundwater containing 5 mg/L F, the authors reported F removal efficacies of 40–58%. Elsewhere, Gandhi and Sekhar [136], found that the F biosorption capacity of *Strychnos potatorum* seed powder was 0.9945–1.052 mg/g. Further recently, the F removal of palm kernel shell-based adsorbent was evaluated and found to be 2.35 mg/g [137]. It is found, therefore, that, plant biomasses exhibit limited F uptake capacities when compared to other adsorbents unless they are formidably treated.

Also, defluoridation studies utilizing algal biosorbents derived from *Spirogyra IO1* [138], *Ulva fasciata* sp. [139], *polyalthia longifolia* [140], and *Spirogyra* IO2 to adsorb F [141] have been reported. In the defluoridation evaluation of *Spirogyra* IO2, [141], for example, sorption capacity of 1.272 mg/g was reported. Also, the defluoridation capacities of fungal biosorbents have been studied. In evaluating *Fusarium oxysporum* to remove F from water, low defluoridation capacity of just 19% was reported [142]. These similar findings were collaborated with those by Ramanaiah et al. [143] fungal biosorbent of *Pleurotus ostreatus* 1804. However, other researchers have shown that the F biosorption potential of *Saccharomyces* sp. biomass reached 91% of F removal [144]. Similarly, *Aspergillus* and Calcium treated *Aspergillus* biosorbents revealed

F adsorption capacities of 8.09 mg/g [145]. Differences in the capacity of various biomasses to sequestrate F from water are related to, among other factors, differences in active functional groups in the biomasses [134].

Thus, even though Mukkanti and Tembhurkar [146] have recently reported a high F adsorption capacity of 26.31 mg/g for an adsorbent developed from clamshell waste, it is apparent that the usual water defluoridation capacities of untreated biomasses are low when compared to the other adsorbents [90, 118]. Furthermore, the source biota for the prized F biosorbents may be non-existent in the regions where they are needed for easy defluoridation of water. Plus, untreated biomasses degrade easily under chemical and biological attacks.

5.7 Layer double hydroxides

Layered double hydroxides (LDHs), also called anionic clay and hydrotalcite-like compounds, are a "host-guest" layered materials, which have the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-}_{x/n}).mH_2O$, where M^{2+} and M^{3+} are metal cations that occupy octahedral positions in hydroxide layers; x is the molar ratio $M^{3+}/(M^{2+} + M^{3+})$ and A denotes interlayer charge-compensating anions [147]. LDHs have attracted a lot of attention as F adsorbents in the recent past. Lu et al. [148] assessed F removal based on NiAl layered double hydroxides (NiAl-LDHs) and reported a low equilibrium F concentration of just 0.2388 mg/L in the treated water. Sadik et al. [149] also reported high F removal rates of 99.2% for calcined LDHs synthesized from seawater (LDHsw). New data have provided the maximum F adsorption capacity of 6.67 mg/g for $Fe_3O_4/Al(OH)_3$ [150] and 12.63 mg/g for tri-metal Mg/Ce/Mn oxide-modified diatomaceous matrix [151]. However, the mechanism of F adsorption onto an LDH and calcined layered double hydroxide (CLDH) had been earlier evaluated with maximum defluoridation capacities of 1.3 mg/g and 20 mg/g, respectively [152]. The F sorption quantities were somehow similar to the 22.78 mg/g and 20.28 mg/g that have recently been reported for Ce-Ti and Ce-Ti/Fe3O4 hybrid oxides, respectively [153].

However, several studies have reported enhanced defluoridation capacities for LDHs. In a study involving calcined Mg–Al–CO_3 LDHs, for example, competitive F adsorption was evaluated and water defluoridation capacity of 1.94 mmol/g was reported [154]. Then, Kang et al. [155] reported water defluoridation capacity of 50.91 mg/g for Mg/Fe l CLDHs. Furthermore, other studies have documented a high F adsorption capacity of 146.6 mg/g for Ca-Al LDHs [156] and 270.3 mg/g for Fe–Mg–La triple-metal hydroxide composite [157]. Consequently, other authors have focused on the optimization of defluoridation conditions for LDHs. Elhalil et al. [158], as such, while evaluating showed that optimum adsorbent dosages of water defluoridation using calcined Mg/Al LDH were in the range of 0.29–0.8 g/L. Also, the suggested F adsorption equilibrium time [149, 156] and solution acidity [149, 155] of LDHs are within 1 h and pH 6–7, respectively.

6. Phytoremediation

This is a technique of defluoridation and removal of other contaminants from the environment, which uses plants to absorb and accumulate excess F from soil and water through their roots into their systems. The plants are then removed at the predetermined time and disposed of safely. Several researchers evaluated technology phytoremediation with varying degrees of success. The tolerance capacity of *Solanum*

tuberosum to accumulate F, has been tested and found that after 87 days, the F levels in the leaves, root, shoot, and potato tuber of the plants had increased to 3.96, 3.02, 2.8, and 1.56 mg, respectively [159]. Some researchers also tested the uptake of Al and F by four green algae species and found that *Pseudokirchneriella subcapitata* showed the highest aluminum and fluoride absorption under the test conditions [160]. Sirisha et al. [161] studied phytoremediation of Cr and F in industrial wastewater using the aquatic plant *ipomoea aquatica plant*. They found that the F removal rapidly reached 37% in just 10 min and similar results have been found by researchers in related tests [162] indicating that phytoremediation id a promising green technology for use in environmental fluoride remediation [163].

7. Conclusions

The current work, which was based on a systematic collection of literature data aimed at providing, in a concise and precise manner, an update on the techniques employed to combat the detrimental effects of human overexposure to F so as to focus the attention of stakeholders to the direction of science in the field of F mitigation in the world. From the foregoing discussions covered in this paper, the following conclusions are made:

i. Water defluoridation techniques applied to the world-over can be classified broadly as chemical, physical, membrane-based, or adsorptive.

ii. The different defluoridation protocols differ in applicability and feasibility, depending on the desired levels of water defluoridation and resource availability.

iii. Adsorptive methods appear to present greater prospects in water defluoridatiore because they are simple, efficient, and cost-effective.

iv. LDH's and soil adsorbents are the most studied adsorbents for water defluoridation, but the latter has a competitive edge over the former as they are readily available, easier to prepare and use, and more environmentally convenient.

v. The efficacy of other adsorbents, such as activated carbons, is greatly controlled by the mode of adsorbent preparation and the adsorbent particle sizes.

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