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Fluoride Sources, Toxicity and Fluorosis Management Techniques - A Brief Review

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Abstract

Fluoride contamination in drinking water is a global issue. Frequent over-exposure to fluoride causes several health problems such as fluorosis, neurological, thyroid, osteoporosis, etc. The guideline values prescribed by the WHO and other nationals for fluoride in drinking water are reasonable but mostly relevant to fluorosis. However, these guideline values cannot be satisfied in some regions due to economic and financial shortcomings. Several fluorosis management techniques were suggested to address excess fluoride in drinking water, but each has specific drawbacks. Defluoridation techniques like the Nalgonda technique, reverse osmosis (RO), and adsorption using activated alumina have found to be promising to reduce fluoride concentration within the prescribed limits, and RO water is most widely used for drinking in fluorosis affected regions. However, these techniques are still associated with certain drawbacks, and prior research on this theme has focused on one dimension of removing excess fluoride from water. Hence, it is essential to understand the basic problems associated with fluoride contamination, such as sources of fluoride exposure, adverse health effects and defluoridation techniques feasibility. Furthermore, perception of the effect of co-existing ions with fluoride in drinking water is crucial in deciding fluoride toxicity level and developing efficient strategies for fluorosis mitigation.

Keywords: Drinking water scarcity; Fluoride contamination; Health Effects; Fluorosis; Fluoride removal

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1. Introduction

Clean and safe drinking water is quintessential to lead a healthy life. Several regions across the globe do not have access to safe drinking water because of certain geographical disadvantages, economic and financial drawbacks. Areas with poor water quality lead to a serious social and health problems. Because of this, the developing and underdeveloped countries are unable to meet certain drinking water standards set by the regulatory boards and supplying safe drinking water is considered as a priority in several countries (Ali et al., 2019; Onipe et al., 2020; Poonia et al., 2021). As per the World Health Organization (WHO), approximately 783 million people are out of reach of basic drinking water service, and it is expected that over half of the world's population will face a shortage of potable drinking water by 2025 (Lacson et al., 2021). Groundwater counts up to the major part of the freshwater, which is usable and potable by both humans and animals due to its superior microbial activity than surface water. Nonetheless, various chemical elements and compounds have increased in concentration and contaminated the groundwater due to various geological activities. Besides, illegal disposal of wastewater from urban, industrial, and agricultural activities chemically contaminates the only water source in these regions. These contaminated water bodies not only affect humans but also destroy aquatic life (Pearcy et al., 2015; Zhang et al., 2016b). Waterborne diseases caused by drinking contaminated water contributes to a measurable and significant burden on human health which has a significant economic impact on society; hence, efforts to improve the drinking water quality would provide significant benefits to health (WHO, 2017). Among the several chemical contaminants, excess concentration of nitrate, arsenic, and fluoride (F^-) ions are found to show harmful health effects to living organisms.

Public health concerns are centered towards the presence of excess F^- in drinking water (for > 1.5 mg F^-/L) and shown several adverse health effects to human beings that sought considerable attention from research community (Ayoob and Gupta, 2006; Grandjean, 2019; Agalakova and Nadei, 2020; Chlubek and Sikora, 2020; Johnston and Strobel, 2020; Kumar et al., 2020; Mondal and Chattopadhyay, 2020; Onipe et al., 2020; Skórka-Majewicz et al., 2020; Wimalawansa, 2020; Vandana et al., 2021; Li et al., 2021). A group of diseases termed as 'fluorosis' is a common sight for those who regularly consume drinking water with excess fluoride. The extent of fluorosis depends on the concentration of F^- ingested, as it can vary from dental fluorosis (1.5 - 4.0 mg F^-/L) to crippling fluorosis (> 10 mg F^-/L) (Meenakshi and Maheshwari, 2006; Mohapatra et al., 2009; Ali et al., 2019; Lacson et al., 2021). The occurrence of F^- ions in drinking water is predominantly geogenic, i.e., groundwater in some areas contains a high amount of F^- due to various natural sources present in specific geographic locations (Chowdhury et al., 2019). Fluoride naturally occurs as fluorapatite ($Ca_5(PO_4)_3F$), sellaite (MgF_2), fluorite (CaF_2), and cryolite (Na_2AlF_6) formed in the sedimentary and igneous-type rocks (Jha et al., 2011). To limit the overexposure to F^- via drinking water, few countries have prescribed F^- limits in their drinking water along with the WHO (Table 1) and found that most of the prescribed limits are in the range of 1 - 1.5 mg/L. However, it is worth mentioning that all these fluoride limits are mostly prescribed with respect to fluorosis disease, and other F^- associated problems were mostly ignored. It is known that there is no accurate analysis to point out how many people are being affected by fluoride contamination; however, it is presently estimated that about 200 million people across the globe are at high risk from crippling fluorosis (Kabir et al., 2020). Some regions in India, China, South Africa, and Bangladesh suffer from endemic fluorosis (Chaudhary and Prasad, 2015). Understanding the level of F^- toxicity and its manifestation on human health is beneficial for resolving this global issue (Susheela and Toteja, 2018; Johnston and Strobel, 2020; Maheshwari et al., 2021). The purpose of this article is to concisely discuss various issues associated with F^- contamination in drinking water, the possible routes of F^- exposure, its toxic effects and fluorosis management techniques with respect to their feasibility for implementation. Although many review articles are published on several of these topics in one dimension, there is a necessity for a complete picture that concisely discusses a compilation of all aspects related to this theme. Therefore, the authors aim to discuss various aspects related to fluoride, such as its sources, health effects on humans, co-existing ions on its toxicity, and management techniques. Further, these discussions provide vital information to several researchers, industrialists, and other concerned groups working on this theme to develop efficient and sustainable methods to overcome the problem of consuming excess F^- via drinking water, which prevents fluorosis-induced deformity and also it can assist in reversing the fluorosis.

2. Various Sources of Fluoride Exposure

It was thought that F^- exposure to humans was only through drinking water, but various studies suggest otherwise (Chowdhury et al., 2019; Kumar et al., 2020). Fluoride can enter the body through food, cosmetic products, and aerosols as well (Maity et al., 2021). Indeed, most cases reported on over-exposure of F^- to humans is via drinking water (Abouleish, 2016; Jagtap et al., 2012). Approximately 75-90 % of F^- exposure to the human body occurs via the consumption of drinking water containing an excess level of F^- (Fawell et al., 2006; Meenakshi and Maheshwari, 2006). The second possible exposure route is the type of food consumed. Minute amounts of F^- is present in beverages, vegetables, and food-grains has grown on agricultural lands (Kabir et al., 2020). Table 2 shows some of the foodstuffs having high amounts of fluoride concentration. These foodstuffs are grown in soil and adsorb fluoride readily. It also depends on the F^- concentration present in the soil, fertilizers, pesticides, and water used to cultivate these products. Industrial effluents containing relatively high F^- concentration can leach into groundwater, get absorbed by the soil and contribute to high F^- in the surrounding regions. In this manner, F^- can be adsorbed by vegetables and plants in agricultural fields. Interestingly, tea is also a source of F^- and can contribute to a certain amount of F^- exposure to humans (Zhang et al., 2016a; Peng et al., 2021). Fluorosis occurring due to consumption of tea is majorly reported in some parts of China (He et al., 2020). Further Viswanathan (2018) argued that dietary supplements for infants expose them to a high amount of fluoride in addition to their regular diet. He suggested that care should be taken on selecting the right dietary supplements for infants and children as it is a crucial stage for the healthy development of the bones and brain. Fluoride can be exposed through the air as well, according to some reports (Weinstein and McCune, 1971; Jayarathne et al., 2014); however, the lethality is relatively less. Industrial and agricultural workers are prone to F^- exposure through this route. Further, excessive coal burning also increases the chance of fluorosis (He et al., 2020). Researchers argue that the occurrence of F^- in this way cannot cause much damage to humans as F^- is not present in an ionized form which makes it less reactive (Jha et al., 2011). Fluorosis due to dental products, say, toothpaste and mouth rinses, have been rarely reported, considering appropriate use of the products and not accidental swallowing. Regular and proper use of these products does not cause fluorosis associated diseases. A few decades ago, pesticides and fertilizers were considered as means of F^- exposure to humans as they contained high amounts of F^- (Patil et al., 2018; Dey Bhowmik and Chattopadhyay, 2019; Gan et al., 2021). Presently, these products are banned and currently do not account for F^- exposure to humans Kabir et al. (2020). Intake of F^- via drinking water is the most significant contributor among all the sources to the total daily F^- intake. Therefore, it is worth mentioning that F^- present in drinking water is the primary cause for adverse health effects compared to other sources of exposure.

3. Divergent Health Effects on Humans

Ingestion of F^- induces various health effects, and it is regarded as that of a "double-edged sword" as F^- ingestion results in beneficial as well as detrimental health effects on human. Consuming water with F^- concentration between 0.5 and 1 mg/L is said to have therapeutic effects on teeth and bones since it reduces dental caries by remineralization (Zhang et al., 2020). It also plays an important role in fertility maintenance, activation of certain enzymes and production of blood cells (Skórka-Majewicz et al., 2020). However, it is known that excess intake of F^- leads to a group of diseases called fluorosis. There are several extents of fluorosis which appear based on the concentration and frequency of F^- ingested. Fluorosis occurring in the teeth is called dental fluorosis. It occurs when drinking water has F^- concentration of more than 1.5 mg/L. The excess F^- in the teeth reduces the protease activity resulting in unusual deformation of the enamel structure. This is caused due to the decay of dental pulp cells: ameloblasts and odontoblasts. This process results in discolouration and formation of irregular lesions on the surface of the teeth (Mondal and Chattopadhyay, 2020; Vandana et al., 2021). Dental fluorosis is more susceptible to kids. The extent of exposure to F^- from childbirth until the age of 8-10 years old is crucial in determining the severity of dental fluorosis (Kabir et al., 2020). Approximately 70 % of the adolescents in India have been injured by dental fluorosis due to intake of drinking water which had F^- concentration > 1.5 mg/L (Chaudhry et al., 2017; Reddy et al., 2017). The abnormality once caused is irreversible. However, dental fluorosis caused by the consumption of F^- contaminated drinking water after adulthood is unlikely, and even if found, the extent is less. Long term exposure to a relatively high level of F^- (4 mg/L) causes another popular type of fluorosis called skeletal fluorosis. This is because excess F^- uptake over a long period gets deposited in the bones resulting in increased bone density. Excess bone growth may occur in various parts of the body leading to osteoporosis, paralysis, and neurological disorders (Srivastava and Flora, 2020). People developing skeletal fluorosis experience muscle weakness, tingling sensation in the limbs, back stiffness, unusual deposits of ligaments, and change in bone structure. Advanced levels of skeletal fluorosis lead to crippling fluorosis for > 10 mg/L. Crippling fluorosis presents itself with other organ disorders such as renal, hepatic, and neuronal. This type of fluorosis has been observed in some regions of India, China, and South Africa (Rasool et al., 2018). Ingestion of F^- contaminated drinking water also causes gastrointestinal effects such as diarrhoea, vomiting, nausea, and abdominal pain. The ingested F^- converts into hydrofluoric acid (HF) due to high acid levels in the stomach. Later, the disassociation of H^+ and F^- ions disrupt enzymatic activity and intracellular pH of the cells. The generation of HF in the stomach damages the stomach lining due to variations in pH. Nonetheless, it is argued that gastrointestinal issues mainly depend upon aqueous stomach F^- level and not on the amount and regularity of F^- exposure (Doull et al., 2006). Kidney stones have been reported in some places due to consumption of high F^- contaminated drinking water (Ahada and Suthar, 2019). One of the most controversial effects of F^- intake is the damage it causes to the brain. It has been established that it reduces the intelligent quotient (IQ) and growth hormone production of school-aged children. In fact, several studies have been conducted to assess the seriousness of F^- exposure and resulting brain functions in children (Grandjean, 2019; Agalakova and Nadei, 2020; Chlubek and Sikora, 2020; Johnston and Strobel, 2020; Skórka-Majewicz et al., 2020; Mondal and Chattopadhyay, 2020; Onipe et al., 2020). A few studies showed that high F^- intake might decrease testosterone production and follicle-stimulating hormones (Susheela and Jethanandani, 1996; Ortiz-Pérez et al., 2003; Skórka-Majewicz et al., 2020). However, these correlations require in-depth study to conclude if they truly have adverse effects on reproductive health. Major adverse health effects on human beings due to ingestion of excess fluoride via drinking water are presented in Figure 1. From the above-adduced facts, it is clear that the demerits of F^- consumption outweigh the merits.

Severe effects of fluoride on human health can be seen majorly in developing and underdeveloped countries. Among these countries, India is the most affected country, where there are many endemic fluorosis regions. India also has one of the largest fluorite deposits making its groundwater highly contaminated with fluoride. Most of the regions in Asia and Africa are prone to fluorosis-based diseases. In Asia, India and China show the majority of cases. Whereas in n the African continent, Tanzania is a popular region with a high concentration of fluoride in groundwater where it is a major source of drinking water (Shen et al., 2015; Ali et al., 2016). The Ethiopian rift valley has about 8 million people regularly over-exposed to natural fluoride present in groundwater (Rango et al., 2012; Demelash et al., 2019), while the East African rift valley has about ten times of that amount of people suffering from various fluorosis-related symptoms (Shen et al., 2015). China has approximately 21 million people affected with fluorosis and close to 10 million people suffering from skeletal fluorosis (Li et al., 2020). Fluorosis has affected around 3000 villages in China, most of which are located in arid and semi-arid island basins. Some of the major reasons for fluorosis cases are high fluoride contaminated groundwater, excess coal burning, and brick tea (Kimambo et al., 2019). In Mexico, approximately 20 million people consume water with 1.5 mg/L of fluoride and around 9,00,000 are exposed to even higher (4.5 - 29.6 mg/L) concentration of fluoride (Alarcón-Herrera et al., 2020). Argentina, in the south American continent, is the most affected where the La Pampa region has fluoride concentrations as high as 25.7 mg/L in groundwater (Smedley et al., 2002; Ali et al., 2016; Alcaine et al., 2020). Some of the European regions such as Spain and Norway have reported excess fluoride in their groundwaters, and cases of fluorosis related disorders are not severe (Kimambo et al., 2019). It is said that water fluoridation is practised in some countries in Europe due to the lack of natural fluoride; however, it is considered as controversial public health intervention, and its benefits and harms have been debated since its proposal (Peckham and Awofeso, 2014). In the USA, some regions of Arizona have reported fluoride concentrations > 4 mg/L in deep wells (McMahon et al., 2020).

4. Correlation Between Fluoride and Coexisting Ions in Drinking Water

Groundwater is the primary source of drinking water in most of the fluorosis affected regions that imply that the cause of excess F^- in drinking water is a case of geogenic contamination. However, the recent studies reported that a significant amount of F^- in groundwater is also contributed by anthropogenic activities such as applying phosphate fertilizers containing a higher amount of F^- in agricultural fields (Kim et al., 2011; Biglari et al., 2016; Chowdhury et al., 2019). Geogenic contamination of F^- is caused by the leaching and weathering of F^--bearing minerals; hornblende ($Ca_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH,F)_2$) and biotite ($K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$) are the most common F^--bearing minerals (Biglari et al., 2016). Interaction of these F^--bearing minerals with groundwater for longer duration results in contamination (Jagadeshan et al., 2015; Biglari et al., 2016). Hence, it is vital in most cases to assess the correlation between F^- and its co-existing ions such as Na^+, K^+, HCO_3^-, Ca^{2+}, and Mg^{2+} (Alhassan et al., 2020). Studies reported that F^- has a strong positive correlation with Na^+, K^+ and HCO_3^- ions, and pH (Kundu et al., 2001; Kim et al., 2011; Jabal et al., 2014); whereas a negative correlation was reported for F^- with Ca^{2+} and Mg^{2+} ions (Kundu et al., 2001; Xu et al., 2013; Jabal et al., 2014). However, dissolution of F^--bearing minerals should produce a positive correlation of F^- with Ca^{2+} and Mg^{2+}, which is contrary to the reported correlation. The observed negative correlation of F^- with Ca^{2+} and Mg^{2+} cations may be due to the reverse ion exchange process, i.e., the exchange of Na^+ present in an aquifer mineral with Ca^{2+} and Mg^{2+} cations from the groundwater (Narsimha and Sudarshan, 2017). Thus, the higher concentration of Na^+ in fluoride-contaminated groundwater can be attributed to the reverse ion exchange process. The reported negative correlation of F^- ion with Ca^{2+} and Mg^{2+} ions implies that wherever the concentration of F^- is relatively high in groundwater, the concentrations of Ca^{2+} and Mg^{2+} ions are low. Thus, it may be worth highlighting here that drinking groundwater with excess F^- would lead to a deficiency of calcium and magnesium minerals in the body.

On the other hand, supplying adequate amounts of Ca^{2+} and Mg^{2+} ions in drinking water that has excess F^- reduced the toxic effects of F^- (Teotia et al., 1998). Fluoride ion having a negative charge and being a highly electronegative anion; it has a high tendency to form complexes with positively charged ions such as Ca^{2+} and Mg^{2+}. Thus, F^- easily gets attracted by Ca^{2+} and Mg^{2+} to form their complexes, which further reduces the bioavailability of F^- when ingested. Due to this, when the concentration of F^- exceeds the desirable limit of 1 mg/L, the toxic effects of F^- may not be severe since the presence of any calcium and magnesium ions minimize the F^- absorption in the body. Albeit, the epidemiological studies by Susheela (2002) and MacDonald et al. (2011) reported the presence of fluorosis even below the desirable limit. This suggests that the reported findings are contrary to the regulatory boards' drinking water standards. In addition to this, it is reported that people with deficiencies in calcium, magnesium, and/or vitamin C are susceptible to the toxic fluoride effects (Dhar et al., 2009). Hence, the drinking water standard prescribed for F^- concentration may need revision by considering the water quality parameters, particularly Ca^{2+} and Mg^{2+} concentrations. Thus, it may be worth mentioning here that the concentrations of Ca^{2+} and Mg^{2+} ions play a significant role in deciding the toxicity level of F^- in drinking water. Further, supplying potable water with F^- concentration below the desirable limit and enhancing the intake of calcium and magnesium minerals protects against the toxic effects of F^-, which can be considered a cost-effective measure for the prevention and control of fluorosis (Sankannavar and Chaudhari, 2019; Khare et al., 2019). In support of this approach, a recent study reported that a low level of calcium in the presence of F^- aggravated fluorosis in rats. The authors counteracted the toxicity of F^- by supplying calcium and F^--free water to the rats (Shankar et al., 2021).

5. Fluorosis Management in Fluoride Affected Areas

Various fluorosis management techniques employed to supply drinking water affected regions are presented in Figure 2 with their schematic representations along with their respective advantages and disadvantages. The literature suggests that interventions for fluorosis management are primarily based on either providing fluoride-free drinking water or defluoridated drinking water with acceptable F^- concentration to the affected population, and these techniques are briefly explained below.

5.1. *Fluoride-free drinking water*

Supplying potable surface water to fluorosis affected rural areas is more complicated since it involves several problems such as technical, administrative, and financial issues. In addition, considerable assistance is required from the community, which is a time-consuming and burdensome option. On the contrary, rainwater harvesting is adopted as an alternate source for drinking water in several fluorosis affected areas (Anjaneyulu et al., 2012; Perera et al., 2013; Marwa et al., 2018; Ndé-Tchoupé et al., 2019; Onipe et al., 2020). Consumers have experienced relief from skeletal fluorosis after drinking harvested rainwater. Despite this, consuming rainwater has its own concerns, such as it requires ample space for harvesting and storing water, frequent cleaning of the roof-like surface, and it is prone to microbial contamination (Gispert et al., 2018). In addition to this, stored rainwater may not be available for the whole year due to seasonal changes; in such cases, the amount of drinking water can be enhanced by water blending, i.e., mixing rainwater with the F^- contaminated water, thereby reducing the F^- level in the drinking water (Ndé-Tchoupé et al., 2019). Further, it is worth mentioning that rainwater is deficient in minerals like Na^+, K^+, Ca^{2+}, and Mg^{2+}. This may be a challenging problem that must be addressed for effective utilization of rainwater for drinking purpose. This suggests that providing alternative sources for drinking water is not feasible, and hence the use of specific processes for the removal of excess fluoride from drinking water, i.e., defluoridation becomes essential.

5.2. *Defluoridation techniques*

Among the defluoridation methods developed to overcome the problem of excess F^- in drinking water, the Nalgonda technique, the use of activated alumina, and reverse osmosis are very well employed to bring down the F^- concentration within the desirable limit. Although these defluoridation methods can successfully remove excess F^- and reduce it well below the acceptable limit, these methods are not feasible in the actual fields due to several drawbacks. For example, the Nalgonda technique is based on a precipitation process that requires careful monitoring of residual alkalinity and concentrations of Al^{3+} and SO_4^{2-} ions in defluoridated water, which exceed desirable limits (Meenakshi and Maheshwari, 2006). Similarly, using activated alumina for defluoridation, residual aluminium concentration in treated water exceeds its permissible limit (Shreyas et al., 2013). Besides, this technique requires either periodic regeneration or disposal of spent alumina. More concerning issue of using defluoridation methods based on aluminium materials is that presence of any residual aluminium along with F^- in treated water forms fluoroalumino complexes (AlF_x) due to the strong affinity of Al^{3+} for F^-. These Al-F complexes are known to enhance the accumulation of both F^- and Al^{3+}, and cause neurotoxic health effects (Wasana et al., 2015). This suggests that adopting a defluoridation method based on Al^{3+} materials may pose additional adverse health effects on the consumers that may worsen compared to the presence of F^- alone in drinking water. To overcome drawbacks associated with alumina and its derivatives, several other materials for F^- removal are proposed in the literature (Bhatnagar et al., 2011), and these materials are based on the adsorption technique. This adsorption process is reported to have higher removal capacities compared to the Nalgonda technique. Further, the adsorption technique is also economically feasible and easy to operate. However, reports published on field studies are limited. However, this technique produces excess sludge, which has to be disposed of or regenerated (Bhatnagar et al., 2011; Shreyas et al., 2013). But disposing of spent adsorbents causes more harm to the environment as it contains dangerously high amounts of fluoride. Thus exploring environmentally safe routes for sludge disposal or using this F^{-}-bearing sludge for alternate use needs to be considered while evaluating an adsorption technique for defluoridation of drinking water. In addition, this methodology is also pH and temperature-sensitive (Alkurdi et al., 2019; Alhassan et al., 2020; Hegde et al., 2020). The ion-exchange process is another high-performance (95 %) defluoridation technique that uses ion-exchange resin for the removal of F^{-}. This technique is not extensively employed since the demerits outweigh merits *viz.* highly expensive and cannot be implemented in remote areas. The membrane-based techniques: reverse osmosis and nanofiltration, face the same issue. Despite this, these techniques are considered the most efficient among all due to their ease of operation, quality of treated water and high durability. However, because of their prohibitive set-up cost, removal of essential minerals and difficulty in managing brine/retentate, they are not a popular choice (Damtie et al., 2019). Similarly, electrocoagulation and electrodialysis are electrochemical-based techniques that are considered highly desirable. The electrodialysis technique is not only used for fluoride removal but also for other contaminants from aqueous media. A major disadvantage of this technique is that a high amount of electricity is required for its operation (Haldar and Gupta, 2020), which is not easily available in several underdeveloped and developing regions. The electrocoagulation process, similar to the Nalgonda technique, produces aluminium complexes after its operation and problem associated with sludge disposal exists.

From the above-adduced facts, there is a necessity to develop a fluorosis management technique that is technically and economically feasible to implement in the affected areas. Particularly, the fluorosis technique would be implemented that should at least selectively remove excess F^- from drinking water without compromising with other water quality parameters. In this direction, a few of the defluoridation techniques, those based on non-toxic elements such as calcium and magnesium, have found to be potential techniques and shown promising defluoridation capacities (Islam and Patel, 2007; Pemmaraju and Rao, 2011; MacDonald et al., 2011; Mourabet et al., 2012; Khare et al., 2019; Sankannavar and Chaudhari, 2019). However, the safe disposal of resulting F^--bearing materials is another problem that demands research.

6. Future Research Directions

Although the problem of fluoride and fluorosis is quite old, limited efforts are made in the fields to mitigate fluorosis. This suggests that the problem of fluorosis due to intake of excess F^- via drinking water is still persisted; thus, there is a need to develop an effective defluoridation technique in which only excess F^- can be removed from drinking water without disturbing the drinking water quality. The existing conventional defluoridation technologies are only based on a laboratory scale. Therefore, the reported fluoride removal capacities mostly do not replicate that of the field studies unless laboratory experiments are conducted with actual field water. Further, it may be noted that drinking defluoridated water with fluoride within the acceptable limit can only prevent further fluorosis, thus removing only excess fluoride from drinking water maynot help the already affected fluorosis patients. Hence, it would be necessary to eliminate already-ingested fluoride from fluorosis affected patients. This may be achieved by supplying fluoride-treated alkaline drinking water enriched with calcium and magnesium minerals. This would reduce the absorption of fluoride ions, and it will also assist in reversing the already absorbed fluoride in the body. There are also few to none published reports on hybrid treatment techniques for defluoridation. Further research should focus on integrating two or more techniques for treating fluoride-contaminated drinking water to improve the water quality for practical usage towards fluorosis mitigation.

In addition, a significant percentage of the people living in underdeveloped countries are not aware of the risks of drinking fluoride-contaminated water. Also, there is not much support and awareness from the local governments on these topics. The government needs to recommend strict guidelines on the endemic fluorosis regions and implement in-house treatment tanks for defluoridation. We also observed that there was no quantifiable data on groundwater fluoride levels in several areas regions in Russia, Australia, North Korea, etc. Although these regions might not be prone to fluorosis, sufficient data should be provided to the government. The effect of co-existing ions with fluoride is not very thoroughly explored, as observed from the literature. Some of the co-ions (Ca^{2+} and Mg^{2+}) have positive effects on defluoridation capacity. Although the mechanism behind this is not well established, reports show that the positive dependency of interfering ions can pave the way for future research directions. The economic and technical feasibility of all the defluoridation technologies should be carried after conducting the experiments at actual fields. This has to be followed as fluorosis majorly exists in underdeveloped regions. The economic feasibility analysis will give an idea about the funds needed to set up the treatment plant and whether or not it is practically possible in those regions.

7. Conclusions

Access to fluoride-free water to the majority of the fluorosis affected regions is a tough challenge. The fluoride-contaminated water is affecting lakhs of people, and extensive management techniques are needed for the hour. Application of surface water and rainwater are eco-friendly techniques; however, they are not feasible. Efforts should be made to provide economic and efficient defluoridation techniques. Although several techniques exist, they have their own shortcomings. To address the limitations of defluoridation techniques, hybridization of two or more techniques is necessary, thereby making the fluoride removal process more effective. Most of the data in the literature does not involve the management of post-treatment fluoride-bearing sludge disposal and the recovery or reuse of spent materials and examining whether the defluoridated water is fit to drink. This opens up a new domain of problems that needs an immediate address. Thus, future research should focus on the practicality of the proposed technique in a detailed manner towards fluorosis mitigation.

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608 **Tables**

Table 1: List of countries with their limit of fluoride concentration in drinking water, adopted from Lacson et al. (2021).

Country	Fluoride concentration (mg/L)
Australia	1.5
China	1.0
India	1.5
Italy	1.5
Malawi	6.0
Mexico	< 1.5
Mongolia	0.7-1.5
Nepal	0.5-1.5
Pakistan	≤ 1.5
Poland	< 1.5
Singapore	1.0
Vietnam	1.5

Table 2: Some examples of food stuffs having fairly high fluoride concentrations, adopted from Yadav et al. (2019).

Food stuff	Fluoride concentration (ppm)
Cow milk	1.73-6.87
Buffalo milk	3.32-6.85
Fermented milk products	1.76-93.68
Wheat	0.51-14.03
Rice	0.51-5.52
Maize	5.6
Bajra	2.76-3.84
Soybean	4.0
Peas	10.77
Red gram	2.34-4.84
Bengal gram	3.84-4.84
Grape	0.84-1.74
Apple	1.05-2.20
Spinach	9.87-29.15
Cabbage	4.25-11.30
Lettuce	5.7
Green tea leaf	72.62-89.02

609 **Figure Captions**

Figure 1. Adverse health effects on human beings due to ingestion of excess fluoride from drinking water.

Figure 2. Various techniques employed to provide fluoride-free drinking water with their advantages and disadvantages.

610 **Figures**

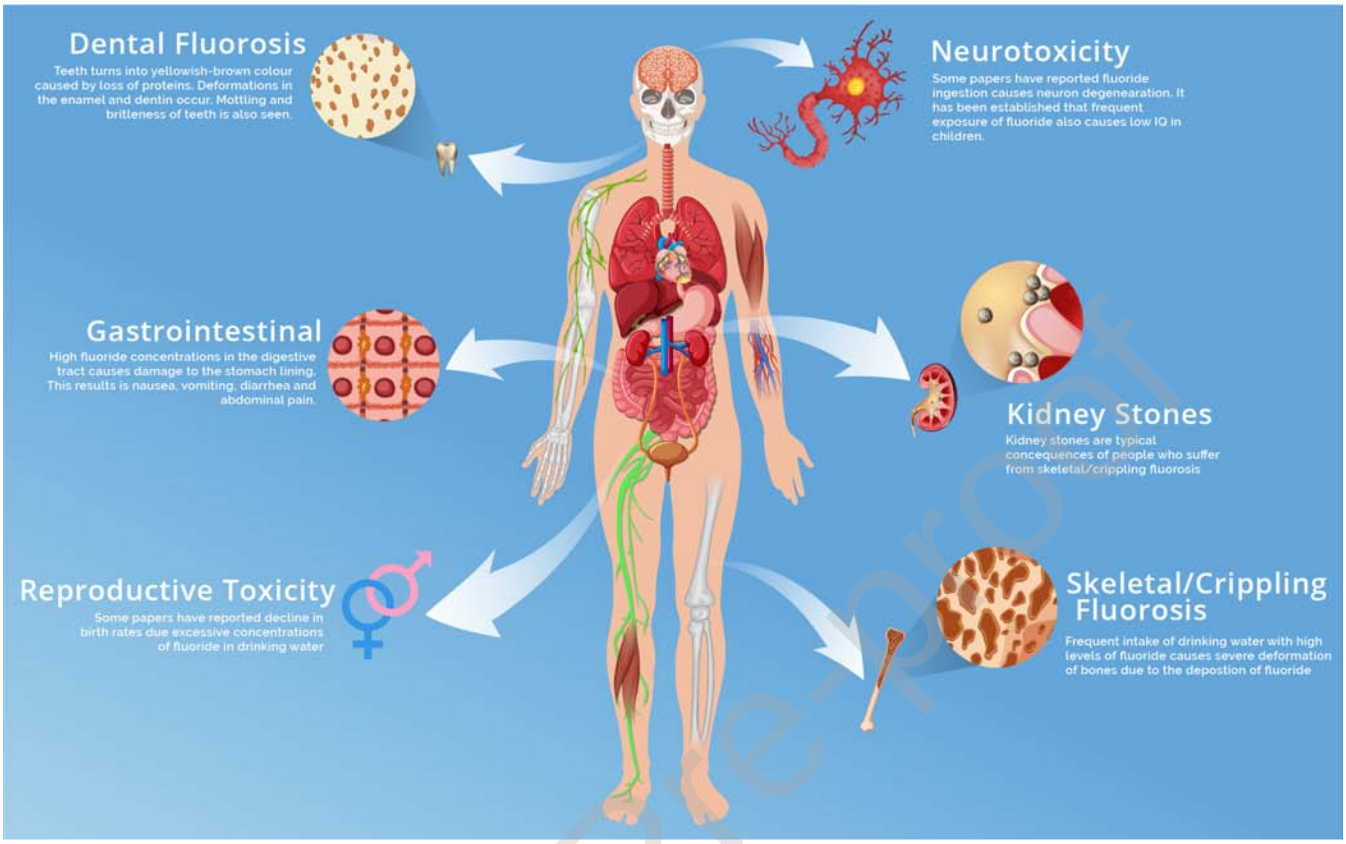


Figure 1: Adverse health effects on human beings due to ingestion of excess fluoride from drinking water.

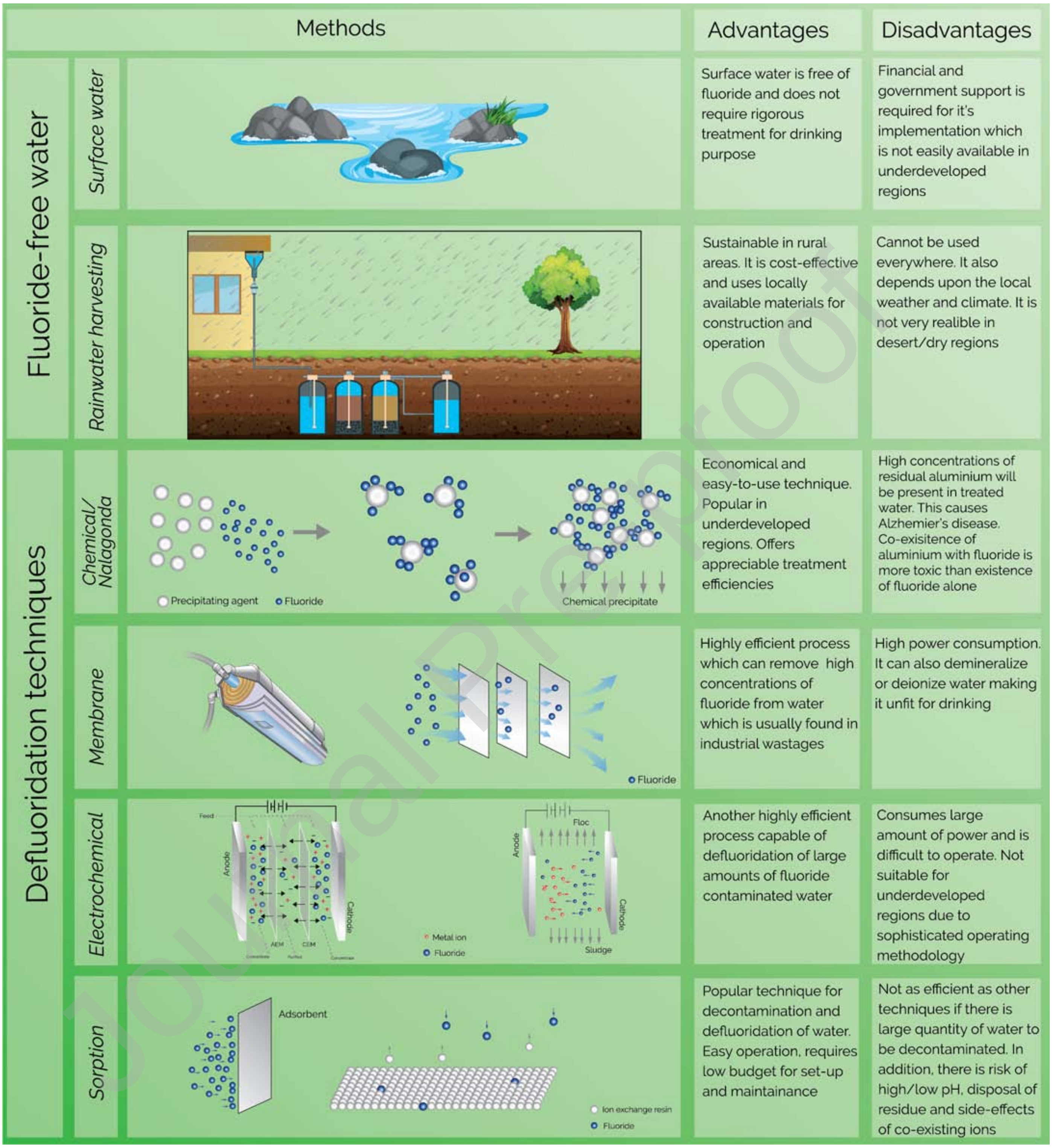
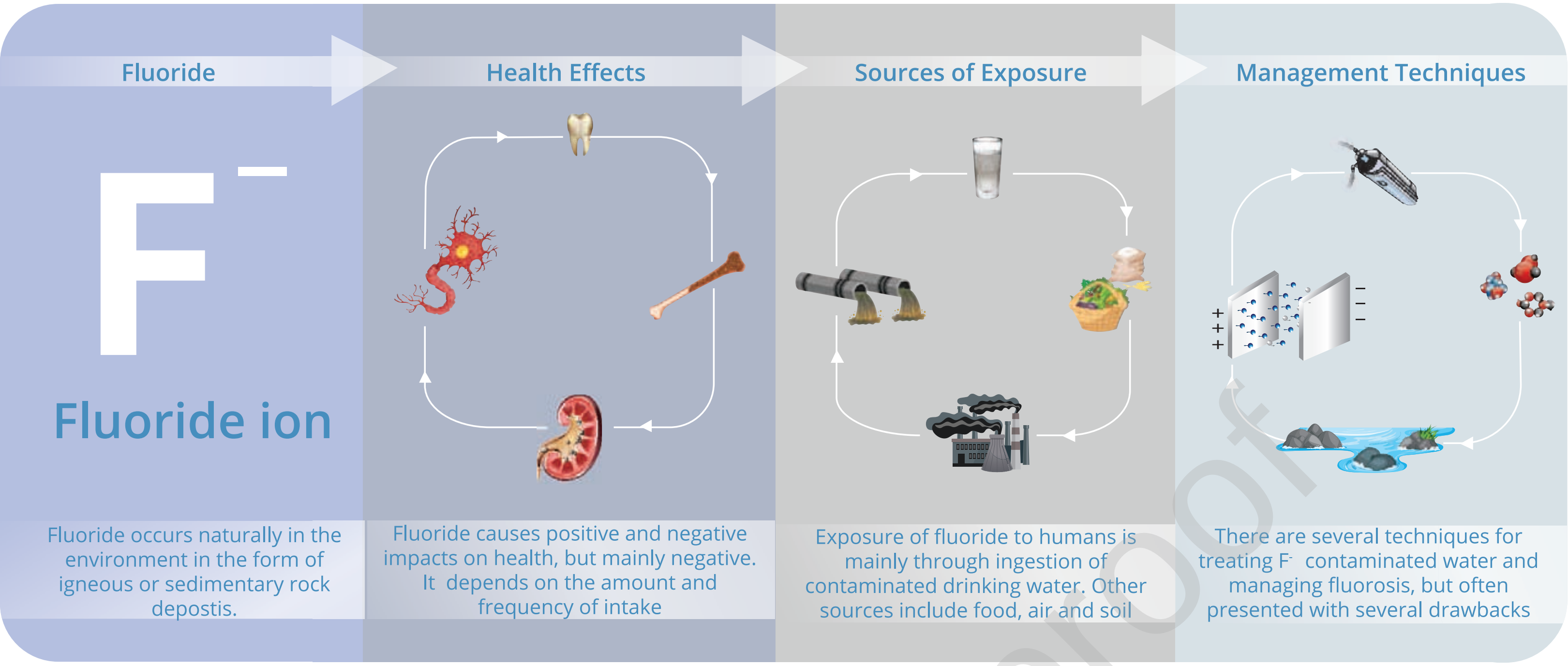


Figure 2: Various techniques employed to provide fluoride-free drinking water with their advantages and disadvantages.

Highlights

- Overexposure to fluoride via drinking water causes several health effects including fluorosis
- Endemic fluorosis is still persisted in several countries even with advancement in research
- Most of fluorosis management techniques suggested in the past have come with their own drawbacks
- Defluoridation techniques based on aluminium materials pose serious health risks to the public
- A method which removes excess F^- from drinking water without affecting water quality has a scope


Fluoride
Health Effects
Sources of Exposure
Management Techniques
F⁻
Fluoride ion
Fluoride occurs naturally in the environment in the form of igneous or sedimentary rock depostis.
Fluoride causes positive and negative impacts on health, but mainly negative. It depends on the amount and frequency of intake
Exposure of fluoride to humans is mainly through ingestion of contaminated drinking water. Other sources include food, air and soil
There are several techniques for treating F⁻ contaminated water and managing fluorosis, but often presented with several drawbacks

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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