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## Fluoride contamination, consequences and removal techniques in water: a review†

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Fluoride contamination has created a drinking water crisis globally. At low concentrations, its presence is essential; however, it becomes toxic to human beings upon consumption of more than 1.5 mg L<sup>-1</sup> in mainly contaminated drinking water due to geochemical reactions and geological or anthropogenic factors. To better understand the toxicity of fluoride, in this study, we examine the recent research on the possible negative consequences of excess fluoride on diverse species. A high fluoride concentration in drinking water cause skeletal fluorosis and long-term kidney, brain, thyroid, and liver damages. This review also focuses on the different techniques for the defluoridation of water, such as electro-coagulation, adsorption, membrane processes, etc., and compares their adsorption capabilities under various situations, while their changes in the literature are reviewed. Furthermore, we present the advantages and disadvantages of different methods and conclude that each technique has shortcomings, with no single approach fitting all aspects. The condition of water pollution with fluoride and recently created technology to remove fluoride from water is evaluated, although research on fluoride contamination of water resources has been reviewed in the literature. Alternatively, this study also examines fluorosis mitigation strategies in the global and Indian settings and existing physicochemical and biological mitigation approaches. Also, the research and development results in fluoride clean-up are reviewed. Specifically, the following topics will be covered in this review: (1) fluoride contamination status, (2) consequences of fluoride contamination in drinking water on human health, and (3) current defluoridation technology.

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### Environmental significance

Fluoride may be beneficial or harmful to human health, depending on its concentration and the amount of fluoride ingested over time. According to the WHO and BIS, the permissible limit of fluoride in drinking water ranges between 1.0 and 1.5 ppm. To date, many defluoridation techniques have been developed, but no one technique has been found to be competent, unassailable, and competitive enough to be widely implemented. An extensive analysis through the archives of defluoridation research indicates that significantly few endorsed sustainable solutions have been developed thus far. On a large scale, fluoride treatment is costly, and thus local governments and communities should focus on being aware and educated to provide satisfactory and reasonable remedial technology.

## 1. Introduction

Drinking water scarcity is now a global challenge in urban and rural areas, where more than 1.5 billion people directly depend on groundwater for drinking purposes worldwide.<sup>1</sup> In the last few years, groundwater has been considered to meet domestic needs and agricultural and industrial requirements, resulting in a drastic change in the chemical composition of underground water.<sup>2</sup> Pollutants originating from various sources can be classed as organic, inorganic, bacteriological, etc., which

enter aquifers, creating a drinking water crisis. The World Health Organization (WHO) considers that fluoride is one water contaminant, adversely affecting human health.<sup>3</sup> Drinking water is measured as the critical fluoride carrier in the human body, where the digestive system absorbs 90% of the fluoride intake through water.<sup>4</sup>

Some rocks such as fluorite, biotite, topaz, fluorapatite, cryolite hornblende, and muscovite contain fluoride-rich minerals, which release fluoride present in them after interacting with water.<sup>5</sup> The fluoride ion concentration available in groundwater is dependent on various factors, which include the physio-chemical condition of the aquifer from where the groundwater is extracted,<sup>6</sup> intensity of rock weathering, depth of water in the aquifer,<sup>7</sup> acidity and porosity of soil and rocks, interaction between different chemical elements, temperature in the surrounding region,<sup>8</sup> mineral composition of rocks, and the geochemistry of the groundwater.<sup>9</sup> In arid and semi-arid

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regions, the concentration of fluoride in the groundwater is maximum. However, most of the world's groundwater is observed to cross the fluoride concentration standard limit, as suggested by the WHO.<sup>10</sup> According to the WHO guideline, the concentration of fluoride in drinking water should be in the range of 0.5 to 1.5 mg L<sup>-1</sup>, which is generally safe.<sup>11</sup> However, the amount may vary between 0.5 to 1.0 mg L<sup>-1</sup> depending on climatic variables such as temperature.<sup>12</sup> Regarding the two climatic conditions, hot and cold climates, the maximum fluoride concentration suggested by the WHO is 1 and 1.5 mg L<sup>-1</sup>, respectively,<sup>13</sup> which accounts for the higher water consumption in the hotter climate than in the colder weather.<sup>14</sup> The national standard limit that meets the maximum fluoride value in drinking water is reported to be 1.0 mg L<sup>-1</sup>. If the fluoride level crosses the limit of 1.0 mg L<sup>-1</sup> by any means, either anthropogenic or geogenic sources, the groundwater will be classified as fluoride-polluted groundwater. In our country, the practical limit for fluoride in drinking water is recognized to be 1 mg L<sup>-1</sup>. However, the concentration range of fluoride in drinking water varies according to different organizations such as the WHO, Bureau of Indian Standards (BIS), Indian Standard Institution (ISI), Indian Council of Medical Research (ICMR), and others, as listed in Table S1.† It has been observed that a large portion of the population globally (mainly >200 million) depends on drinking water with a concentration of fluoride greater than the safe limit described by the WHO, which is 1.5 mg L<sup>-1</sup>. Fish and tea contain a high fluoride content, and hence members of the population eating this food are more prone to fluoride exposure.<sup>15</sup>

Consequently, studying the sustainability of excessive fluoride in groundwater and its hazardous impact on people is critical worldwide. Herein, we aim focus on the severity and seriousness of this issue by analyzing the current studies and presenting information on the exclusive and extraordinary Indian research on the effect of a higher natural concentration of fluoride in groundwater and the public scientifically. Furthermore, we aim to dissect the origins, bioavailability, and geochemistry of fluoride and its worldwide rank, focusing on human health consequences.

## 2. Fluorine: chemical profile

Fluorine (F<sub>2</sub>) is a halogen group member in the periodic table. It is a gas with a corrosive nature and has a characteristic pale, yellow-green colour. It has high reactivity and electronegativity. Fluoride is obtained as a reduced form of fluorine, which is a monovalent ion having a charge of -1, like other halides. It possesses distinct properties in compound form compared to other halides. It resembles hydroxide ions both structurally and chemically. Both the fluoride ion (F<sup>-</sup>) and bi-fluoride ion (HF<sub>2</sub><sup>-</sup>) are obtained as a result of a solution of inorganic fluoride in water.<sup>16</sup> Some inorganic fluorides without insignificant hydrolysis are water-soluble. Due to the smaller radius/charge ratio of fluoride, it has a high solvation effect, and also in comparison to chloride and other halides, fluoride appreciable differs in terms of reactivity. Naked fluoride refers to fluoride ions that are almost relatively unsolved and behave as a solid Lewis base.<sup>17</sup>

For the detection of the fluoride and its compound fluorine-19, nuclear magnetic resonance (<sup>19</sup>F NMR) spectroscopy is used.

## 3. Sources of fluoride

Natural resources and manufactured-generated industrial pollutants are the primary sources of excessive fluoride in the environment. Fluoride is naturally added to ground and surface water by fluoride-rich natural rocks and soil that water interacts with them. Because of the deterioration or leaching of fluoride-bearing rocks during the percolation of water into the earth, groundwater becomes more contaminated than surface water, as shown in Fig. S1.† The rate of evaporation, the length of time water spends in aquifer zones, and intense and long-term irrigation are all variables that influence how much fluoride is added to groundwater. The fluorine concentration in some mineral rocks is shown in Fig. S2.† Fluorine (F<sub>2</sub>) is a greenish diatomic gas, which owing to its highly reactive nature, seldom occurs in its pure gaseous form except in a few industrial operations.<sup>18</sup> The chemical, glass, and ceramic industries, coal power stations, semiconductor manufacturing units, electroplating, brick and iron industries, aluminum smelting facilities, and beryllium extraction operations are some of the sectors that contribute the most fluoride-rich effluent. Fluoride is also introduced into the human body *via* everyday items such as toothpaste, mouthwash, medicines, cosmetics, and chewing gum.

### 3.1 Paths of fluoride uptake

Water, medicines, food, air, and cosmetics products are vulnerable sources of fluoride absorption. Water and other food sources are the most common sources of ingested fluoride.

**3.1.1 Water.** Fluoride is found in water as a fluoride ion and has a concentration of about 625 mg kg<sup>-1</sup> in the crust of Earth. Fluorosis in humans is mainly induced by consuming fluoridated water. Fluoride may be found in various concentrations in all-natural water sources. The geological, chemical and physical properties of aquifers, soil and rock acidity and porosity, temperature of the corresponding areas, the depth of wells, and the impact of other chemicals influence the fluoride concentration in groundwater. The fluoride concentration present in drinking water is minimal, while in seawater, it is approximately 1.3 parts per million (ppm). The range of fluoride in the freshwater supply generally varies between 0.01–0.3 ppm, whereas in the ocean it is in the range of 1.2–1.5 ppm.<sup>19</sup> The solubility of fluoride in water limits its concentration to 3.1 mg L<sup>-1</sup> in the presence of calcium, which has a concentration of 40 ppm. If calcium is not present in the solution, then its higher concentration is also stable. Hence, the groundwater in regions having fluoride-bearing minerals and calcium-poor aquifers is expected to have a higher fluoride concentration. The fluoride concentration is also expected to increase in groundwater where cation exchange of sodium for calcium occurs. On the ground, fluoride-rich bands extend from Syria to Libya, Egypt, Jordan, and Kenya, and from Turkey to China, Northern Thailand, and India.<sup>20</sup> The fluoride concentration in



freshwater sources is shown in Fig. S3† (ppm in percent),<sup>21</sup> and the fluoride concentration in minerals and soils ( $\text{mg L}^{-1}$  in percent) is shown in Fig. S4.†<sup>22</sup>

**3.1.2 Foods and beverages.** Fluoride is found in almost all foods in tiny amounts. The amount of fluoride in food is determined by the soil, water, and fertilizers used for irrigation and agriculture. Compared to water and soil, the effect of fluoride entering the body *via* food and drinks is smaller. Various food items such as wheat, cabbage, tea, carrots, spinach, and some drinks contain fluoride, which enters the human body.<sup>23</sup> The fluoride in these products is most likely due to the use of fluoridated water from the soil or fertilizer for food and beverage production. Tea plants absorb a high content of fluoride, with 97% of it accumulating in their leaves.<sup>24</sup> Tea leaves have a fluoride concentration of about 97% that of the soluble fluoride in the soil, and it also has 2 to 7 times the full amount of fluoride in the soil.<sup>25</sup> The fluoride content in regular strength instant tea in distilled water is 3.3 ppm,<sup>26</sup> which causes dental fluorosis.<sup>25</sup> Tibetan children exhibit dental fluorosis as a result of drinking brick tea, which has a high fluoride content of 493.2–1000  $\text{mg kg}^{-1}$  compared to black tea (23.6–52.1  $\text{mg kg}^{-1}$ ) and green tea (232–240  $\text{mg kg}^{-1}$ ).<sup>27</sup> The fluoride concentration in tea beverages from India, Tibet, and China range from 1.55–3.21 ppm,<sup>28</sup>  $2.59 \pm 1.73$  ppm,<sup>29</sup> and 1.60–7.34 ppm, respectively.<sup>25</sup> Fig. S5(a) and (b)† show the specifics of fluoride-rich foods.

**3.1.3 Drugs.** Long-term usage of some medications, such as aspirin, has been linked to fluoride toxicity. Sodium fluoride is used to cure osteoporosis, niflumic acid is used to treat rheumatoid arthritis, and a fluoride-based mouth rinse is used to prevent cavities. Fluoride supplements containing inorganic fluoride in drinking water, pills, and other medications prevent tooth decay. The anti-inflammatory drug niflumic acid is used to treat rheumatoid arthritis. *Sodium fluoride* is a fluoride salt that is used in mouthwash to prevent cavities in the mouth.

**3.1.4 Air.** Fluorides are extensively distributed in the atmosphere due to the industrial manufacture of phosphate fertilizers, manufacture of aluminum, coal ash from coal combustion, and volcanic activity. However, air exposure only accounts for a tiny portion of the overall fluoride exposure.<sup>30</sup> In comparison to non-industrial regions, fluoride exposure in the air is higher in industrial zones. In parts of Morocco and China, there is a large amount of fluoride in the air.<sup>31</sup> In particular Chinese regions, the indoor burning of high-fluoride coal for cooking produces 16 to 46  $\text{g cm}^{-3}$  of fluorides in the air.<sup>32</sup> Fluorosis affects ten million individuals in China due to the burning of high-fluoride coal.<sup>33</sup>

**3.1.5 Cosmetic.** Fluorides are present in daily use goods such as mouthwash, toothpaste, and cosmetics. Raw materials such as calcium carbonate, talc, and chalk are used for manufacturing these goods, increasing the fluoride levels between 800 and 1000 ppm. In fluorinated brands, fluoride is added in the range of 1000 to 4000 ppm. Various products that contain fluorides are employed to minimize dental decay in children. They include toothpaste with 1.0 to 1.5  $\text{g kg}^{-1}$  fluoride, fluoride solution, and fluoride gels, corresponding to the topical treatment between 0.25 and 24.0  $\text{g kg}^{-1}$  of fluoride, and

fluoride tablets with around 0.25, 0.50, and 1.0 mg fluoride per tablet, which are responsible for direct fluoride contact in the children. It was estimated that toothpaste swallowed by a few children had nearly 0.50 or 0.75 mg of fluoride per day in one child.<sup>34</sup>

**3.1.6 Soil.** The fluoride levels in soil typically range from 200 to 300 parts per million.<sup>35</sup> Fluoride is not easily leached from soils because it is held in the soil *via* solid through interactions with the various components present in the soil.<sup>36</sup> The amount of fluoride in the soil increases with the depth, with just 5% to 10% of the complete fluoride inside soil being water-soluble.<sup>37</sup> The chemical form, deposition rate, soil chemistry, and temperature influence the destiny of inorganic fluorides discharged into the soil, where most fluorides in acidic soils with  $\text{pH} < 6$  are present in complexes related to aluminium or iron or on the displacement of hydroxide with the surface of the clay, fluoride bonds to it. The pH and fluoride concentration have a significant impact on the adsorption of fluoride, which is most noticeable between pH 3 and 4 and diminishes at pH 6.5.<sup>36</sup> The presence of  $\text{Cl}^-$ ,  $\text{SO}_2^{4-}$ ,  $\text{F}^-$  and  $\text{NO}_3^-$  in groundwater is caused by fertilizer application under heavy irrigation. Groundwater from irrigated fields and soils has a higher fluoride concentration owing to alkalization.

**3.1.7 Humans.** According to the research by Watanabe *et al.*,<sup>38</sup> fluoride and hydrofluoric acid are absorbed *via* the skin in human beings and animals. Fluoride is absorbed and quickly transported throughout the body through blood, with approximately 99% of it ending up in bones and teeth.<sup>39</sup> Fluoride is absorbed from the stomach through an inert diffusion procedure, which is inversely proportional to pH,<sup>40</sup> but quickly absorbed from the small intestine following gastric emptying.<sup>41</sup> Fluoride absorption is reduced with the availability of a calcium-rich diet and contact with  $\text{CaCO}_3$ .<sup>42</sup> In soft tissues, there is no fluoride accumulation, although hydrogen fluoride may penetrate the intracellular fluid of soft tissues.<sup>43</sup> The fluoride concentration in soft tissues reflects the fluoride concentration in the blood. It is highly concentrated in the renal tubules, at a concentration higher than that in plasma.<sup>44</sup> Due to its higher contact with fluoride, the kidney may be a possible location and target of chronic fluoride damage.<sup>45</sup> The placenta may regulate fluoride transfer from maternal blood to fetal blood in humans,<sup>46</sup> while fluoride is only weakly transferred from plasma to milk.<sup>47</sup> Human milk has been shown to have fluoride levels between 5 and 10  $\text{g L}^{-1}$ .<sup>48</sup> Saliva excretes around 1% of ingested fluoride or less,<sup>49</sup> where the saliva fluoride concentrations seem to reflect the plasma fluoride levels.<sup>50</sup> Low amounts of fluoride were found in sweat, according to Henschler *et al.*,<sup>51</sup> which were around 20% that of the plasma levels. Fluoride excretion by the kidneys accounts for 35% to 70% of the fluoride consumed in adults.<sup>52</sup> Consequently, indicators of acute fluoride exposure may be seen in the urine, plasma, and saliva. The fluoride concentrations in drinking water and the level of fluoride in the clippings of a fingernail are directly related, as shown by studies in Hungarian<sup>53</sup> and Brazilian children,<sup>54</sup> which suggested that the levels of fluoride in the fingernails are a reliable biomarker of direct contact with it, and thus they are not well consistent for plasma or bone.



However, the level of fluoride in the nails reflects its consumption three to six months before.<sup>55</sup> Adults living in regions with 1.0 mg L<sup>-1</sup> fluoride in the water have an average dietary intake of 0.02–0.048 mg per kg per day, whereas those living in places with less than 0.3 ppm fluoride in the water have an average dietary intake between 0.004 and 0.014 mg per kg per day. In regions with fluoridated water, that from food consumption by children varies from 0.03 to 0.06 mg per kg per day, whereas in areas without fluoridated water, it is 0.01 to 0.04 mg per kg per day.<sup>56</sup> Infants bottle-fed with fluoride water reconstituted milk formula consume between 0.12 and 0.18 mg per kg per day. The total fluoride intake for babies with an average weight of 8.1 kg at six months is between 1.0 and 1.5 mg per day, which is an adult dose.<sup>57</sup> In humans, Li *et al.*<sup>58</sup> proposed the lowest observed-adverse-effect level (LOAEL) of 0.25 mg fluoride per kg per day and no-observed-adverse-effect limit (NOAEL) of 0.15 mg fluoride per kg per day, but these values are presently under dispute.

**3.1.8 Other sources.** The sources of fluoride in the environment include industrial plants, aluminum smelters producing glass brick, hydrofluoric acid, tile works and phosphate fertilizer plastic factories, textile dyeing, and industries that consume high sulfur non-coking coal for thermal power. Currently, high-tech companies developing semiconductors and integrated circuits produce significant fluoride-containing industrial wastewater.<sup>59</sup> Cigarettes, which contain an average of 236 ppm fluoride, play a significant role in human fluoride consumption.<sup>60</sup> Teflon-coated cookware may potentially increase the fluoride absorption in humans. The fluoride concentrations in Teflon-coated cookware is as high as almost 3 ppm, whereas it is lower in aluminum cookware. Also, the fluoride concentrations are high in stainless steel and Pyrex ware, although to a lower extent.<sup>61</sup> In normal and high quantities, fluoride in water may cause aluminum to leach from cooking utensils and copper from pipework.<sup>55</sup>

## 4. Contamination in ground water

The contamination of groundwater with fluoride is now one of the most significant global issues, given that this contamination is natural and inevitable. Fluorosis is an endemic disease in tropical climates but only to a certain extent. A high fluoride concentration in water in extensive geographical belts is associated with (1) volcanic rocks, (2) marine origin sediments in mountainous regions, and (3) granitic and gneissic rocks. This contamination occurs due to two main factors, which are reported to be geogenic<sup>62</sup> and anthropogenic sources.<sup>63</sup>

### 4.1 Geogenic source

Fluoride is present in various rocks in the Earth's crust, posing an average value of 625 mg kg<sup>-1</sup>.<sup>64</sup> The increase in the fluoride content in groundwater is attributed to several geological processes. Geothermal springs, volcanic activities, tectonic processes, weathering, and other geological processes involving rock and water contact are the main routes for fluoride contamination.<sup>64</sup> The fluoride concentration in water is

positively associated with ions such as chloride and phosphate, whereas that with the calcium ion is negative.<sup>65</sup> The generation of water with the loss of water from the system *via* evaporation has been studied using isotopic data such as carbon (C), oxygen (O), and hydrogen (H) isotopes. Also, it was determined how various aquifers are connected and how climate influences fluoride concentration.<sup>66</sup> After much research, it has been found that the geogenic sources of fluoride contamination are the main reason for population exposure due to the intake of groundwater polluted with fluoride.<sup>67</sup> Several minerals such as fluorite, topaz, and their parent rocks including granite, basalt, and shale release fluoride in the groundwater.<sup>68</sup> The mobilization of fluoride through the leaching of rocks and over-utilization of groundwater is the root cause of fluoride contamination.<sup>69</sup> Fig. S6† depicts the different rocks and their fluoride content (mg kg<sup>-1</sup>).<sup>70</sup> Soil and rocks are natural sources of fluoride. Moreover, natural leaching, which occurs during the percolation of water through the soil and rocks, plays an essential role in groundwater contamination. There are also some indirect ways by which groundwater contamination occurs, including storage of water between soil and rocks for a long time, evaporation of water, and use of irrigation systems for an extended period. The fluoride ion can occupy the hydroxide ion site by replacing it in the mineral structure given that these two ions are negatively charged and are almost similar in size.<sup>71</sup> The modification of rock minerals and discharge of the dissolved compound occur *via* geochemical processes due to the exposure of rocks to weather agents such as water. The dissolution of minerals containing fluoride in rocks is accelerated by temperature and residence time.<sup>72</sup> When the alkalinity of groundwater is high, hydroxyl ions quickly replace the fluoride ions in minerals such as mica, elite, and amphiboles.<sup>73</sup> Moreover, many bicarbonate and sodium minerals enhance the concentration of fluoride in the groundwater.<sup>74</sup> The possibility of fluoride dissolution increases when calcium-rich groundwater changes to sodium-rich groundwater.<sup>75</sup>

Under average temperature and pressure conditions, hydrogen fluoride and sodium fluoride are sufficiently soluble, whereas calcium and magnesium fluoride are poorly soluble. The hydraulic conductivity of aquifers, groundwater circulation, and various other geochemical processes regulate the advancement of fluoride concentration in groundwater<sup>76</sup> and F<sup>-</sup> bearing minerals.<sup>77</sup> After a detailed study, it was found that the fluoride concentration also changes with a change in the groundwater level. The presence of clay also impacts the dissolution of fluoride in the groundwater because it can reduce the hydraulic conductivity and enhance the time of residence of water in aquifers.<sup>78</sup> Fluoride with a content of almost 295 ppm is also present in coal.<sup>79</sup> In humid areas, the fluoride level is less prominent because they receive massive rainfall, which finally dilutes the fluoride level to a great extent. Volcanic eruption also contributes fluoride to groundwater. Volcanic ash containing fluoride is released during volcanic eruptions, which occur during rainfall. Moreover, due to the high solubility of volcanic ash, it readily comes in contact with groundwater. Even after the completion of volcanic activity, the fluoride concentration remains high in the surrounding water and grass for many years.<sup>80</sup>





## 4.2 Anthropogenic sources

Anthropogenic factors may potentially raise the fluoride level in groundwater such as the use of fluoride-containing phosphate fertilizers, rodenticides, fumigants, herbicides, and insecticides.<sup>81</sup> Fluoride pollution may also be caused by coal combustion, fly ash, and fluoride particle emissions from the steel, aluminium, glass, and tile industries.<sup>82</sup> Anthropogenic activities such as coal combustion, the extensive use of fertilizers containing phosphate in agriculture, and cement manufacture generally produce fluoride to a large extent.<sup>83</sup> Industries such as semiconductor manufacturing, coal-fired power stations, and aluminium smelters release wastewater enriched with fluoride.<sup>84</sup> Compared to natural water, the fluoride concentrations in these industrial effluents are very high, ranging between 10 and 1000 ppm.<sup>85</sup> It has been observed that the use of fertilizers containing phosphate in an unscientific manner is one of the primary anthropogenic sources of groundwater contamination with fluoride.<sup>86</sup> The superphosphate fertilizers used to increase agricultural productivity contribute almost 0.34 ppm of fluoride.<sup>59</sup> The region near brick kiln industries has an elevated fluoride concentration in groundwater.<sup>81</sup>

## 5. Health effects

Fluoride may be helpful or harmful for humans depending on the overall concentration of fluoride consumed over a period. A deficiency in fluoride causes dental caries and weakening of the bones when its concentration is less than  $0.5 \text{ mg L}^{-1}$ , whereas if there is an intake of more than  $1.5 \text{ mg L}^{-1}$ , it causes fluorosis. The accumulation of fluoride more than the permissible limit leads to hazardous health issues in infants, children, and adults. The different effects of fluoride on the human body are shown in Fig. 1. Fluoride will not affect a person briefly, but it gets stored in the brain and slowly deteriorates the body with time, as shown in Fig. 2.

The primary basis of fresh water is groundwater, which is the most consumed form for irrigation purposes. According to the report presented by the WHO, more than 25 countries have a concentration of fluoride more than the permissible limit, and nearly 200 million people depend on the contaminated water, which is a severe threat causing health issues to consumers. Many African countries have a higher fluoride concentration than the guideline set by the WHO of  $1.5 \text{ mg L}^{-1}$ .<sup>87</sup> The Asian countries with a high fluoride concentration in their groundwater include Bangladesh, China, India, Indonesia, Iran, Iraq, Jordan, Korea, Pakistan, Palestine, Saudi Arabia, Sri Lanka, Syria, Thailand, Turkey, and Yemen.<sup>88</sup> The regions of Canada, Mexico, and the United States especially need defluoridation due to the high fluoride concentration in their groundwater.<sup>89</sup> Even countries of Latin America, namely Argentina, Ecuador, and Peru, have high fluoride concentrations in their groundwater.<sup>90</sup> An excessive concentration of fluoride in groundwater is a significant problem in European countries. Some regions of Germany also face this problem.<sup>91</sup> Fig. 3 displays a world map with all the countries having drinking water with fluoride.<sup>92</sup>

In 1937, the Prakasam area of Andhra Pradesh reported the first incidence of fluorosis endemic in humans.<sup>93</sup> Only four states of India, namely Andhra Pradesh, Uttar Pradesh, Punjab, and Tamil Nadu, were recognized with fluorosis patients in 1950. Currently, fluoride is present in 20 of India's 29 states, which is projected to rise,<sup>94</sup> as shown in Fig. 4. Fig. 4 displays a map of India with fluoride in the drinking water in all districts.<sup>95</sup> In India, just a few families with fluorosis were found in 1937. However, fluorosis was projected to affect 25 million individuals in India by the United Nations International Children's Emergency Fund (UNICEF) in 1995. Currently, fluorosis affects 66 million people in India, with 6 million children less than 14. Around 411 million individuals in 201 districts across 20 states are affected by fluoride in India, and thus are possibly in danger of fluoride poisoning.

### 5.1 Dental

Dental caries is the world's most common issue in children. Fluoride plays a significant role in minimizing the chance of enamel fluorosis and preventing dental caries. During the developmental period of teeth, continuous exposure to fluoride helps develop resistance against dental decay and fluorosis of the enamel. The enamel is the most mineralized hydroxyapatite crystal, which is rich in carbonate, but deficient in calcium.<sup>96</sup> To maintain the state of stable equilibrium with the fluid in the surrounding region of the crystal, a sufficient amount of ions such as  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$ ,  $\text{OH}^-$ , and  $\text{F}^-$  are present. During cariogenic acid attack, the pH value in the vicinity of the tooth decreases due to the release of  $\text{H}^+$  ions from organic acids, which are formed by plaque bacteria from carbohydrates. These  $\text{H}^+$  ions are released to interact with the phosphate ions ( $\text{PO}_4^{3-}$ ) available in plaque fluid and reduces them to  $\text{HPO}_4^{2-}$ , and finally  $\text{H}_2\text{PO}_4^-$ . This reduction process helps to release calcium from potent tooth substances and also balances the neutrality.<sup>97</sup> Compared to the incorporated fluoride, the smaller quantity of fluoride present in the solution in the vicinity of the tooth more effectively prevents the process of demineralization. Moreover, it also can inhibit dental caries more than the large amount of fluoro-hydroxyapatite in the enamel. This protection is ascribed to the fact that the fluoride ions present in solution are more effective to prevent caries than the fluorides present in the enamel crystals. Now, a small amount of fluoride ions is adsorbed on the crystalline surface, and a state of dynamic equilibrium is achieved between the fluoride ions in solution in the vicinity region and the adsorbed fluoride ions. Finally, this adsorption inhibits the process of demineralization.<sup>97</sup> The presence of fluoride in the correct amount ( $\geq 0.7 \text{ mg L}^{-1}$ ) is significant for developing dental enamel and normal mineralization of bones.<sup>98</sup> Up to 40% of tooth decay can be prevented by fluoride.<sup>99</sup>

### 5.2 Teeth and bones

An essential constituent of the tooth enamel and skeleton is hydroxyapatite. The hydroxide ions replaced by fluoride form a significantly harder compound called fluorapatite. If present in a small amount, fluorapatite prevents the tooth from



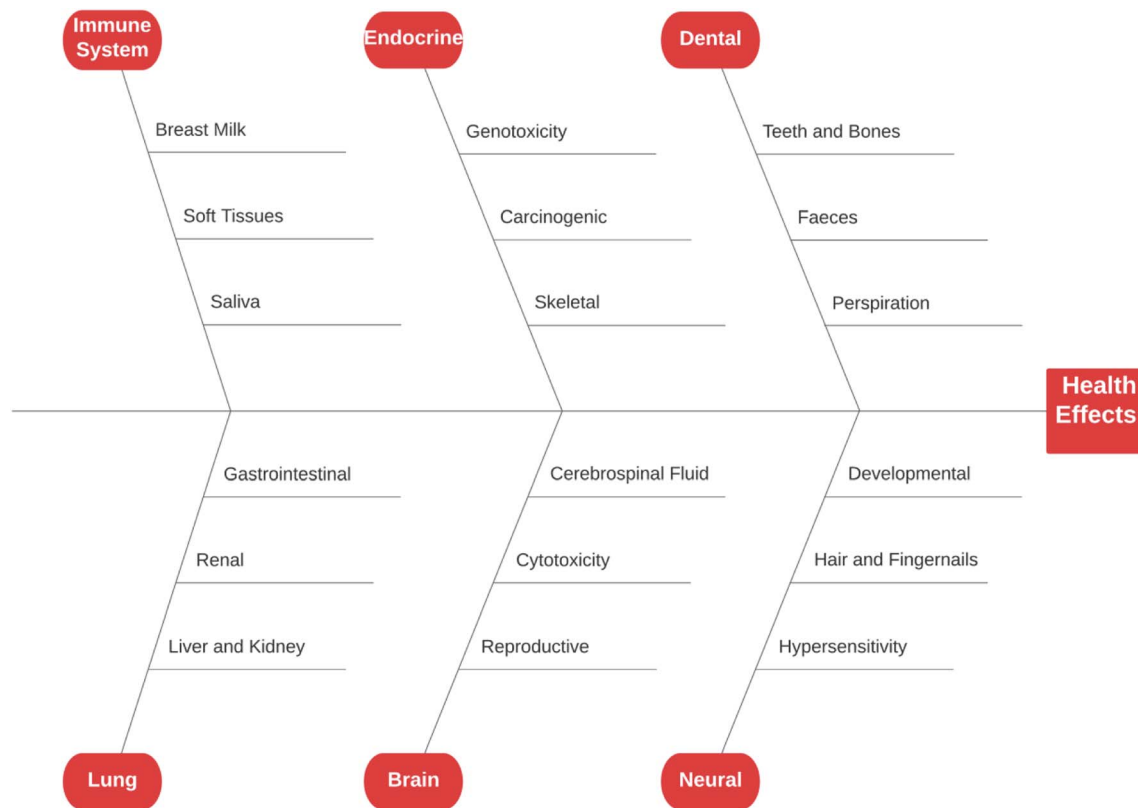


Fig. 1 Schematic representation of the general health effect of fluoride.

decaying and reinforces the tooth's enamel. However, if fluoride at elevated doses is taken for a long time, then the hydroxyapatites get converted to fluorapatite in a more significant amount, making the bone and teeth stiffer and brittle and promoting the disease called dental fluorosis. Dental fluorosis gets converted to skeletal fluorosis as the fluoride concentration increases to  $3.0 \text{ mg L}^{-1}$ . About 65% of the endemic fluorosis, which occurs due to fluoride-contaminated drinking water, is reported in arid and semi-arid regions.<sup>100</sup> Table S2† shows the effect of prolonged use of drinking water on human health, which is related to its fluoride content.<sup>101</sup> Crippling skeletal fluorosis is considered one of the leading causes of morbidity in a large area of the globe. If the fluoride present in drinking water is less than  $0.5 \text{ mg L}^{-1}$ , then the possibility of dental caries increases in children.<sup>102</sup> If the amount of fluoride present is up to  $1.5 \text{ mg L}^{-1}$ , it helps strengthen the skeleton. The threat of skeletal and dental fluorosis increases with an increase in the fluoride concentration in water. The most common problem encountered is the mottling of the teeth when the fluoride concentration is in the range of  $1.5$  to  $4.0 \text{ mg L}^{-1}$ . When the fluoride intake crosses  $6.0 \text{ mg L}^{-1}$ , it opens the path for multidimensional health effects, mainly dental and skeletal fluorosis.<sup>103</sup> Drinking water containing excess fluoride is responsible for almost 65% of the total endemic fluorosis.<sup>104</sup> Out of the total fluoride consumed by the body, its maximum amount is retained by the bones or teeth, with almost 80–90% in new-born babies and 60% in adults, and the remaining fluoride gets excreted *via* the urine.<sup>105</sup> The early symptom of

dental fluorosis is enamel discoloration,<sup>106</sup> which may convert to discrete or aggregated pitting.<sup>107</sup>

In the three districts of Rajasthan, India, namely Dungarpur, Banswara, and Udaipur, a survey was conducted and it was reported that more than 21% of teenagers and 36% of adults of the area having fluoride concentration of  $1.5 \text{ ppm}$  in the drinking water were affected by dental fluorosis. Also, the fastest spreading rate (77.1%) of dental fluorosis was found in the age group of 17–22 years.<sup>108</sup> The other effects of fluorosis are restricted joint movement, joint pain, and limb motor dysfunction. In India and some other countries, these symptoms make life very complex for people suffering from severe health issues such as paralysis.<sup>108</sup>

### 5.3 Neural

When present in a concentration of more than  $1 \text{ mg L}^{-1}$ , fluoride increases the chance of neurotoxicity, which may disturb the learning and memorizing capacity. Compared to the mature brain, the developing brain is more prone to damage by toxicants, which may lead to permanent damage.<sup>109</sup> Current research has established that the mental ability of children in high fluoride areas is relatively lower than those living in low fluoride areas.<sup>110</sup> A comparative study was carried out between 1988 and 2008 in China to relate the intelligence quotient (IQ) level with fluoride concentration and it was found that the children living in fluoride-enriched areas have a chance of low IQ by at least five times more than the children from the region



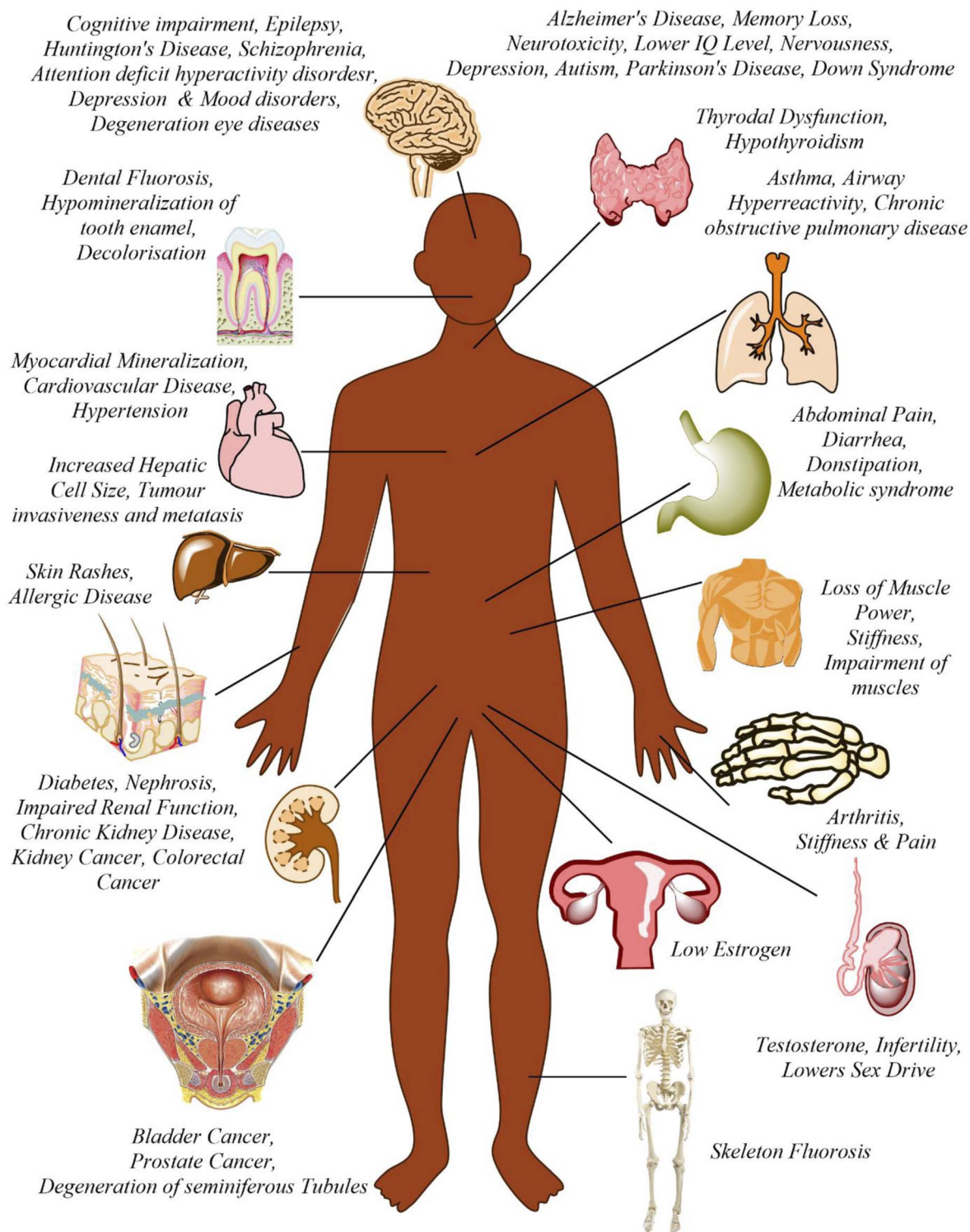


Fig. 2 Effect of fluoride on human body.

having a lower fluoride concentration.<sup>111</sup> The excess fluoride concentration increases the lipid peroxidation level and hinders various chief neuronal enzymes.<sup>112</sup> This study suggested that fluoride directly affects neurons, myelin, and neurotransmitters, suggesting that fluoride may directly damage the functioning of the brain.<sup>113</sup> A characteristic study was performed to

understand the correlation between neonatal neurodevelopment and fluoride intake by mothers during pregnancy. It was found that the neonatal neurodevelopment of babies was very slow when the fluoride intake by their mothers was large during pregnancy compared to the babies not exposed to an elevated fluoride concentration.<sup>114</sup> After chronic fluoride



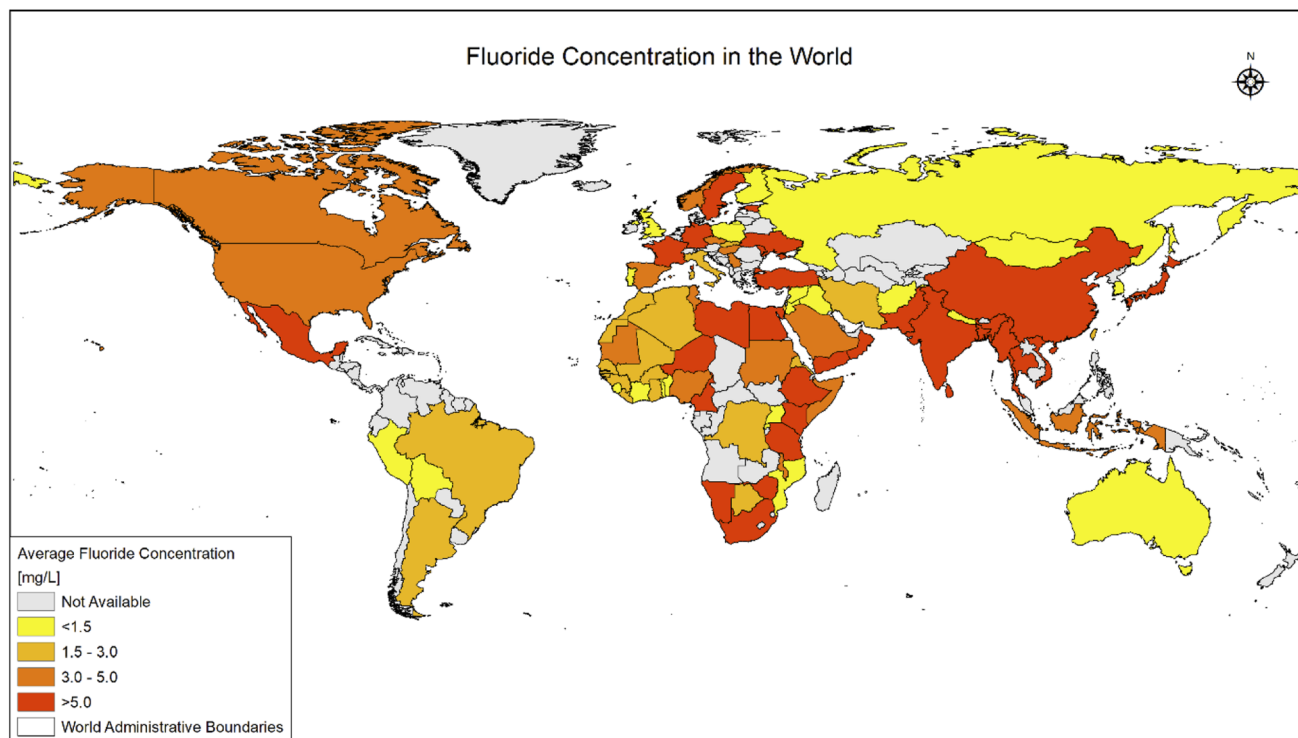


Fig. 3 Map of world showing fluoride (in ppm) distribution in all countries. This map was modified or prepared based on published scientific reports.<sup>91</sup>

administration, various changes occur in the blood, brain, and liver of animals, including metabolic lesions, abnormal behavior designs, and changed neuronal cerebrovascular integrity.<sup>115</sup> When the groundwater contains fluoride of more than  $10 \text{ mg L}^{-1}$ , it accelerates more diseases such as neurological problems, hypertension, and cancer, which become challenging for human health.<sup>116</sup>

#### 5.4 Reproductive

Currently, the world is struggling with the growing issue of infertility, where fluoride is considered to be it is one of the main factors. Increased fluoride exposure is related to an increased luteinizing hormone (LH) level and follicle-stimulating hormone (FSH),<sup>117</sup> decreased thyroid hormone (TH),<sup>118</sup> reduced estrogen level (EL),<sup>119</sup> and disturbed ratio of estrogen receptor to androgen receptor (ER/AR).<sup>120</sup> The morphology, solidity, and metabolism of spermatozoa change in rats affected by fluorosis and their fertility was reduced by 33%.<sup>121</sup> In a male patient affected by skeletal fluorosis, a reduced circulating testosterone concentration was observed.<sup>122</sup> The level of potassium and sodium in spermatozoa is reduced, as fluoride enables the leakage of potassium ions.<sup>123</sup> Due to the genotoxic effect of sodium fluoride (NaF) on mouse germ cells, the sperm abnormality increases, and the chromosomal aberrations increase in the primary testicular cells.<sup>124</sup> When an excess amount of NaF was applied to the ovaries of albino rats, stomal congestion, ovarian follicles, and dilated blood vessels were observed.<sup>125</sup>

#### 5.5 Liver and kidney

When the three crucial parts of the body, namely the kidney, liver, and heart, are exposed to excess fluoride concentrations for a long time, they start showing histopathological and functional changes.<sup>126</sup> A study showed that the continuous ingestion of fluoride through the diet accelerates chronic kidney disease (CKD).<sup>127</sup> An experiment on mice by exposing them to high fluoride showed a higher fluoride concentration in their urine, renal cell apoptosis, reduced serum glutathione peroxidase (GPx3), and increased malondialdehyde (MDA).<sup>128</sup> Also, NaF induces hypertension by increasing the production of reactive oxygen species (ROS) and elevating the NF- $\kappa$ B expression in the kidney and heart.<sup>129</sup> A person suffering from kidney problems is more susceptible to fluorosis even if fluoride is consumed in the permissible limit due to a reduction in their ability to excrete fluoride *via* urine.

#### 5.6 Lung

Fluorosis is associated with asthma in laborers working in the aluminum industry.<sup>130</sup> In most factories, the key source of fluoride pollution is the production of aluminum and phosphate.<sup>131</sup> Studies showed that respiratory ROS production may be linked with many respiratory diseases.<sup>132</sup> The levels of pro-inflammatory cytokines and ROS were elevated in the lungs of fluoride-treated mice, whereas there was a decrease in anti-inflammatory factors. The NrF<sub>2</sub>/keap-1 signaling pathway supports cell survival by maintaining anti-oxidant function and activity during oxidative stress. It was observed that elevated





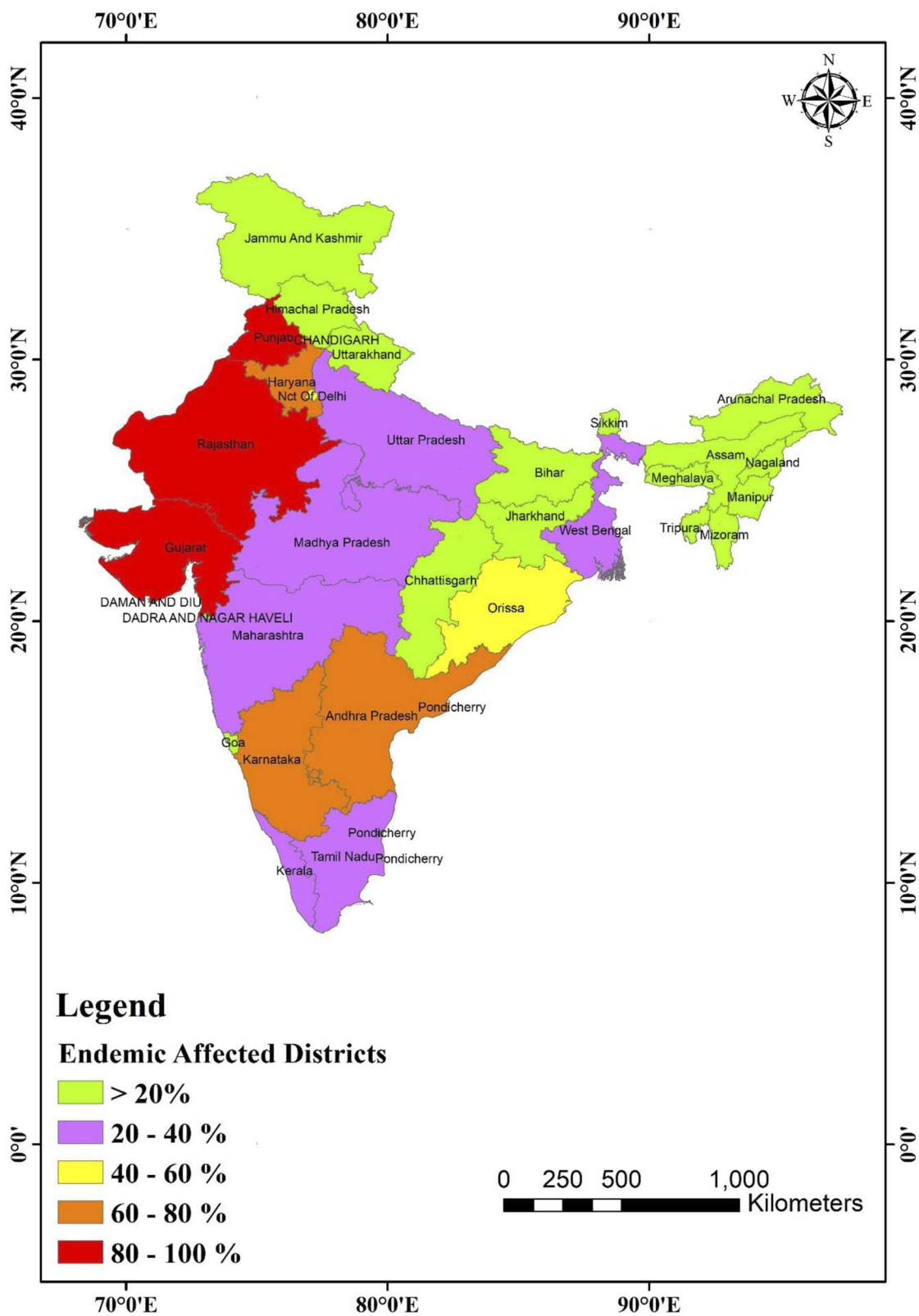


Fig. 4 Map of India showing fluoride (in ppm) distribution in the different states and union territories. This map was modified or prepared based on published scientific reports.<sup>95</sup>

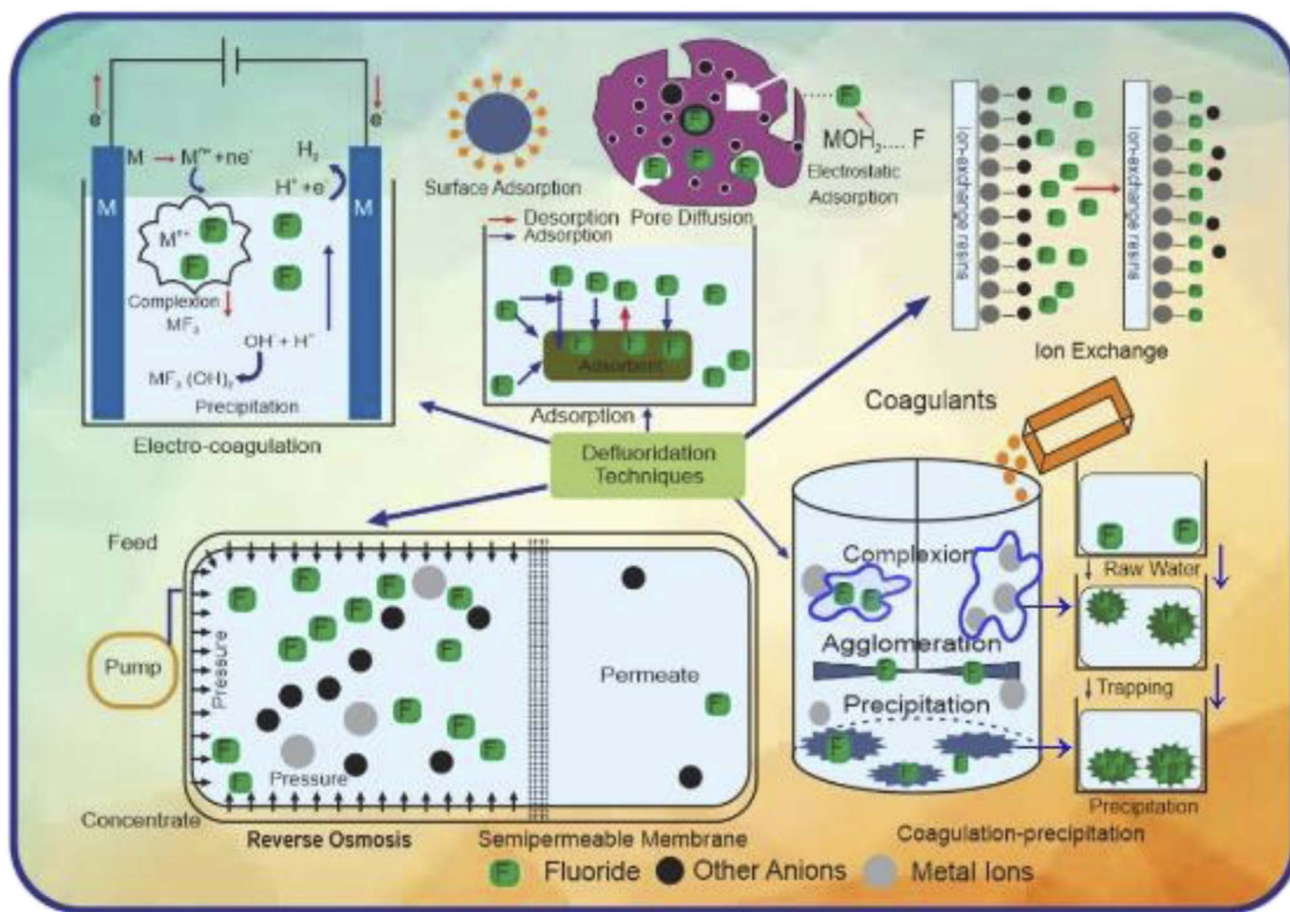


Fig. 5 Various defluoridation techniques.

endogenous anti-oxidants, decreased ROS and number of lung lesions, and up-regulation of NrF2 occurred after mice were pre-treated with epigallocatechin gallate (EGCG).<sup>133</sup>

### 5.7 Immune system

Fluoride produces an adverse effect on the immune system of the body. A study showed that the immunity of silk worms is reduced upon exposure to NaF, which hinders their cellular immunity.<sup>134</sup> This study concluded that at lower fluoride concentration ( $5 \text{ mg L}^{-1}$ ), the level of cellular expression of anti-inflammatory factor IL-10 decreases in mouse macrophages. Alternatively, a greater fluoride concentration ( $50\text{--}75 \text{ mg L}^{-1}$ ) helped enhance the macrophage inflammatory protein 2 (Mip 2) and pro-inflammatory cytokine IL-6 and increased ROS and reactive nitrogen species. This resulted in elevated lipid peroxidation and redox imbalance, decreasing the macrophage population.<sup>135</sup> Moreover, fluoride ions also form a complex with magnesium and other metals, inhibiting many enzymes.<sup>136</sup>

### 5.8 Skeletal

An increase in the mass and density of bones and a variety of joint and skeletal complaints define skeletal fluorosis. The mechanism(s) causing skeletal fluorosis are unknown. Nevertheless, the phases of growth and development have been

thoroughly characterized.<sup>137</sup> Pain and stiffness in the backbone and hip area, joints, and increased bone density are common early signs (osteosclerosis). “Poker back” is the situation where the entire spine stiffens until it forms one continuous column of bone. Different ligaments of the spine may tend to be calcified and ossified as this illness worsens. Fluorosis causes neurological problems, muscular atrophy, paralysis, debilitating deformities in the spine and major joints, and spinal cord compression in its later stages. Water consumption, water quality, and other dietary variables influence the content of fluoride required to develop skeletal fluorosis.<sup>138</sup> It has been indicated that skeletal fluorosis has not developed among the population in the United States (US) where the drinking water concentration is less than  $4 \text{ mg L}^{-1}$ ; however, those with renal impairments consuming substantial amounts of drinking water at  $2\text{--}8 \text{ mg L}^{-1}$  may be at risk.<sup>139</sup>

### 5.9 Developmental

There is a good association between the concentration of fluoride estimated in the umbilical and maternal cord with the blood plasma, as discovered by many studies, suggesting that the placenta facilitates inactive fluoride transmission from the mother to fetus.<sup>140</sup> Studies on laboratory animals show that even at extremely high ingestion rates, detrimental developmental



effects are feasible; nonetheless, the assessment of developmental problems in the human population has been inconsistent, owing to the poor study quality.<sup>141</sup> The probable relationship between fluoride intake and the occurrence of Down's syndrome,<sup>142</sup> particularly in children born through women below the age of 30,<sup>143</sup> is an avenue of inquiry that merits additional exploration.

### 5.10 Renal

The renal system excretes most of the excessive fluoride from the body, and thus it is vulnerable when in contact with a high concentration of fluoride compared to the other organs.<sup>144</sup> It has also been shown that it is more susceptible to fluoride poisoning than soft tissues. Moreover, only two published studies demonstrate that chronic fluoride consumption has non-carcinogenic consequences on the kidney, both of which are related to kidney stones.<sup>141</sup> Residents in high fluoride regions in Finland, where the fluoride concentrations in groundwater surpass  $1.5 \text{ mg L}^{-1}$ , had higher hospital acceptance rates for urolithiasis, which is commonly known as kidney stones, than residents in the other regions, according to Juuti and Heinonen,<sup>145</sup> however, the difference was only 16%. Singh *et al.*<sup>146</sup> examined over 18 700 persons in an Indian location where the fluoride levels varied from  $3.5$  to  $4.9 \text{ mg L}^{-1}$  and discovered that patients with evidence of skeletal fluorosis were 4.6 times more likely to face the issue of kidney stones. However, it was difficult to make clear conclusions given that the individuals in this study were presumably at higher risk of suffering from kidney stone development due to malnutrition.

### 5.11 Endocrine

Fluoride seemed to impact normal endocrine function and response in laboratory animals and human populations, although there is substantial difficulty in interpreting the findings of this study. Reduced thyroid function, increase in calcitonin activity, increase in parathyroid activity, secondary hyperparathyroidism, and poor glucose tolerance are the principal effects of fluoride on the endocrine system (type II diabetes).<sup>141</sup> However, these impacts differ in intensity among various people, and most of them may be characterized as subclinical, given that they are not deemed harmful to human health. The link discovered by various studies, such as endemic goiter and fluoride exposure in human beings, is perhaps the most acceptable illustration of the difficulty required in considering the properties of fluoride on the endocrine scheme.<sup>147</sup> Although these geographical correlations state the reason and resulting connection, the actual causative approaches for the thyroid action of fluoride have yet to be determined.<sup>141</sup>

### 5.12 Gastrointestinal

In acute fluoride poisoning, gastrointestinal symptoms such as diarrhea, vomiting, nausea, and abdominal discomfort have already been recorded.<sup>148</sup> In animal tests, fluoride has been shown to accelerate the stomach acid output, restrict the flow of blood away from the stomach lining, and kill gastrointestinal tract epithelial cells.<sup>149</sup> The amount of chronic fluoride

consumption necessary to elicit these effects in people has not been determined, where it is possible that this threshold changes depending on other circumstances. For example, in regions with endemic fluorosis where nutrition is often poor, unpleasant gastrointestinal symptoms are prevalent,<sup>143</sup> although equivalent amounts of fluoride exposure in the United Kingdom (UK) and the United States may not always induce the same reaction.<sup>150</sup> Another significant aspect seems to be peak concentration rather than the time of exposure given that slow-release fluorides and calcium supplements have been shown to reduce adverse stomach effects in clinical studies when fluoride is supplied through tablets.<sup>151</sup>

### 5.13 Carcinogenic

An epidemiological survey aimed at determining the carcinogenic risk of chronic fluoride disclosure encountered a variety of obstacles. The most severe issues are that cancer is diagnosed every year, if not in decades, after exposure to the relevant variables when people move in and out of the research region. This often results in the miscalculation of the research group's orientation. Another challenge is the wide variety of malignancies and their probable causes, which involve independently evaluating each form of cancer. Consequently, it is not unexpected that attempts to link fluoridated water and general cancer rates have failed.<sup>152</sup> Researchers have paid close attention to the potential that fluoride contributes to bone cancer because it is accumulated in the skeleton. Although there is controversy in applying these results to people, specific laboratory investigations of animals have found indications of increased osteosarcoma and osteoma.<sup>141</sup> Fluoride use may also raise the risk of kidney and bladder cancer due to the propensity for hydrogen fluoride, a caustic and possibly poisonous chemical, to develop in acidic environment of urine. Grandjean *et al.*<sup>153</sup> performed investigations that provide strong support for this.

### 5.14 Hair and fingernails

Measuring fluoride in the hair and fingernails is a typical way of assessing the overall fluoride load in the body.<sup>154</sup> Although the fingernails reflect exposure in the last 3 to 6 months, namely short-term biomarkers, crippled fingernails definitively designate high fluoride concentrations.<sup>155</sup> Several reports in the literature discuss the shifting decorations of current biomarkers, namely hair and nail, and sensitivity to high fluoride concentrations. The use of pins as a biomarker was initially suggested.<sup>156</sup> According to the research, fingernails show a higher daily fluoride ( $3$  to  $6 \text{ mg L}^{-1}$ ) intake 3.5 months after the initial exposure. Because the reference values for fluoride correlation have yet to be established, researchers are actively investigating the use of nails to predict the fluorosis levels. Although toenails, particularly the big toe, are less susceptible to exogenous fluoride, other affecting variables such as dietary habits, age, sex, and environmental factors should be addressed.<sup>157</sup>

### 5.15 Soft tissues

In soft tissues, the fluoride concentration is relatively low, which does not change with age. The intracellular fluoride in soft tissue





and the extracellular fluoride in the fluid are easily interchangeable. During the increased uptake of fluoride, the fluoride content in soft tissue changes within a limited range and demonstrates slight fluctuation.<sup>158</sup> The rate of fluoride deposition in soft tissue is determined by the alkalinity and blood flow velocity in the tissue.<sup>159</sup> Thus, advanced epidemiologic research is needed to corroborate the findings of deposited fluoride possessions for soft tissue.

### 5.16 Cerebrospinal fluid

The blood–brain obstacle actively defends against excessive flooding of fluoride into the brain by transporting fluoride to the cerebrospinal fluid. The fluoride concentrations in brain fluid are less than half that of complete plasma fluoride.<sup>160</sup> The fluoride concentration in the cerebral fluid increases with excess fluoride intoxication in patients with compromised blood–brain barriers.<sup>161</sup>

### 5.17 Urine

Fluoride reduction *via* urination is mainly a pH-controlled mechanism, where renal excretion rises as the urine becomes more alkaline. Reduced renal clearance of fluoride is caused by increased hydrofluoric acid (HF) reabsorption at acidic pH.<sup>162</sup> Jarnberg *et al.*<sup>163</sup> accurately detailed the renal excretion process of fluoride. Urine is formed by available blood filtration in tubular and glomeruli reabsorption, according to the mechanism. HF is reabsorbed throughout the nephrons through an ionic diffusion process, and the grade of reabsorption is proportional to the fluid pH.

### 5.18 Faeces

The unabsorbed portion of ingested fluoride in the gastrointestinal tunnel is about 10% of the total ingested fluoride, which is excreted in the stool. The number of other food components such as fat, protein, and fiber; the availability of divalent cations, namely Ca and Mg; age, and physiological conditions, all influence faecal excretion.<sup>164</sup> The solubility of ingested fluoride is also an essential element that controls the F<sup>-</sup> outflow in the urine and faeces.<sup>165</sup>

### 5.19 Saliva

In humans, the typical fluoride concentration in the saliva is around 75% of the plasma fluoride content, suggesting that saliva can be used as a fast biomarker. Without being exposed to a high concentration of fluoride, humans exhibit salivary fluoride values in the range of 0.01 to 0.06 mg L<sup>-1</sup>. Within 15 minutes of intake, the level of fluoride in the saliva tends to rise by 15 times than its typical value, and then reverts to its average amount between 20 and 60 minutes.<sup>166</sup>

### 5.20 Perspiration

In people and animals with adequate sweat glands and high sweating rates, perspiration is an essential path of fluoride excretion. The fluoride concentration in human sweat is roughly 20% of the plasma fluid concentration, whereas perspiration may eliminate 13–38% of the total absorbed fluoride at high temperatures and humidity.<sup>167</sup>

### 5.21 Breast milk

Milk fluoride concentrations are highly correlated with the total fluoride intake.<sup>168</sup> A good association among plasma, breast milk, and fluoride content in water was documented in several investigations.<sup>169</sup> The fluoride level of milk in women with dental fluorosis was 0.550 mg L<sup>-1</sup> in a current survey of 62 mothers, compared to 0.006 for mothers without dental fluorosis.<sup>170</sup>

### 5.22 Cytotoxicity

In mammalian cells, the excessive consumption of fluoride may cause chromosomal abnormalities and genetic mutations.<sup>171</sup> Fluoride has a significant impact on deoxyribonucleic acid (DNA) and protein production, even at low concentrations. Excess fluoride has also been linked to changes in cell shape and DNA breakage in nucleosomes.<sup>172</sup> The cytotoxic impact is mainly determined by the exposure intensity, frequency, and duration.

### 5.23 Hypersensitivity

Existing investigations in this sector provide insufficient evidence on the logical association between hypersensitivity and fluoride ion concentration. Thus, to link hypersensitivity and fluoride exposure in experimental animals, researchers often choose a high dosage, an ineffective mode of administration, or both.<sup>173</sup> However, the results obtained may not be extended to fluoride exposure in people given that the experimental dose is disputed. Human hypersensitive response research is similarly inconclusive and contentious. Eczema, roseola, stomatitis, and gastrointestinal issues are the most frequent responses.<sup>174</sup>

### 5.24 Brain

Excessive fluoride consumption has been shown in several studies to impair the structure organization and function of the central and peripheral neurological systems.<sup>175</sup> The build-up of excess fluoride in the hippocampus has also been linked to neuron degeneration, decreased aerobic metabolism, and alterations of free radical metabolism.<sup>176</sup> Several other investigations on experimental animals have shown that traces of metal concentration in the brain and the antioxidant defense system are altered.

### 5.25 Genotoxicity

The word genotoxicity refers to the presence of a toxin that damages the integrity of cells by destroying their genetic contents.<sup>177</sup> The technique and judgments used *in vivo* and *in vitro* research linked to fluoride toxicity significantly impact genotoxicity studies.<sup>178</sup> Fluoride does not generate mutagenic alterations in the Ames assay, which is a highly reliable way to detect genotoxicity,<sup>179</sup> despite inconsistent findings in the literature.

### 5.26 Other toxic effects

Fluoride may produce a toxic effect on the human body in several ways. Initially, fluoride acts on the intestinal mucosa,





but later, due to hydrofluoric acid formation in the abdomen, it causes gastro-intestinal irritation or corrosive effects.<sup>180</sup> Fluoride can also disturb lipid functioning and adipogenesis.<sup>104</sup> Fluoride exposure is also related to the problem of obesity in children. However, the result remains inconclusive given that some researchers show a positive correlation between obesity and fluoride,<sup>181</sup> while others reported either no effect or negative correlation between them.<sup>182</sup>

## 6. Fluoride mitigation knowledge

Fluoride has a variety of negative impacts on humans and plants; thus, it must be monitored and mitigated. Consequently, it is essential to take appropriate steps to minimize the concentration of fluoride in potable water from affected zones within the permissible limit. Different strategies are used to reduce the risk of fluorosis. They include using some alternate water resources, improving the nutritional status by using some specific foods in the diet, and water defluoridation.<sup>183</sup> One attempt tried to supply treated surface water, not groundwater, at the community level as an alternative water resource. However, this method is not possible for developing countries due to the considerable expense.<sup>184</sup> Sometimes we can go through two water systems in which the water with a less amount of fluoride can be used for household purposes such as cooking and drinking, while water containing a higher amount of fluoride can be used for other chores.<sup>185</sup> Rainwater harvesting can also be considered another alternative.<sup>186</sup> However, the main limitation of this method is the requirement of ample space to store rainwater and the uneven distribution of rainfall in different areas.<sup>187</sup> Consuming foods rich in vitamin C and calcium (nutritious food) also reduces the fluoride effect to some extent.<sup>183</sup> However, if no alternative source of water is available, then the only option left is the process of defluoridation.<sup>188</sup> Although several defluoridation processes exist, no one solution is prosperous, safe, and cost-effective enough to be extensively used. An examination of the history of defluoridation research indicates that just a few reliable, long-term treatments have been discovered.<sup>189</sup>

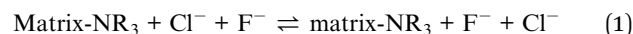
Furthermore, in endemic parts of the developing world, adsorption/ion exchange and coagulation procedures are extensively utilized as fluoride removal strategies. Many nations, including India and Tanzania, utilize defluoridation treatments that are both residential and community-based at various levels. People in India and Sri Lanka have recently had a paradigm change in their attitudes about community-based water treatment schemes that use activated alumina as an electro-coagulation and sorbent. Moreover, most defluoridation methods are out of reach for people living in fluoride-affected rural regions. Other processes such as nanofiltration, electro-dialysis, and reverse osmosis, can provide superior quality water, but they are costly and require a high level of technical expertise, limiting their application in fluoride removal. Fig. 5 presents a schematic diagram explaining the fundamental principles of several defluoridation procedures.

Each approach has its own set of benefits, drawbacks, and influencing variables, and it only works well under ideal

circumstances. Various physical and chemical methods may accomplish defluoridation of drinkable water. Biological approaches for phytoremediation and defluoridation of the air, water, and soil employing bio-sorbents generated from plant materials and bioremediation *via* bacteria have also been documented.

### 6.1 Chemical and physical process of defluoridation

**6.1.1 Ion exchange.** In this process, a material called an ion exchanger is used, where water is allowed to pass through its bed to eliminate the undesirable ions according to the following reaction:



The fluoride ion replaces the chloride ion in the resin, and the substitution process continues until every site of the resin is occupied. To regenerate the resin, it is back-washed with water containing dissolved sodium chloride salt, enabling fluoride to be replaced by chloride and start acting as an ion exchanger.<sup>190</sup> The fluoride ion possesses higher electronegativity, which is the specific driving force to replace chloride ions in the resin. By using lanthanum, Chikuma *et al.*<sup>191</sup> modified the method of fluoride removal by anion exchange. Chikuma and Nishimura<sup>192</sup> used Amberlite IRA-400 in an aqueous solution for fluoride removal and found that the fluoride ion replaces the chloride ion present in the resin. Ho *et al.*<sup>193</sup> increased the capacity of the ion exchange method through titanium oxyhydroxide. Zirconia and silica having tiny particle sizes are doped on iron oxyhydroxide, a mesoporous material, to increase its ion exchange capacity, but this process is expensive and the issue of membrane arises. Meenakshi *et al.*<sup>194</sup> investigated the fluoride removal capacity of chelating Ceralite IRA 400 (CER) and Resin FR 10 (IND) and concluded that in comparison to the anion exchange resin, the chelating resin is highly selective for the removal of fluoride. The ion exchange technique has a high potential for eliminating fluoride from aqueous solutions (up to 95%). However, the resins are costly, making the treatment uneconomical although the resins may be readily renewed. Furthermore, the regeneration process generates a lot of fluoride-loaded waste, which is a downside of the technique.<sup>195</sup>

**6.1.2 Precipitation/coagulation.** In the early 1930s, researchers tried to develop a technique for fluoride removal from water, which will be economical and sustainable. This process involves the removal of contaminants from water, thereby reducing turbidity. In the coagulation process, a particular chemical called a coagulant is used to destabilize the tiny particles present in water. The different materials used as coagulants to remove fluoride from water include aluminum, iron, alum, lime, zeolites, silica gel, sodium aluminate, ferric chloride, and silica gel.<sup>196</sup> Among them, alum and lime are the most commonly used. The best example of fluoride removal from the coagulation/precipitation method is the Nalgonda technique. This method involves the addition of aluminum salts, bleaching powder, and lime to water contaminated with fluoride, in six consecutive steps, as follows: coagulation/flocculation, disinfection, filtration, rapid mixing,



sedimentation, and sludge concentration.<sup>196</sup> This whole process is carried out in the following sequence. (a) Formation of insoluble flocs of aluminum hydroxide, (b) sinking of sediments at the bottom, and (c) co-precipitation of fluoride and bleaching powder.<sup>197</sup> However, considering that the efficiency of the Nalgonda technique for water de-fluoridation is approximately 70%, it is not suitable for the treatment of water with elevated fluoride concentrations. Also, due to the high cost of alum, this method is expensive.<sup>196</sup> In the precipitation method, the fluoride in calcium fluoride is precipitated from water.<sup>196</sup> To precipitate the fluoride, phosphate, and calcium are used, followed by the process of filtration by employing bone char pre-saturated with fluoride ions. A medium containing saturated bone charcoal behaves like a catalyst for fluoride precipitation in the form of fluorapatite and  $\text{CaF}_2$ .<sup>198</sup>

**6.1.3 Electrocoagulation.** Electro-coagulation is a simple and effective method for the removal of flocculating agents obtained by the electro-oxidation of a sacrificial anode, in general, consisting of aluminum and iron. This process does not involve any chemical flocculants or coagulant and help in reducing the amount of sludge to be disposed. Three fundamental processes are involved in this method, namely, electro-chemistry, hydrodynamics, and coagulation. The electrocoagulation reactor consists of an electrolytic cell having a cathode and anode.<sup>199</sup> Ghosh *et al.*<sup>200</sup> proposed the removal of fluoride through an electrocoagulation process from drinking water with a fluoride concentration ranging between 2 to 10  $\text{mg L}^{-1}$ , employing both mono and bipolar connections. They noticed that in comparison to mono-polar connection, bipolar connection prefers fluoride removal. Under the bipolar connection, the final suggested breaking point of fluoride ( $1 \text{ mg L}^{-1}$ ) was achieved at  $625 \text{ A m}^{-2}$  within an interval of 30 minutes. Moreover, for mono and bipolar connection, the operational costs are 0.38 and 0.62 US \$  $\text{m}^{-3}$ , respectively. Vasudevan *et al.*<sup>201</sup> observed the effect of a direct current and alternating current on the removal of fluoride from water, taking an aluminum alloy as the cathode and anode. Due to the direct current, an impermeable oxide layer was developed on the cathode surface, where anode corrosion takes place due to oxidation. This reduced the efficiency of the method given that the current between the cathode and anode could not be controlled. However, this issue could be removed using an alternating current. It was observed that at pH 7.0, the current density of  $1.0 \text{ A dm}^{-2}$ , by employing aluminum alloy electrodes, the removal efficiencies of the alternating and direct current were 93% and 91.5%, respectively. The energy consumption was 1.883 and  $2.541 \text{ kW h kL}^{-1}$ , respectively. Moreover, a temperature study revealed that the process of electrocoagulation was spontaneous and exothermic.

**6.1.4 Reverse osmosis.** In the reverse osmosis process, a tank is separated into two parts through a semi-permeable membrane. With the aid of hydraulic pressure, the contaminated water can move from one side to the other through a semi-permeable membrane. Water and small impurities can pass through the membrane, but salts and many other contaminants cannot pass through the semi-permeable membrane.<sup>202</sup> The speed of the reverse osmosis process can

be increased by increasing the osmotic pressure on the contaminated side, enabling the water to move through the semi-permeable membrane from the impure side to the fresh side.<sup>203</sup> This removal efficiency by this process reaches 90% or more in the absence of hindrance due to other ions.<sup>204</sup> The two critical parameters that affect the membrane performance are pH and temperature, affecting the fluoride removal efficiency. For water purification, the membrane is selected based on cost, temperature, pressure, recovery, salt rejection, and nature of water to be tested.<sup>205</sup> In the reverse osmosis process, all the ions present in the water are removed, which is its major drawback. For the average growth of the body and other metabolic processes, minerals are necessary. However, for the fulfilment of minerals, the treated water has to undergo re-mineralization, making it expensive.

**6.1.5 Nanofiltration.** Among the various membrane processes, because of the high specific membrane selectivity of nanofiltration, it is regarded as the perfect membrane technique for removing fluoride.<sup>206</sup> The pore size of nanofiltration membranes is slightly more significant than that of reverse osmosis membranes, enabling the easier movement of both the solvent and solute. Consequently, low pressure is required and the flow is fast in nanofiltration.<sup>207</sup> It was observed that in fluoride removal and desalination of some brackish water, nanofiltration gave a superior result compared to other membrane techniques.<sup>208</sup> It was observed that between two commercial nanofiltration membranes, namely NF-270 and NF-90, NF-270 decreased the fluoride level from 10 to  $1.5 \text{ mg L}^{-1}$ , while NF-90 decreased the level from  $20 \text{ mg L}^{-1}$  to  $0.5 \text{ mg L}^{-1}$ .<sup>209</sup> Also, it was reported that the fluoride level could be reduced from  $417.9 \text{ mg L}^{-1}$  to below  $1.5 \text{ mg L}^{-1}$  by using BW30 and NF-90 membranes.<sup>210</sup>

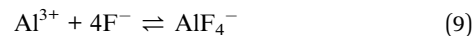
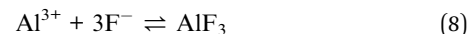
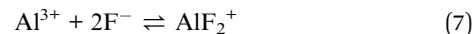
**6.1.6 Adsorption process.** The adsorption method involves particle accumulation from the bulk segment to the solid or liquid segment and is treated as a boundary phenomenon.<sup>211</sup> On the surface of adsorbents, a substance layer is formed, which is known as adsorption. Thus, the method of adsorption can be explained in the following steps. Firstly, the accumulation of a fluoride layer across the surface of adsorbent particles from the heterogeneous solution. The second step involves the adsorption of fluoride ions on the surface of the adsorbent particles. The last step involves intra-particle diffusion, where the adsorbed fluoride shifts to the inner surfaces of the porous adsorbent materials.<sup>212</sup> Specifically, the quantity of fluoride adsorbed on the adsorbent surface per unit mass of the adsorbent reflects the water purification extent from fluoride contamination.<sup>213</sup> The various types of adsorbents are shown in Table S3.† The extent to which an adsorbent is efficient in removing fluoride depends on factors such as the initial concentration of fluoride, the type of adsorbent used, pH of the water, the existence of interfering ions, and the time of contact.<sup>214</sup> Among the different methods for defluoridation, adsorption is considered the most effective for a small population due to its more straightforward operational process, simple design, presence of a variety of adsorbents, and comparatively low setup cost.<sup>215</sup> However, some adsorbents are very expensive, while some of them for defluoridation are not fit technically in rural areas.<sup>216</sup> Also, the use of some adsorbents is



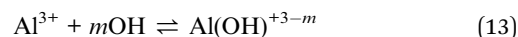
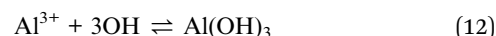
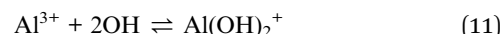
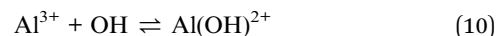
limited due to their inadequate removal capacity. Active alumina is used on a large scale as an adsorbent at the domestic and community levels to remove fluoride from drinking water. It was noted that the use of active alumina as an adsorbent involves both the adsorption process and ion exchange method.<sup>217</sup> The use of active alumina effectively removes fluoride from water; however, it can also cause adverse health effects. The complex compound formed between aluminum and fluoride is recognized as the reason for Alzheimer's disease and is also responsible for some health complexes.<sup>218</sup> Ferric hydroxides,  $[\text{Fe}(\text{OH})_3]$ , as granules, are a mixture of poorly crystallized iron oxide ( $\text{FeOOH}$ ), showing a positive result in removing fluoride from drinking water.<sup>219</sup>

The adsorption capacity, fluoride removal effectiveness under ideal experimental circumstances, and regeneration capacity of important adsorbents are summarised below.

**6.1.6.1 Aluminium-based adsorbents.** Alumina has been extensively investigated and recognized as the most efficient adsorbent for water defluoridation.<sup>220</sup> It must be activated to be an efficient adsorbent. Steady or quick gibbsite pyrolysis or gibbsite-comprising materials such as flash calcination produces activate alumina (AA).<sup>221</sup> Because highly porous aluminum oxide possesses a high surface area, activated alumina is an appealing adsorbent with higher fluoride removal capability than other adsorption media. The cationic networks across the alumina crystal generate a positive charge, which attracts anionic species. The adsorption capacity of activated alumina is affected by its crystalline form and pH of the water. The development of fluoride complexes is considered a significant factor in fluoride adsorption through activated alumina from solution, as represented below:

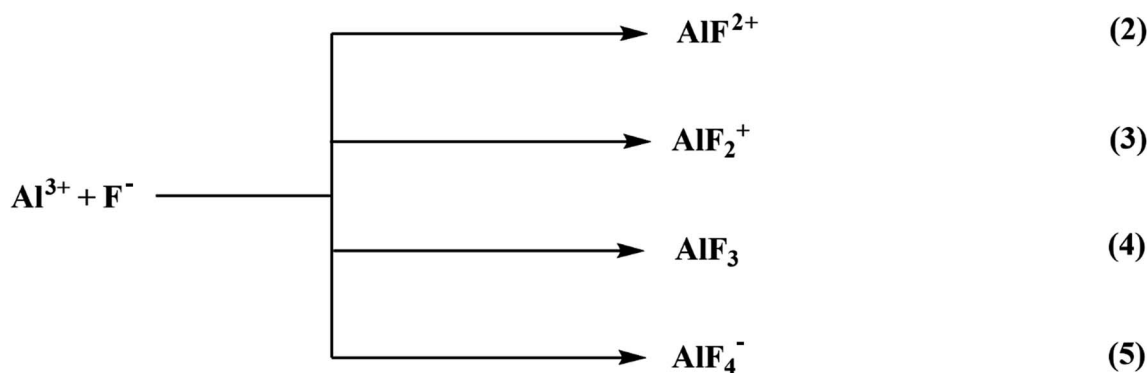


The formation of complexes of the specific aluminum ions together with the hydroxyl ions in the solution is represented as follows:

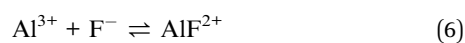


The solution pH is responsible for the adsorption of fluoride on activated alumina due to the electrostatic interactions between the alumina surface and dominant species with fluoride in the solution.

Goswami and Purkait<sup>222</sup> used acidic alumina to defluoridate water and found that pH 4.4 resulted in the removal of the most fluoride. The adsorption process fitted well with the Langmuir model, showing an adsorbent capacity value of  $8.4 \text{ mg g}^{-1}$ , while the kinetics adopted a pseudo-second-order model. Farrah *et al.*<sup>223</sup> investigated the association between fluoride and amorphous  $\text{Al}(\text{OH})_3$ , alumina, or gibbsite in the pH range of 3 to 8 and fluoride concentration of  $0.1\text{--}1.0 \text{ mg L}^{-1}$ . A high amount of the amorphous  $\text{Al}(\text{OH})_3$  gel was dissolved by forming  $\text{AlF}$  complexes at a pH value of 6 and an overall  $\text{F}^- : \text{Al}$  ratio of  $> 2.5$ ,



The activated alumina may not be soluble in the aqueous solution comprised of fluoride ions, resulting in the formation of a variety of aluminum and fluoride and hydroxyl-aluminum complexes. The steps of the equilibrium equation to represent the Al-F complexes are as follows:



with the distribution of fluoro ions governed through the equilibrium  $\text{F}^-$  value. Some solid remained in the pH 4–7 range at lower  $\text{F}^- : \text{Al}$  ratios, and  $\text{F}^-$  was severely sorbed from solution. According to the authors, the highest absorption of  $\text{F}^-$  was seen in the pH range of 5.5 to 6.5, which was approximately  $9 \text{ mol kg}^{-1}$ . The fluoride absorption was reduced at a lower pH owing to the preferred production of  $\text{AlF}_x$  soluble entities, where at the



maximum pH, OH<sup>-</sup> displaced the fluoride ion from the solid, and the quantity of fluoride ion adsorbed on the complexes quickly decrease to around zero in the pH range of 6 to 8. The fluoride uptake fluctuated according to the Langmuir isotherm at a constant pH (5 and 7.5). In acid conditions, the quantity of substrate transformed into AlF<sub>x</sub> complexes increased as the pH decreased and the initial fluoride concentration increased. Gibbsite exhibited the same dissolving patterns as feldspar but was considerably slower. This substrate absorbed less F<sup>-</sup> (10–20 mmol kg<sup>-1</sup>). Many researchers have altered activated alumina, chemically or thermally, to improve its adsorption effectiveness. Tripathy *et al.*<sup>224</sup> synthesized alum-impregnated activated alumina (AIAA) and discovered that it was more effective for water defluoridation. Its surface area was enhanced by impregnating alum from 113 m<sup>2</sup> g<sup>-1</sup> to 176 m<sup>2</sup> g<sup>-1</sup>. At pH 6.5, with an adsorbent dosage of 8 g L<sup>-1</sup>, a contact time of 180 min, and an initial concentration of 20 mg L<sup>-1</sup> in 50 mL water, AIAA could remove 99% of fluoride. The Bradley equation revealed that the adsorption capacity reduced as the pH increased, linking the isotherm and fluctuation in the adsorbent dosage data. Fluoride removal was shown to be attributed to simple surface precipitation rather than adsorption, according to the energy-dispersive X-ray analysis (EDAX). The modest adsorption rate of activated alumina is readily available for usage in large-scale water treatment. Magnesia showed some promising features in removing fluoride, although its application as an adsorbent is limited owing to its powder form. Maliyekkal *et al.*<sup>225</sup> created magnesia-amended activated alumina (MAAA) to combine the benefits of these two materials and examined the capability of the generated adsorbent to remove fluoride. MAAA, which was fabricated by calcining magnesium hydroxide-impregnated alumina at 450 °C, has a much higher capability for the adsorption of fluoride than AA. More than 95% fluoride removal occurred within a contact time of 180 min and neutral pH. The production of Mg(OH)<sub>2</sub> with the help of interacting magnesia with water was proposed for adsorption of fluoride. The fluoride ions in the polluted water substituted the hydroxyl ions in the brucite crystal lattice during the production of Mg(OH)<sub>2</sub> without disrupting the crystal structure of the molecule. According to the Sips equation, the maximum adsorption capacity of MAAA for fluoride removal was 10.12 mg g<sup>-1</sup>. The pH range of 5.0–7.5 was optimal for fluoride elimination. Higher bicarbonate and sulfate concentrations lowered the fluoride adsorption capability. As an eluent, a 2% sodium hydroxide solution was used to regenerate the fluoride-bearing MAAA.

Table 1 shows a comparison of several aluminum-based adsorbents for the removal of fluoride under ideal experimental circumstances. Based on physical factors that impact the complicated chemistry of fluoride in water, the performance of different adsorbents may vary.

**6.1.6.2 Calcium-based adsorbent.** Owing to the high affinity of fluoride together with its biocompatibility in the human body, several researchers have looked at calcium-based adsorbents to remove fluoride.<sup>240</sup> Gandhi *et al.*<sup>241</sup> investigated chalk powder as a fluoride adsorbent. Due to its high porosity, chalk powder was selected as an adsorbent. The adsorption of fluoride

on the chalk powder showed linear behavior for the concentration of fluoride, adsorbent dosage, and contact duration in batch adsorption investigations. The kinetic isotherms showed the pseudo-first-order and second-order models, and the adsorption data fitted well with the Langmuir and Freundlich models. In nature, the adsorption process is exothermic and spontaneous. The efficacy of stimulated and conventional quick lime in the forms of adsorbents to remove fluoride was also examined.<sup>242</sup> When the original fluoride content was 50 mg L<sup>-1</sup>, the fluoride removal from the synthetic solution was 80.6% under the optimal conditions. According to the Langmuir model, the best adsorption efficiency for fluoride on activated quick lime was noted to be 16.67 mg g<sup>-1</sup>. According to the XRD examinations and SEM graphs, the elimination of fluoride was primarily because of chemisorption and precipitation. PO<sub>4</sub><sup>3-</sup> > SO<sub>4</sub><sup>2-</sup> > NO<sub>3</sub><sup>-</sup> were the anions that decreased the fluoride adsorption in that order. Gogoi and Dutta<sup>243</sup> transformed limestone powder hydrothermally using phosphoric acid. The FTIR and XRD measurements revealed that hydroxyapatite (HAP) was produced during the hydrothermal treatment. The hydrothermally treated adsorbent had an adsorption capability of 6.45 mg g<sup>-1</sup>. The isotherm model was used for governing the process through physical adsorption on interacting HAP to fluoride ions. According to the data, second-order kinetics was observed. The adsorption process proven to be spontaneous, endothermic, and irreversible according to the thermodynamic analysis. Jayarathne *et al.*<sup>244</sup> employed natural apatite for the adsorption of fluoride. The pH of the adsorption method was found to be very important, and the ideal pH for the maximum removal was found to be 6. The adsorption increased with an increase in adsorbent dosage due to the increase in the number of adsorbent sites, which is also illustrative. With a contact time of 10 min, the maximum adsorption was obtained at pH 6 for a solution containing 15 mg L<sup>-1</sup> fluoride. The Langmuir model was well-suited to fit the adsorption data, which indicated an adsorption capacity value of 0.212 mg g<sup>-1</sup>. Pseudo-second order kinetics were seen in the experimental data.

Table 2 shows a comparison of several calcium-based adsorbents for fluoride removal under ideal experimental circumstances. Based on the physical factors that impacted the complicated chemistry of fluoride in water, the performance of different adsorbents may vary.

**6.1.6.3 Oxide/hydroxide-based adsorbent.** According to many studies, it has been observed that metal oxides/hydroxides have a high capability for the adsorption of fluoride.<sup>257</sup> Kumar *et al.*<sup>258</sup> utilized granular ferric hydroxide (GFH) for the adsorption of fluoride. At 25 °C and pH in the range of 4–8, the most outstanding fluoride removal was 7 mg g<sup>-1</sup>. The isotherm supported the Langmuir isotherm, and the kinetic analysis indicated that pore diffusion governs the pseudo-first-order isotherm. The presence of phosphate ions had the most significant impact on the fluoride adsorption on GFH, followed by carbonate and sulfate ions. Tang and Zhang<sup>259</sup> synthesized and analyzed Ce–Fe bimetal oxides with a hierarchical pore structure and good fluoride removal efficiency. XRD, XPS, and HRTEM were used to determine the properties of the adsorbent. The maximum capability for defluoridation was observed to be







Table 1 Optimum experimental conditions of various aluminium-based adsorbents with their maximum adsorption capacities and fluoride removal efficiency

S. no.	Adsorbent	Adsorption capacity		pH	Dose [g L <sup>-1</sup> ]	Contact time (h)	Initial fluoride conc. [mg L <sup>-1</sup> ]	Langmuir adsorption	Freundlich adsorption	1 <sup>st</sup> Order model	2 <sup>nd</sup> Order model	Characterization	Removal [%]	Regeneration	Reference
		[mg g <sup>-1</sup> ]	[mg L <sup>-1</sup> ]												
1	Acidic alumina	8.4	4.4	4.5	1.5	15	Yes	No	No	No	Yes	XRD, SEM, BET, FTIR, EDAX	94	85	222
2	Alumina impregnated alginate beads	17	7.4–8.2	2	5	1–100	Yes	No	No	No	Yes	SEM, EDX, ATR-FTIR, XRD	99.9	—	226
3	Calcium aluminate material	4.37	3–11	3	24	8.9	Yes	No	No	No	Yes	XRD, SEM	85	84	227
4	Chitosan based mesoporous alumina-450	8.26	3–9	4	24	5	Yes	No	No	No	Yes	XRD, SEM, FTIR, EDAX	78	—	228
5	Copper oxide coated alumina	7.22	4–9	0.4	24	10	Yes	No	No	No	Yes	XRD, SEM	98	97	229
6	Calcium oxide loaded mesoporous alumina	137	6.8	3	8	10	Yes	No	No	No	Yes	XRD, HRTEM	90	—	230
7	Gamma alumina with magnesium oxide nanocrystals	5.6	6.3–7.3	0.5	2.33	5	Yes	No	No	No	Yes	XRD, BET, SEM, EDAX, FTIR	85	—	231
8	Hydroxyapatite modified activated alumina	14.4	8	7	8	9	Yes	Yes	Yes	—	—	SEM, EDX, FTIR	—	—	232
9	Lanthanum-impregnated activated alumina	16.9	7.6–8.6	1	—	10	Yes	No	No	—	—	SEM, TEM, XRD, TGA EXAFS	77.2	98	233
10	La <sup>3+</sup> -modified activated alumina	6.7	4–8	2	2	10	Yes	No	No	No	Yes	SEM-EDS, EXAFS	—	—	234
11	Magnesium dioxide-coated alumina	0.16	7	8	3	10	Yes	No	No	No	Yes	SEM, EDAX, MMS	98	—	235
12	Modified immobilized activated alumina	0.76	7	10	1	12	Yes	Yes	Yes	—	—	—	95	85	236
13	Magnesia-amended activated alumina	10.12	7	4	3	10	—	—	No	No	Yes	XRD, SEM, EDAX, GAPA	95	90	225
14	Manganese oxide-coated alumina	2.85	4–7	5	3	—	Yes	No	No	No	Yes	XRD, BET	91	94.6	237
15	Hydrous manganese oxide-coated alumina	7.09	5.2	—	—	10–70	Yes	No	No	No	Yes	SEM, BET, XRD, FTIR, XPS, pHpzc	95	85	238
16	Aluminum-impregnated coconut fiber	3.192	5.0	0.5	1	1	Yes	Yes	Yes	Yes	Yes	XRD, FTIR, SEM	88	98	239



Table 2 Optimum experimental conditions of various calcium-based adsorbents with their maximum adsorption capacities and fluoride removal efficiency

S. no.	Adsorbent	Adsorption capacity				Dose [g L <sup>-1</sup> ]	Contact time (h)	Initial fluoride conc. [mg L <sup>-1</sup> ]	Langmuir adsorption	Freundlich adsorption	1 <sup>st</sup> Order model	2 <sup>nd</sup> Order model	Characterization	Removal [%]	Regeneration	Reference
		[mg g <sup>-1</sup> ]	pH	[g L <sup>-1</sup> ]	[mg L <sup>-1</sup> ]											
1	Quick lime	16.67	12.71	5	1.25	50	Yes	No	No	Yes	No	XRD, SEM, BET	80.6	6	242	
2	Ca-deficient hydroxyapatite	26.11	4-7	—	—	—	Yes	No	No	No	Yes	BET, SEM, EDS, XRD, UV-Vis	85	—	245	
3	Hydroxyapatite	4.7	5-7.3	0.1	16	—	No	Yes	Yes	No	Yes	XRD, SEM, IRS	96	50	246	
4	Glass derived hydroxyapatite	17.34	6.72	5	12	100	No	Yes	Yes	No	Yes	XRD, SEM, IRS	96.6	—	247	
5	Aluminum modified hydroxyapatite	32.57	5	0.5	—	10	Yes	No	No	No	Yes	XRD, TEM, FTIR	75	—	248	
6	Bone char	2.8	6	0.6	—	2	Yes	Yes	Yes	Yes	Yes	—	—	—	249	
7	Crustacean derived calcium phosphate systems	18.2	0.2	2	180	5	Yes	Yes	Yes	Yes	Yes	FTIR, XRD	92	—	250	
8	Gypsiferous limestone	1.07	3-5	15	12	11.28	Yes	No	No	Yes	No	—	89	86	251	
9	Charred beef shoulder blade bones	3.15	—	8	3	10	No	Yes	Yes	No	Yes	—	60.27	—	252	
10	Natural crystalline apatite	0.212	6	—	0.166	15	Yes	No	No	No	Yes	FTIR, XRD, XRF	65	—	244	
11	Hydroxyapatite (Hap)	3.12	4.16	0.28	1.5	20	Yes	Yes	Yes	No	Yes	FTIR, XRD, pHpc	86.34	—	253	
12	Hydroxyapatite (HAP)	12.4	12.5	4	4	4.6	Yes	Yes	Yes	—	—	—	94.5	—	254	
13	Magnesium-incorporated hydroxyapatite	1.16	7	10	3	10	Yes	No	No	No	Yes	FTIR, XRD, TEM, EDX	94.5	91	255	
14	Ce-Zr oxide nanospheres encapsulating calcium alginate beads	137.6	7	0.5	4	10	Yes	Yes	Yes	No	Yes	FTIR, XPS, XRD, SEM, TEM	78	63	256	

Table 3 Optimum experimental conditions of various oxide/hydroxide-based adsorbents with their maximum adsorption capacities and fluoride removal efficiency

S. no.	Adsorbent	Adsorption capacity		pH	Dose [g L <sup>-1</sup> ]	Contact time (h)	Initial fluoride conc. [mg L <sup>-1</sup> ]	Langmuir adsorption	Freundlich adsorption	1 <sup>st</sup> Order model	2 <sup>nd</sup> Order model	Characterization	Removal [%]	Regeneration	Reference
		[mg g <sup>-1</sup> ]	[mg g <sup>-1</sup> ]												
1	Aluminium hydroxide	7	—	1.6	1	1	20	No	Yes	No	Yes	—	90	—	261
2	Iron-aluminium-cerium trimetal oxide	178	7	1.5	—	—	84.5	Yes	No	—	—	ASAP, XRD	90	97	262
3	Aluminium (hydro)oxide	4.10	6	2	2	2	6	Yes	Yes	Yes	Yes	EXD, XRD, FTIR, SEM	98	97.36	263
4	Hydrous iron-tin mixed oxide	10.47	6.4	0.8	2	2	25	Yes	No	No	Yes	FTIR, XRD	95.36	75	264
5	Hydrated iron-aluminium-chromium ternary mixed oxide	31.89	5.6	4	1.5	1.5	10	Yes	No	No	Yes	FTIR	95.7	91	265
6	Lithium-aluminium layered double hydroxide	47.24	7	2	1	1	20	Yes	Yes	No	Yes	TEM, XRD, TGA	97.36	—	266
7	Crystalline titanium dioxide	15.35	7–8	1	3	3	5	Yes	No	No	Yes	XRD, SEM	75	79	267
8	Hydrous bismuth oxide	1.93	4–12	50	3	3	10	Yes	No	No	Yes	XRD, FTIR, SEM	65	—	268
9	Mg–Cr–Cl layered double hydroxide	13.15	6	6	0.66	10	10	Yes	No	No	Yes	FTIR, XRD, SEM	88.5	2	269
10	Alumina-magnesia mixed hydroxide	5.62	7	6	24	24	5.13	Yes	No	No	Yes	—	90	98	270
11	ZnCr <sub>3</sub> -NO <sub>3</sub> layered double hydroxide	31	3–10	1	3	3	10	Yes	No	No	Yes	XRD, FTIR	95	80	271
12	Aluminium oxide-manganese oxide	18.6	5–7	4	2	2	—	No	Yes	No	Yes	XRD, TGA, SEM	96.4	—	272
13	Calcined layered double hydroxide	79.37	6–7	0.5	1	10	10	Yes	No	—	—	XRD	99.2	—	273
14	Non-thermal plasma modified Ni–Al layered double hydroxide	93.41	3–7	2	0.5	0.5	60	—	—	No	Yes	XRD, FTIR, TG-DTA	37.12	—	274
15	Calcium-aluminium-lanthanum composite	29.30	6.8	1	3	3	10	Yes	No	No	Yes	XRD, FTIR, SEM, XPS	96.65	—	275
16	Trimetal oxide	2.19	7	1	1.16	10	10	Yes	No	No	Yes	XRD, XRF	78	—	276
17	Fe <sub>3</sub> O <sub>4</sub> @LDH/poly	167.62	7.8	0.005	0.66	10	10	Yes	Yes	Yes	Yes	FTIR, XRD, SEM	—	—	277





Table 3 (Contd.)

S. no.	Adsorbent	Adsorption capacity [mg g <sup>-1</sup> ]	pH	Dose [g L <sup>-1</sup> ]	Contact time (h)	Initial fluoride conc. [mg L <sup>-1</sup> ]	Langmuir adsorption	Freundlich adsorption	1 <sup>st</sup> Order model	2 <sup>nd</sup> Order model	Characterization	Removal [%]	Regeneration	Reference
18	β-Cyclodextrin modified hydrous zirconium oxide	31.45	5.5	0.5	2	10	Yes	No	No	Yes	FTIR, XRD	94	95	278
19	Fe-Mg-La trimetal composite	270	4	0.1	5	10	Yes	No	—	—	FTIR, XPS	85	96.7	279
20	Micron-sized magnetic adsorbent	41.8	3	1	2	4	Yes	No	No	Yes	SEM, XPS	92.4	96.8	280
21	Calcined Mg-Al layered double hydroxide	55.22	7	4	2.5	10	No	Yes	No	Yes	SEM, XRD, FTIR, TG-DTA, TEM	93.92	86	281
22	Fe-modified clinoptilolite	1.72	11	2	5	50	Yes	Yes	Yes	Yes	XFS, SEM, XRD, BET	80.23	—	282
23	Goethite anchoring regenerated graphene oxide	24.67	10.90	—	1	50	Yes	No	No	Yes	XPS, FTIR, XRD, FTIR, SEM, TEM	87.4	95	283

60.97 mg g<sup>-1</sup>. The Langmuir model explained the experimental data well, and the kinetic analysis showed the pseudo-second-order model. Carbonate ions had the most significant impact on the adsorption followed by nitrate, bicarbonate, sulfate, and chloride ions. Hussain *et al.*<sup>260</sup> investigated the effectiveness of the fluoride adsorption by co-precipitated Mg(III)-Al(III)-La(III) triple-metal hydrous oxide. In the pH range of 2–12, the adsorbent effectively removed 98.28% of fluoride from a fluoride solution of 20.66 mg L<sup>-1</sup>. The adsorption was endothermic and suited the Langmuir model. Also, the adsorption followed the pseudo-second-order model. The adsorbent could be readily regenerated with a combination of methanol and HCl until 95.71% recovery.

Table 3 shows a comparison of several oxide/hydroxide-based adsorbents for fluoride removal under ideal experimental circumstances. Based on the physical factors that impacting the complicated chemistry of fluoride in water, the performance of different adsorbents may vary.

**6.1.6.4 Carbon-based adsorbents.** Carbon-based adsorbents have been explored to remove fluoride given that carbon possesses a strong affinity towards fluoride anions. Karthikeyan and Elango<sup>284</sup> utilized graphite in adsorbents to remove fluoride from solution. The optimum fluoride adsorption was achieved at a low pH value and high temperature. The adsorption data fit the Freundlich and Langmuir models, and the pseudo-first-order model was observed. According to the thermodynamics, the adsorption is an exothermic reaction. Zirconyl-impregnated activated carbon was created by Joshi *et al.*<sup>285</sup> Lapsi (*Choerospondias axillaris*) seed stone provided the activated carbon. The maximum defluoridation was discovered in the pH range of 3–4 after a 3 hour contact duration. The adsorption isotherm results matched well with the Langmuir isotherm model. Said and Machunda<sup>286</sup> investigated the defluoridation of water using activated carbon from coconut shells. Batch studies were performed to determine how different adsorbents affected the adsorption efficiency. The acidic range favored adsorption, with the highest adsorption of 58.4% found at a pH value of 2. The Freundlich and Langmuir models were an excellent match to explain the fluoride adsorption on activated carbon from coconut shells.

Table 4 shows a comparison of several carbon-based adsorbents for fluoride removal under ideal experimental circumstances. Based on the physical factors that impact the complicated chemistry of fluoride inside water, the performance of different adsorbents may vary.

**6.1.6.5 Natural material-based adsorbents.** Various natural materials have been employed as adsorbents to remove fluoride from solution, including dirt, chitosan, clay, and zeolite due to their large surface area, mechanical and chemical durability, molecular sieve arrangement, and diverse range of surface and structural features.<sup>307</sup> The ability of clay and its minerals to eliminate fluoride has been widely demonstrated by several researchers. According to Peter,<sup>308</sup> bauxite-rich soil possesses a higher adsorption efficiency compared to kaolinite-rich soil. In both kaolinite-rich and bauxite-rich soil, activated soil was showed added extraordinary adsorption ability compared to non-activated soil. At low fluoride concentrations, bauxite-rich



soil was more efficient than at high fluoride concentrations. Due to the enhanced and stabilized positive sites, magnesium-enriched clay has higher adsorption effectiveness than raw clay, according to Atasoy and Sahin.<sup>309</sup> Also, calcination changes the properties of clay.

Table 5 shows a comparison of several natural-based adsorbents for the removal of fluoride under ideal experimental circumstances. Based on the physical factors impacting the complicated chemistry of fluoride in water, the performance of different adsorbents may vary.

**6.1.6.6 Agriculture and biomass-based adsorbents.** In recent years, products of agriculture and biomass have been extensively employed by scientists to remove fluoride from water. These materials are widely employed in practice because of their widespread accessibility, natural biodegradability, and commercial viability. Several studies were carried out to modify plant-based adsorbents through an appropriate chemical to improve fluoride removal efficiency. Singh *et al.*<sup>339</sup> examined the fluoride adsorption capability of sugarcane bagasse in a batch adsorption experiment. The contact duration, pH, temperature, adsorbent dosage, and starting concentration of fluoride were all investigated. The highest fluoride adsorption was determined to be 4.12 mg g<sup>-1</sup>. The adsorption rate of fluoride was highly characterized by the Redlich–Peterson isotherm theory and the pseudo-second-order equation. The thermodynamic parameter indicated that the adsorption procedure is endothermic. For the defluoridation of drinking water, Pandey *et al.*<sup>340</sup> produced biomasses from *Tinospora cordifolia*. The pH value of 7, the adsorbent dosage of 7 g/50 mL, and 120 minutes of contact duration were determined to be the best conditions. The Langmuir and Freundlich isotherms accurately reflected the experimental results. Fluoride binding was found in several frequency ranges using FT-IR spectrum analysis.

Table 6 shows a comparison of several agricultural and biomass-based adsorbents for fluoride removal under ideal experimental circumstances. Based on the physical factors that impact the complicated chemistry of fluoride in water, the performance of different adsorbents may vary.

**6.1.6.7 Building material-based adsorbents.** Several studies have investigated the fluoride removal capacity of various construction materials, including brick powder, cement, fly ash, sand, and concrete, with and without treatment and modification. The capacity of hydrated cement for eliminating fluoride from drinkable water was investigated by Bibi *et al.*<sup>362</sup> With a 60 minute contact period and a 30 g L<sup>-1</sup> adsorbent dosage, the adsorbent was shown to have an 80% fluoride removal efficacy at pH 7. 1.72 mg g<sup>-1</sup> was determined as the maximum fluoride absorption. Because the adsorbent is affordable, no regeneration was necessary. Using batch adsorption tests, Kagne *et al.*<sup>363</sup> examined the potential of hydrated cement to remove fluoride from aqueous solution at different intervals. They discovered that the hydrated cement removed considerable amounts of fluoride in a broad pH range (3–10). The linear transformed Freundlich and Langmuir isotherms were successfully fitted by the experimental data collected from the batch adsorption studies. Togarepi *et al.*<sup>364</sup> carried out an experiment comprised of sand to remove fluoride. It was treated both chemically and

thermally for use as an adsorbent. Different parameters were examined by performing batch experiments including pH, initial fluoride, and adsorbent dose. It was observed that the experimental data of the activated sand fitted well with the Freundlich isotherm and the multilayer sorption.

Table 7 shows a comparison of several building-based adsorbents for the removal of fluoride under ideal experimental circumstances. Based on the physical factors that impacted the complicated chemistry of fluoride in water, the performance of different adsorbents may vary.

**6.1.6.8 Nanomaterial-based adsorbents.** The advancement of nanotechnology in the present scenario has inspired researchers. The area of nanotechnology involves the synthesis, development, and classification of nano-sized particles, generally with a size of 1 to 100 nm, which has been found to be a highly active avenue for researcher to purify contaminated water. Patel *et al.*<sup>377</sup> blended CaO nanoparticles through the sol-gel method. The adsorption capacity was 92% with 0.6 g L<sup>-1</sup> dose, 30 min contact duration, and 100 mg L<sup>-1</sup> initial fluoride concentration. The Freundlich model and pseudo-first-order model best-fit the experimental results. The reaction was spontaneous and endothermic, according to the thermodynamic parameters. Fluoride absorption is most likely caused by an ion-exchange process, which produces CaF<sub>2</sub> by substituting OH<sup>-</sup> ions with F<sup>-</sup> ions from CaO nanoparticles. On the addition of 0.1 M NaOH or 0.1 M HCl, 95% desorption can be attained due to the adjusted pH range between 2 and 12. Devi *et al.*<sup>378</sup> explored nano-MgO for the adsorption of fluoride. On employing a 0.6 g L<sup>-1</sup> dose, the adsorption efficacy reached 90% for nano-MgO. The availability of OH<sup>-</sup> ions influences the fluoride adsorption through nano-MgO. The adsorption of fluoride was negligible owing to the variations in pH and the occurrence of other ions. It was also observed that the equilibrium data followed the Freundlich model rather than the Langmuir model, suggesting that the multilayer adsorption followed the pseudo-second-order model. The regeneration study showed that 1 M HCl was the appropriate material for fluoride removal with a desorption capacity of 95% and 2 M NaOH had 25% adsorbent regeneration. Kumar *et al.*<sup>379</sup> performed batch experiments involving the parameter pH, co-existing anions, temperature, and contact time to synthesize nano-alumina for fluoride removal efficiency. XRD, EDX, FTIR, SEM were used to analyze the structural characteristics of nano-alumina. The obtained results clarified that at 25 °C and pH of 6.15, fluoride of 14 mg g<sup>-1</sup> was removed. The adsorption process revealed a pseudo-second-order model and followed the Langmuir model. In the presence of carbonate, sulfate and phosphate ions, the adsorption efficacy of nano-alumina was enhanced.

Table 8 shows a comparison of several nanomaterial-based adsorbents for the removal of fluoride under the ideal experimental circumstances. Based on the physical factors that impact the complicated chemistry of fluoride in water, the performance of different adsorbents may vary.

The following sections examine the various strategies for removing F<sup>-</sup>, and Table 9 summarises the areas of interest and limitations of each methodology. The following observations





Table 4 Optimum experimental conditions of various carbon-based adsorbents with their maximum adsorption capacities and fluoride removal efficiency

S. no.	Adsorbent	Adsorption capacity		Dose [g L <sup>-1</sup> ]	Contact time (h)	Initial fluoride conc. [mg L <sup>-1</sup> ]	Langmuir adsorption	Freundlich 1 <sup>st</sup> Order model	2 <sup>nd</sup> Order model	Removal [%]	Regeneration	Reference	
		[mg g <sup>-1</sup> ]	pH										Characterization
1	KMnO <sub>4</sub> modified activated carbon derived from steam pyrolysis of rice straw	23.3	2	1.5	3	20	Yes	Yes	No	Yes	100	—	287
2	Waste carbon slurry	4.86	—	1	—	15	Yes	No	No	Yes	—	92	288
3	Zirconium ion-impregnated coconut fiber carbon	1.95	4	20	6	20	Yes	No	No	Yes	SEM, EDX, BET, pHpzc	100	289
4	Zirconium-impregnated coconut shell carbon	0.99	4	1	6	10	Yes	No	No	Yes	EDX, BET	100	290
5	Zirconium-impregnated cashew nut shell carbon	1.83	7.6	0.015	3	3	Yes	No	No	Yes	XRD, FTIR	80.33	291
6	Activated carbon from Bermuda grass	4.702	5-5.5	12.5	1.75	3	Yes	No	—	—	—	83.77	292
7	Iron-impregnated granular ceramics	2.16	4	20	48	10	Yes	Yes	No	Yes	SEM, BET, EDX	94	293
8	Microwave assisted activated carbon derived from <i>Acacia auriculiformis</i> scrap wood	18.95	4	2	0.33	—	Yes	No	No	Yes	—	97.2	294
9	Zirconium-impregnated walnut shell carbon	6.38	3	15	3	3	No	Yes	No	Yes	XRD, SEM, EDAX	94	295
10	Carbon nanotubes/alumina	9.6	6	0.5	1.25	10.3	No	Yes	—	—	—	—	296
11	Aligned carbon nanotubes (ACNTs)	4.5	7	2	1	15	Yes	Yes	Yes	Yes	SEM, HRTEM	94	297
12	Activated bagasse carbon	1.15	6	4	1	2.5	No	Yes	No	Yes	—	57.6	298
13	Zirconium-impregnated activated carbon mixed with oxalic acid	7.40	7	—	—	40	Yes	Yes	—	—	BET, FTIR, XPS, SEM, pHpzc, XRD, DFT, ICP-OES	94	299
14	Cow dung carbon @ 500 °C	15	7.53	2	0.66	2	No	Yes	No	Yes	SEM, XRD, FTIR, EDS, pHpzc	99	300
15	Powder activated charcoal	—	2	2.0	2	—	Yes	Yes	Yes	Yes	—	94	301
16	Natural coal	5.9	4	3	1	5	Yes	No	—	—	—	82	302
17	Physically activated coal	8.36	2	3	1	5	Yes	No	—	—	—	86	303
18	Chitosan doped graphite composite (FCDGNC)	3.5	6.5	2.5	2.33	—	Yes	No	—	—	FTIR, SEM, TGA, XRD	91	304
19	Activated carbon prepared from bael shell	2.4	6	2	1	8	Yes	No	No	Yes	SEM, FTIR	52	305
20	Activated carbon derived from bark of <i>Ficus racemosa</i> plant	1.65	7	4	1	5	Yes	No	Yes	No	SEM, FTIR, EDX, BET, FESEM	88	306

Table 5 Optimum experimental conditions of various natural-based adsorbents with their maximum adsorption capacities and fluoride removal efficiency

S. no.	Adsorbent	Adsorption capacity			Initial fluoride conc.			Langmuir adsorption	Freundlich adsorption	1 <sup>st</sup> Order model	2 <sup>nd</sup> Order model	Characterization	Removal [%]	Regeneration	Reference
		[mg g <sup>-1</sup> ]	pH	Dose	Contact time (h)	[mg L <sup>-1</sup> ]	adsorption								
1	Montmorillonite	0.263	6	8	3	4	No	Yes	—	—	—	65	93	310	
2	Laterite soil	0.8461	6.8	1	—	20	Yes	No	Yes	No	XRD, SEM	80.4	80.4	311	
3	Bauxite	33.6	4	12.5	2	8	Yes	No	Yes	No	XRD, TGA	93.8	—	312	
4	Montmorillonite clay	1.836	2	70	0.83	3	Yes	No	—	—	—	97	—	313	
5	Clay soil	93.45	3	—	24	—	Yes	No	—	—	—	85	—	314	
6	Sodium activated Algerian non calcium montmorillonite clay	1.324	4	3	0.5	6	Yes	No	—	—	FTIR, XRD, BET	88	—	315	
7	Ceramic adsorbent	2.16	4–11	20	48	10	Yes	Yes	No	Yes	BET, SEM, XRD, EDS, UV-Vis	94.4	—	316	
8	Magnesium incorporated bentonite clay	2.26	3–10	3	12	5	Yes	No	Yes	No	XRD, SEM	95.47	97	317	
9	Acid treated diatomaceous earth	51.1	3.4	500	10	400	Yes	No	—	—	—	92	—	318	
10	Pumice	0.31	7	20	3	7	No	Yes	No	Yes	—	85.75	—	319	
11	Acid treated raw laterite	39.10	5	0.5	24	10	Yes	Yes	—	—	FTIR, SEM, SAA	96	96	320	
12	Pyrophyllite	2.2	4.9	4	2	10	Yes	No	No	Yes	BET, XRD, ZPC	85	—	321	
13	Kanuma mud	3.06	5–7	20	2	10	No	Yes	No	Yes	BET, TEM, EDS, BJH	90	85	322	
14	Calcined meixnerite	16.1	—	—	50	75	Yes	Yes	Yes	No	XRD, SEM	97.3	61	323	
15	Siliceous material	12.4	3.4	500	0.33	200	Yes	No	—	—	—	100	—	324	
16	Hydrogen peroxide modified pumice	11.765	6	6	2.5	10	No	Yes	No	Yes	SEM, XRD, FTIR, BET, XRF, PZC	70.8	98	325	
17	Raw bauxite	0.275	5.5	120	1.5	6.17	—	—	Yes	No	—	96.1	—	326	
18	Al <sup>3+</sup> modified bentonite clay	5.7	2–12	10	0.5	60	Yes	Yes	No	Yes	XRD, XRF, BET, EDS, CEC, PZC	99.97	—	327	
19	Calcium aluminium modified zeolite	8.03	4–8	1.5	6	10	No	Yes	No	Yes	—	96	90	328	
20	Clay mixed hydroxyapatite	18.409	6	1.25	0.5	5	No	Yes	No	Yes	—	96.5	—	329	
21	Vermiculite	2.36	4	2	1.16	4	No	Yes	No	Yes	FTIR, SEM	51	—	330	
22	Iron ore	1.72	6	5	2	14.22	No	Yes	Yes	No	XRF	89	—	331	
23	Lanthanum-impregnated bauxite	18.18	8.5	2	120	20	Yes	No	No	Yes	—	99	95	332	
24	Granular aluminium coated bauxite	0.426	2	10	176	5	Yes	No	No	Yes	SEM, XRD, EDS, XRF, BET, FTIR	94.1	—	333	
25	Chitosan iron complex	2.34	3–10	10	1.5	50	Yes	Yes	No	Yes	FTIR, SEM	90	84.3	334	
26	Brushite	36.26	5.36	1.5	2	49.06	Yes	No	No	Yes	XRD, SEM, EDX	90.83	—	335	
27	Zirconium modified zeolite	28.57	7	10	1	40	No	Yes	No	Yes	XRD, SEM, BET	97.62	—	336	
28	Mg/Ce/Mn oxide-modified diatomaceous earth	12.633	6.52	6	1	40	Yes	No	No	Yes	SEM, EDX, BET, XRD, FTIR, PZC	97.1	60.8	337	
29	Fe <sup>3+</sup> modified bentonite clay	2.91	2–10	20	0.5	10	Yes	No	—	—	XRF, XRD, PZC, CEC, BET, SEM	100	—	338	





Table 6 Optimum experimental conditions of various agricultural and biomass-based adsorbents with their maximum adsorption capacities and fluoride removal efficiency

S. no.	Adsorbent	Adsorption capacity			Initial fluoride			Langmuir adsorption	Freundlich adsorption	1 <sup>st</sup> Order model	2 <sup>nd</sup> Order model	Characterization	Removal [%]	Regeneration	Reference
		[mg g <sup>-1</sup> ]	pH	Dose	Contact time (h)	concentration [mg L <sup>-1</sup> ]	adsorption								
1	Al <sup>3+</sup> loaded saponified orange juice residue	1.03	6	1	4	0.52	Yes	No	—	—	—	FTIR	80	—	341
2	Bark of babool	1.12	8	5	8	5	Yes	No	No	Yes	—	—	77.04	—	342
3	Activated neem stem charcoal	1.27	2	5	3	2	Yes	Yes	No	Yes	—	—	94	—	343
4	Carbon obtained from pecan nut shells modified with a calcium solution extracted from egg shells	2.3	7	8	—	20	Yes	No	—	—	—	EDX, SEM, XRD	84	—	344
5	Tea-Al	13.79	4-8	2.0	2	10	Yes	Yes	Yes	Yes	—	SEM, EDS, XPS, XRD	—	—	345
6	Banana peel	1.340	6	14	1	20	Yes	No	No	Yes	—	—	94.34	—	346
7	Carbonized cattle dung (CDC)	15.0	7.53	2.0	—	2	Yes	Yes	Yes	Yes	—	SEM, BET, XRD, FTIR, elemental analyses	99	100	347
8	Palm kernel shell	285.7	7	0.2	2	100	No	Yes	No	Yes	—	FESEM-EDX, XRD, FTIR, XPS	95	—	348
9	Mechanically modified guava seeds	15.6	6	80	6	100	Yes	Yes	No	Yes	—	—	85	—	349
10	Mosambi peel powder	1.35	7	10	0.5	5	No	Yes	No	Yes	—	—	82.5	—	350
11	Restructured lignite	15.8	7.93	8	—	3	Yes	No	No	Yes	—	BET, SEM, XRD	95	—	351
12	Peepal leaf powder	2.24	7	10	0.75	20	No	Yes	—	—	—	—	85.7	—	352
13	Grape pomace	7.54	3	17.5	1	19.91	Yes	Yes	Yes	Yes	—	FTIR, SEM, EDS	—	—	353
14	Pyrolyzed <i>Delonix regia</i> pod carbon	33.34	2	15	5	2-10	No	Yes	No	Yes	—	BET, ZPC, FTIR, SEM, EDAX	97	—	354
15	Lanthanum modified carbon from <i>Sargassum</i> sp.	94.34	7	0.4	4	20	Yes	No	No	Yes	—	EDX, ZPC, XPS	90	—	355
16	Sal leaf powder	1.28	7.5	60	0.42	5	No	Yes	—	—	—	—	98.6	—	356
17	Zirconium[iv] loaded carboxylated orange peel carbon	5.605	6	0.7	0.83	10	Yes	No	No	Yes	—	FTIR, TGA, SEM, XRD	97.2	91	357
18	Pithecellobiumdulce carbon	0.81	7	3	0.66	3	Yes	No	Yes	No	—	—	81.60	—	358
19	Alkali steam-treated elephant grass	7	2-10	1.5	2.5	5	Yes	No	No	No	—	PZC, FTIR, XRD, SEM	85	—	359
20	Carbonised <i>Punica granatum</i> carbon	1.68	7	0.75	1.25	2-10	No	Yes	—	—	—	—	78.1	—	360
21	<i>Padina sanctae crucis</i> algae	1.65	7	48	0.08	8	No	Yes	No	Yes	—	FTIR	97	—	361



Table 7 Optimum experimental conditions of various building-based adsorbents with their maximum adsorption capacities and fluoride removal efficiency

S. no.	Adsorbent	Adsorption capacity [mg g <sup>-1</sup> ]		pH	Dose	Contact time (h)	Initial fluoride conc. [mg L <sup>-1</sup> ]	Langmuir adsorption	Freundlich adsorption	1 <sup>st</sup> Order model	2 <sup>nd</sup> Order model	Characterization	Removal [%]	Regeneration	Reference
		capacity	capacity												
1	Alum sludge	0.53	1.23	3-8	16	1	10	—	—	No	Yes	—	85	—	365
2	Broken concrete cubes	1.23	7.8	7	60	2	8	—	—	—	—	—	80	—	366
3	Surface-functionalized polyurethane foam	7.8	8.07	6.7	10	1	20	—	—	—	—	SEM, FTIR	96	96	367
4	Basic oxygen furnace slag	8.07	16.26	6-10	5	0.58	10	Yes	No	No	Yes	SEM, XRD, ICP-AES, BET	93	4	368
5	Bottom ash	16.26	10.3	6	0.7	1.75	—	Yes	No	—	—	—	83.2	—	369
6	Gas concrete	10.3	0.6	6.9	40	1	120	—	—	—	—	SEM, XPS	96	—	370
7	Zirconium hydroxide modified red mud porous material	0.6	5.15	3	—	1	20	Yes	No	No	Yes	XRD, EDX, SEM	90	90	371
8	Low weight concrete	5.15	10.86	6.9	—	1	2.5	Yes	Yes	—	—	BET	—	—	372
9	Calcium hydroxide treated fly ash	10.86	44.25	7	3	2	10	Yes	No	No	Yes	PZC	80	—	373
10	Calcinated electro coagulation sludge	44.25	10.215	6	4	2	25	Yes	Yes	No	Yes	—	99.99	—	374
11	Alumina cement granules (ALC)	10.215	0.358	7	2	—	8.65	Yes	No	—	—	—	—	—	375
12	Heat-activated Mahabir colliery shale	0.358	—	3	70	24	10	No	Yes	No	Yes	XRD, BET, SEM, PZC	88.3	0	376



Table 8 Optimum experimental conditions of various nanomaterial-based adsorbents with their maximum adsorption capacities and fluoride removal efficiency

S. no.	Adsorbent	Adsorption capacity			Initial fluoride conc.			Langmuir adsorption	Freundlich adsorption	1 <sup>st</sup> Order model	2 <sup>nd</sup> Order model	Characterization	Removal [%]	Regeneration	Reference
		[mg g <sup>-1</sup> ]	pH	Dose	Contact time (h)	[mg L <sup>-1</sup> ]	adsorption								
1	Nano-scale aluminium oxide hydroxide	3.25	5.2	5	6	13	Yes	No	No	Yes	Yes	XRD, TEM, NAD, PZC, FTIR, XPS, BET	90	97	380
2	Manganese oxide modified aluminium oxy (hydroxide)	18.62	5-7	—	—	—	Yes	Yes	Yes	Yes	Yes	SEM, XRD	94.8	86.2	381
3	Nano-hydroxyapatite	2.30	5	4	1.66	10	Yes	Yes	No	Yes	Yes	XRD, FTIR, TEM, SEM	91	—	382
4	Nano-sized goethite	59	—	1	2	30	No	Yes	No	Yes	Yes	XRD, TEM	49	—	383
5	CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	37.0	3-10	2	24	120	No	Yes	Yes	Yes	Yes	—	—	—	384
6	Multi-walled carbon nanotubes	3.5	5	—	0.3	—	No	Yes	—	—	—	—	94	—	385
7	Zirconia/multi-walled carbon nanotubes	4.94	3	2	5	10	Yes	No	—	—	—	EDX, SEM, FTIR, BET, XPS	99.67	Small regeneration	386
8	Single-walled carbon nanotubes	3	5	0.5	1.16	1	—	—	—	—	—	—	58	—	387
9	Iron-titanium oxide	47	—	1	12	50	Yes	No	—	—	—	EDS, BET, SEM	98.7	—	388
10	Mn-Ce powder	79.5	6	0.01	3	6	—	—	—	—	—	FTIR, XPS	90	92	389
11	Iron oxide-hydroxide nanoparticles	16.7	7.28	1	3	10	No	Yes	—	—	—	—	80	76	390
12	Magnesium oxide coated magnetite nanoparticles	10.96	6	2	2.5	13.6	Yes	No	No	Yes	Yes	SEM, EDAX	98.6	—	391
13	Nano-scale aluminium oxide hydroxide	11.88	7	1.6	1	20	Yes	No	No	Yes	Yes	XRD, TGA	95	—	392
14	Nanoscale zero-valent iron	18.91	4	0.6	0.58	—	No	Yes	—	—	—	—	84	—	393
15	Hybrid Fe-Ce-Ni nanoporous adsorbent	285.7	7	0.4	0.5	10	No	Yes	No	Yes	Yes	—	98.7	95	394
16	MgO nanoparticles loaded with mesoporous alumina	37.35	6.8	3	8	30	Yes	Yes	No	Yes	Yes	XRD, NAD, TEM, BET, BJH, HRTEM, EDS, PZC	90	—	395
17	Cupric oxide nanoparticles	357	5	0.05	1.33	20	No	Yes	No	Yes	Yes	—	89	—	396
18	Nanoparticles of gamma alumina	14	7	0.1	1.5	—	Yes	No	No	Yes	Yes	TGA, DSC, XRD, FESEM, FTIR, BET, SEM	85	—	397





Table 8 (Contd.)

S. no.	Adsorbent	Adsorption capacity [ $\text{mg g}^{-1}$ ]		pH	Dose	Contact time (h)	Initial fluoride conc. [ $\text{mg L}^{-1}$ ]	Langmuir adsorption		Freundlich adsorption		1 <sup>st</sup> Order model	2 <sup>nd</sup> Order model	Characterization	Removal [%]	Regeneration	Reference
		$q_m$	$K_L$					Yes	No	Yes	No						
19	Nano-sized hydroxyapatite on to graphene oxide seeds	44.06	3-7	0.5	0.42	50	No	Yes	Yes	No	Yes	No	Yes	XRD, TEM, SEM, EDAX, FTIR	96.3	95	398
20	Nano gamma alumina	32	4	1	1	10	No	Yes	Yes	No	Yes	No	Yes	XRD, BET, SEM	96	98	399
21	Single-walled carbon nanotubes	2.4	5	0.5	0.5	1	No	Yes	Yes	No	Yes	No	Yes	SEM, BET, TEM, XRD, FTIR	58	—	400
22	HA-multi-walled carbon nanotubes	39.22	7	0.25	3	5	Yes	Yes	Yes	No	Yes	No	Yes	SEM, TEM, XRD, BET, FTIR	—	—	401
23	Single-walled carbon nanotubes	16.63	6	0.6	0.42	1	Yes	No	No	No	Yes	No	Yes	—	100	—	402
24	Trinitate nanotubes	58	2	1	2	10	Yes	No	No	No	Yes	No	Yes	—	95	—	403

were concluded regarding the different methodologies for fluoride removal based on the literature reviewed.

(1) A perusal of the above-mentioned table shows that adsorption gives favorable results in efficiency, technology, and cost, but the main issue is the dumping of the sludge generated in the process.

(2) The ion-exchange method removes fluoride very efficiently, but the treated water is found to have a high chloride residue, and this method is also expensive.

(3) The coagulation/precipitation technique has the limitation of fluoride removal of up to 33% and also produces a large quantity of residue, having an excess amount of residual aluminum.

(4) Reverse osmosis and nanofiltration techniques have higher efficiency for fluoride removal, but they are expensive and few essential ions are removed.

(5) The electrocoagulation technique is the most suitable for removing fluoride if the above-mentioned issues are considered, but the continuous supply of power required is one of its drawbacks.

(6) In the last few years, the adsorption technique for the removal of fluoride has attracted significant attention due to the very high adsorption power shown by some of the adsorbents, but the main issue is to choose an appropriate adsorbent because commonly, a particular adsorbent gives excellent adsorption in the laboratory but simultaneously fails in the field.

(7) Lastly, it should be noted that every technique has limitations, and hence a single technique is not suitable for all countries because different countries have different concentrations of fluoride and other ions present in their groundwater.

A broad overview of the available technologies for fluoride removal and the advantages and limitations of each one were presented based on a literature survey and the experiments conducted in the laboratory with several processes. It has been concluded that the selection of the treatment process should be site-specific according to the local needs and prevailing conditions given that each technology has some limitations and no one process can serve this purpose in diverse conditions.

## 6.2 Defluoridation through biological mediators

**6.2.1 Biosorption.** Because of the constraints associated with traditional defluoridation approaches, microbial treatment or biosorption of  $\text{F}^-$  has become an economically feasible and ecologically beneficial alternative in recent years.<sup>404</sup> Numerous skeletal fluorosis adsorbents have been created for groundwater defluoridation, which can be divided into several categories, including bacteria, algae, fungus, and agricultural goods.<sup>405</sup> There has been a constant increase in the interest in overcoming the many technological challenges preventing biosorption systems from being commercially viable. The cost-effectiveness, availability, practicality, and defluoridation efficiency of a specific type of bio adsorbent play a role in its selection.<sup>404</sup> The contaminants linked to biomass are often eradicated, and the bio-adsorbents are repeatedly rejuvenated.<sup>405</sup> Granular bio-adsorbents are helpful because they work

Table 9 Various methods for F<sup>-</sup> removal and their advantages and disadvantages

Method	Advantages	Disadvantages
Adsorption	<ul style="list-style-type: none"> <li>• Cost effective</li> <li>• Higher accessibility</li> <li>• Easy operation</li> <li>• Large number of adsorbents</li> <li>• Locally available and cheap</li> </ul>	<ul style="list-style-type: none"> <li>• To achieve good and adjustment of pH is required</li> <li>• Fluoride adsorption are sometime hundred due to some other ion present</li> <li>• Reduce in removal % of regenerated adsorbent</li> <li>• Interference of other inorganic ions</li> <li>• Treated water comprises greater total dissolved solids (TDS)</li> </ul>
Ion exchange	<ul style="list-style-type: none"> <li>• High efficiency</li> <li>• Removal efficacy up to 95%</li> <li>• Colour and taste of water continue complete</li> </ul>	<ul style="list-style-type: none"> <li>• Costly</li> <li>• Easy exposed to interfering ions (bicarbonate, sulphate, chloride <i>etc.</i>)</li> <li>• Filter media to replace after multiple recycle, presence of toxic solid waste used filter media, development of toxic liquid waste due to the regeneration of media, efficiency depends to large extent on pH</li> </ul>
Coagulation/precipitation	<ul style="list-style-type: none"> <li>• Highly effective and efficient process</li> <li>• Low running cost</li> <li>• Efficiency is high</li> <li>• Chemical used are available commercially</li> <li>• Work at domestic and community level</li> <li>• Simple design</li> <li>• Simple operation process</li> </ul>	<ul style="list-style-type: none"> <li>• Treated water becomes acidic</li> <li>• Treated water exhibits greater chloride concentration</li> <li>• Costly and largely depends on the co-ion and also pH of water</li> <li>• High amount of residual aluminum obtained</li> <li>• Sludge obtained contain toxic aluminum fluoride complex</li> <li>• Large amount of water is retained and hence dewatering is before disposal</li> <li>• High chemical dosages</li> </ul>
Reverse osmosis	<ul style="list-style-type: none"> <li>• Quick regeneration of membrane</li> <li>• <math>N &gt; 90\%</math> helping in eliminating other dissolved solids also wide range of pH</li> <li>• Chemical process is not used</li> <li>• Work under wide range of pH</li> <li>• No chemical assist</li> </ul>	<ul style="list-style-type: none"> <li>• High cost</li> <li>• Saline solution is used to treat water</li> <li>• Salt may be creating issue</li> <li>• Valuable mineral is needed after treatment for demineralization</li> <li>• Needs pH enhancement</li> </ul>
Nano-filtration	<ul style="list-style-type: none"> <li>• No chemical is used</li> <li>• Productive is very high</li> <li>• No ion interference is noted</li> <li>• Divider for organic micro pollutant</li> <li>• Inorganic toxic suspended solid</li> </ul>	<ul style="list-style-type: none"> <li>• High cost</li> <li>• Issue of membrane degradation scaling and fouling</li> <li>• Some ions helpful in ordinary development also get removed</li> <li>• May necessitate remineralisation of treated water</li> <li>• Discards all vital minerals</li> </ul>

similarly to ion exchange resins.<sup>406</sup> Non-living algal biomass with more excellent F adsorption capabilities, such as *Ulva fasciata*,<sup>407</sup> *Spirogyra* IO2,<sup>408</sup> *Spirogyra* IO1,<sup>409</sup> and *Nostoc* sp. BTA394 (ref. 410) has been observed. Dead biomass is preferable over live microbes because it requires less care and nutrients.<sup>411</sup> Although Mukherjee *et al.*<sup>410</sup> employed live *Nostoc* sp. (BTA934) microalgae to remove fluoride, defluoridation by utilizing live microalgal species is uncommon.

**6.2.2 Bioremediation.** Bioremediation of F<sup>-</sup> utilizing bacterial strains is still in progress.<sup>410</sup> Different resistance mechanisms, namely bioaccumulation and biotransformation, allow some bacterial species to tolerate greater F<sup>-</sup> concentrations.<sup>405</sup> However, there are few reports on the possible bioremediation of F utilizing live bacterial cells. *Acinetobacter* sp. RH5, *Pseudomonas aeruginosa*, and KX926492 are the bacterial strains employed for the successful defluoridation of wastewater.<sup>412</sup> The complexation of the F<sup>-</sup> ion may be enabled by critical functional elements in biomass molecules, such as acetamido and sulfhydryl carboxyl.<sup>413</sup> Active absorption of F<sup>-</sup> ions by ionophores is followed by creating organic/inorganic fluoro-complexes within the cytoplasm during defluoridation with bacteria. F<sup>-</sup> ions are transported to the cell vacuole, and deposited as permitted F<sup>-</sup> complexes or ions in the second step.<sup>405</sup> Both the biomass production and the specific F<sup>-</sup> absorption rate are affected by the concentration of F<sup>-</sup> ions.<sup>414</sup>

Fungi are more suitable for defluoridation than bacteria because they have shorter multiplication cycles and more natural growing procedures. Fungal biomass has a high

proportion of cell-wall components, which increase its surface area and diversity of functional groups, supporting its bioadsorption capacity.<sup>415</sup> The fungal classes with defluoridation possibly comprise *Pleurotus ostreatus* 1804.<sup>416</sup>

Defluoridation potential has also been boosted by the waste produced and processed from agricultural items such as fruits and crops.<sup>417</sup> Agricultural leftovers have unique chemical compositions including lipids and hemicellulose and are cost-effective and ecologically friendly. Some functional groups in these polymers promote F-binding through biosorption.<sup>405</sup>

**6.2.3 Phytoremediation.** Phytoremediation is a low-cost and efficient remediation approach for decontaminating soils from contaminants.<sup>418</sup> According to the suggestion by Agarwal and Chauhan,<sup>419</sup> the highest bioaccumulation of F<sup>-</sup> of 9.948 mg kg<sup>-1</sup> was found in the leaves of *Hordeum vulgare* diversity RD 2052, while the lowest bioaccumulation of F<sup>-</sup> of 6.302 mg kg<sup>-1</sup> was found in the grains of *Hordeum vulgare* diversity RD 2052 in the presence of 18 mg kg<sup>-1</sup> NaF.

Boukhris *et al.*<sup>420</sup> found that the fluoride accumulation in aerial native plants in the soil was more in coastal superphosphate factories, which was in the range of 37 and 360 mg kg<sup>-1</sup>. *Spirodela polyrhiza* was shown to remove 12.71–19.87% F<sup>-</sup> from 3 mg F<sup>-</sup> L<sup>-1</sup> polluted water by Karmakar *et al.*<sup>421</sup>

### 6.3 Integrated methods

Integrated methods, which combine two or more procedures to improve the F<sup>-</sup> decontamination efficiency, are gaining traction



compared to employing a single technology. When the sprouting root of *Amaranthus* was submerged in F<sup>-</sup>-contaminated water containing 0.1 mM, 1 mM, and 10 mM FeCl<sub>3</sub>, Kopenja *et al.*<sup>422</sup> showed an increase in F coagulation. After only 12 hours, the removal efficiency was noted to be 20%, 37%, and 40%, respectively, but it was just 10% without the plant. The development of Fe(III) oxide coating on the root surface may improve the removal effectiveness by containing organic molecules and CO<sub>2</sub>. When altered with various microbial consortiums, *P. juliflora* was clarified to have a bioaccumulation factor in the range of 0.12 to 3.3.<sup>418</sup> From a starting concentration of 20 mg L<sup>-1</sup>, the SABA approach employing leaves and *Citrus limetta* peels together with the bacteria lowered the F level below 1.5 mg L<sup>-1</sup>.<sup>423</sup>

## 7. Regeneration issue

Further regeneration studies are needed to recover the adsorbent under field settings and increase the economic viability of the process. Based on this review, four technological adsorption techniques can be considered, as shown in Fig. S7,<sup>†</sup> including nano-surface effect, structural memory effect, anti-competitive adsorption, and ionic sieve effect. These four methodologies for designing adsorbents may considerably increase the fluoride removal efficiency in water and give guidelines for developing novel efficient fluoride removal technologies.

## 8. Sustainable technologies for the removal of fluoride

A worldwide challenge prevailing nowadays is the unavailability of safe water for consumption. The goal was to halve the “environmental sustainability” by the end of 2015 by providing safe and pure water for drinking. In this case, to provide safe, clean, high-quality water, the 6th United Nations Sustainable Development Goal (UNSDG) was aimed at 2.8 billion people by the year 2030. It was found that a minimum sustainable option was present for removing fluoride in developing countries given that they are concerned about its high impact. The WHO has limited the minimum concentration level of fluoride in drinking water to 1 mg L<sup>-1</sup> to prevent dental decay, a deliberating topic and matter of concern.<sup>424</sup>

Fluoride-containing sludge is manufactured from municipal and industrial wastewater. Water fluoridation can lead to fluoride levels in the municipal wastewater treatment plant (MWTP), and it is observed that most fluoride is released from industrial wastewater.<sup>425</sup> The projection of wastewater discharge was estimated to be between 75–80% for the supplied water, which infers that the water obtained will accumulate in the wastewater treatment plant (WWTP). The above-mentioned process suggests that the fluoride level of the WWTP depends on the overall grade. The non-accumulated water is targeted as a section of run-off and pipe leaks that enter the environment without any full-fledged treatment. Later, the fluoride constrains the process of nitrification where the fluoride removal is not reported in the primary treatment phase.<sup>426</sup> The

leading cause of this action is the availability of bacteria in the anaerobic digestion, which are very sensitive towards fluoride, resulting in about 50% reduced microbial metabolism.<sup>426</sup> Therefore, it can be inferred that the level of fluoride removal in persistent pollution in conventional municipal wastewater treatment plants (CMWTP) also leads to disadvantageous effects on WWTP efficacy.

The above-mentioned industrial procedures generate fluoride as wastewater effluents. Therefore, various technologies were formulated for removing fluoride and even for its reuse. It was found that the fertilizer industries used precipitation to remove fluoride in their effluents and recovered fluoride to obtain economic welfare. Sorbents were used for water containing fluoride. The absorbent and sludge-producing water treatment were responsible for synthesizing a high quantity of waste using landfill disposal. Another method for sludge disposal besides landfill is incineration, which is responsible for sterilizing and reducing the weight and volume, and later transforming sludge into ash, basically burning substances at 1000 °C.<sup>427</sup> The substantial leaching of sewage sludge ash varies given that it contains inert waste, namely fluoride. Therefore, it is observed that highly soluble fluoride-containing waste is not suitable for direct discharge in the sanitary landfill. The most convenient source to avoid fluoride leaching is pre-treating the waste through stabilization and solidification. This pre-treatment method for fluoride-containing water is usually employed in pesticide industry.<sup>428</sup>

Hence, redirecting fluoride sludge to its recovery and reuse is emerging nowadays. Recusing calcium fluoride sludge (CFS) has garnered interest from researchers worldwide because of the harmful and pollution potential of fluoride and the sudden decline in landfill capacity. The possibility of replacing cement with CFS has also been considered.<sup>429</sup>

The respective features represent that the development of fluoride treatment is based on its incineration and landfill disposal. However, it is observed that the recent methodologies do not guarantee absolute its confinement and reintroduce the contaminant in a different way in the environment, finally requiring further development. The contemporary methods are responsible for slowing the entry into the background again. The recovery of fluoride is still limited in practice and technical aspects, and thus investigations are an essential but continuous challenge towards sustainability. It has been found that the mechanism of disposal is not a sustaining aspect with the rapid growth of waste volume in developing countries.

Regulatory bodies play a significant role in defining the characteristics and parameters of fluoride. The fluoride regulation for drinking water varies from country to agency. However, it is the same regarding the standard for effluents and environmental levels. According to the consent of public health, there are varying perspectives on the level of fluoride based on human health, from non-nutrient to micronutrient and essential nutrients.<sup>430</sup> A literature survey revealed that regular investigations are carried out to overcome the negative effects and more researchers are interested in this area based on its valuable aspects. The use of fluoride-containing dentifrice shows minimum risk, whereas the use of municipal fluoridation is





a severe threat, which requires policy making. Thus, an organized definition of fluoride is needed with perceptible objectives.

According to the analysis done in the literature, the shift in the linear economy (LE) and circular economy (CE) shows great potentials. As an efficient specification of sustainability development (SD), the CE is not capable of coping with economic stability and is included for environmental protection and social equity.<sup>431</sup> The economic benefits are the main reason for CE, highlighting the ecological and the beneficial social aspects, generating the momentum for the use of the CE. The maintenance of public health is recognized as an important node on the web. The use of fluoride may lead to hazardous health issues, creating public health problems that also impact macroeconomics. The environmental degradation arising because fluoride affects plants, animals, agriculture, aquaculture, and stocks shows economic and ecological connections. The protection method shows more expenditure efforts and has benefited the economy. Many scholars from the last few decades have already reported the poverty–environment–deterioration relation, whose web linkage cannot be overestimated or neglected.<sup>432</sup> Environmental deterioration (ED) can be a problem for public health, affecting the poorer class and posing socio-economic and ecological impacts. Therefore, the deterioration in the lifestyle of people with health issues has deteriorated the unexploited labour quality in the entire country.

Finally, artificial municipal water fluoridation is a significant problem and is considered the critical node for the network of fluoride, showing enormous considerable aspects. The re-consumption of fluoride from industrial by-products helps adhere to the economic benefits. It is believed that municipal fluoridation is not capable of reflecting the principle of CE. Given that the fluoride is retrieved from a fluoride conduit, it finally ends up at the disposal area, making its reuse economically appealing. Water is the natural medium for transporting fluoride in various forms such as agriculture, food, and beverages.

The fluoridation technique may undergo social justice because of ethical problems and disregarding the poor. The method of artificial fluoridation is practiced for the

unprivileged society without any access to dental care. However, a lack of understanding and knowledge can also avoid the primary objective of helping the poor. According to a literature study, the fate of fluoride in humans and its severe effect leads to disease. The resource governance is working to develop advanced resource flows and involves comprehensive aspects in a diverse range.<sup>433</sup> Following the CE, it is recommended to shift from artificial fluoridation towards other fluoride applications.

Technological development plays a significant role in improving the recovery of fluoride and emerges as a challenging aspect for the disposal of fluoride. Multiple applications must pose inclusive, deliberate, and aligned principles. Thus, the decision-making body needs to create a strong and mutual linkage to attain this task.

Therefore, the critical problem of developing sustainable defluoridation technologies confronts the global scientific assets for a long duration.

## 9. Preventive procedures

A highly organized way to deal with the problem based on fluoride is represented in Fig. 6. For the prevention and management of excessive fluoride ingestion, the following actions should be implemented:

### 9.1 Awareness

Raising the awareness on the safer limit of fluoride content in drinking water and about its incurable health effects using posters, interpersonal interactions and group discussion in villages and school, and other is the first step in preventing the adverse health effects of fluoride contamination.

### 9.2 Substitute water source

Water harvesting is the best technique for providing residents with a minor fluoride content in drinking water. In general, groundwater contains a higher fluoride level than surface water utilized after typical surface water treatment.

# Preventive Procedures

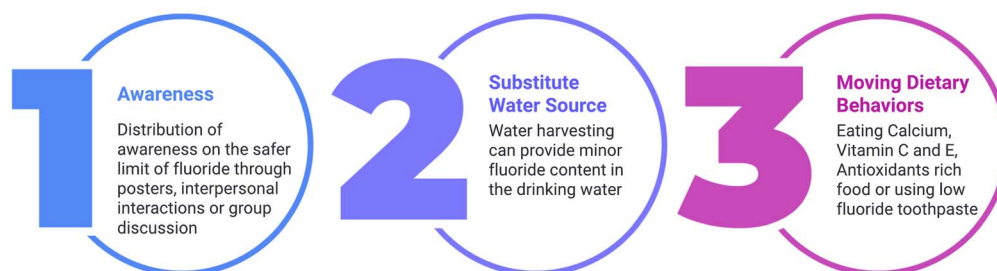


Fig. 6 Schematic diagram of preventive procedures.



### 9.3 Moving the dietary behaviors

If the amelioration procedure fails to reduce the fluoride level to an acceptable level, residents may take the following precautions by changing their eating habits.

**9.3.1 Calcium.** In fluorosis areas, eat calcium-rich foods such as curd and sesame seeds. Fluoride absorption is lowered when the calcium consumption was high.

**9.3.2 Vitamin C and E.** Vitamin C and E have been shown to prevent oxidative stress and endometrial injury in fluoride-intoxicated rats.<sup>434</sup> Vitamin C is abundant in oranges and tomatoes, whereas vitamin E is found in almonds and cereals, among other foods.

**9.3.3 Antioxidants.** Antioxidants such as ginger, pumpkin, and others have an aggressive action, preventing fluorosis.<sup>435</sup>

**9.3.4 Toothpaste.** 4–6 year-old youngsters in fluoride belt areas may employ toothpaste with a low fluoride content for dentifrices.<sup>436</sup> Various dental specialists recommend using toothpaste with a low fluoride concentration (500–550 ppm) instead of the conventional fluoride concentration (1.0–1.1 ppm).<sup>437</sup>

## 10. Fluorosis mitigation programmes

Fluorosis mitigation is gaining a better awareness of the health effects of high fluoride ingestion *via* education, communication, and information. Since the late 1980s, government and non-governmental groups have attempted to fight fluorosis. However, given that most activities concentrate on water defluoridation, it cannot be recommended as the only or most effective method of fluoride prevention. The current research focuses on skeletal fluorosis, which has become more common in recent years. It also includes fresh discoveries and existing techniques for battling skeletal fluorosis and data that may aid research into successful fluorosis treatment and the development of cost-effective and straightforward methods for fluoride removal from water.

### 10.1 Worldwide scenario

If fluoride mitigation is deemed necessary, one or more of the following options<sup>438</sup> may be used: providing a new or alternative source of water with acceptable levels, blending the existing water supply with another containing lower levels of fluoride, providing bottled water, treating the level of water at the domestic level in small treatment devices such as a domestic defluoridation unit, treatment of water at the point-of-use at the industrial level, and treatment of water at the point-of use. Table S4† shows the various fluorosis mitigation programs that have been implemented across the globe.<sup>439</sup>

**10.1.1 Defluoridation unit in Ngurdoto Village, Tanzania.** The Tanzanian Water Authorities, University of Dar es Salaam, and the Technical University of Denmark collaborated to initiate this defluoridation initiative. Due to its economic efficiency and simplicity of handling, the Nalgonda process was used to defluoridate this project. However, this approach had a few drawbacks, as follows: (1) fluoride limits that exceeded the standard ranges of the process and (2) the addition of lime in

the suggested concentration raised the pH to levels that were much higher than the ideal pH necessary for fluoride removal.

A device with taps and a cotton cloth put on the sieve to which alum and lime were introduced concurrently and combined is known as the “two-bucket” defluoridation procedure. Flocculation occurs after quick mixing, gradual stirring, and settling for roughly 1 hour. Few observations have shown that the fluoride trapped in the flocs may be released back into the water; hence, the two buckets are utilized to guarantee that the treated water is quickly separated.<sup>440</sup>

**10.1.2 ICOH mobile bus unit project.** This initiative began in Thailand, intending to raise public awareness about the harmful effects of fluoride on human health, conduct on-site analyses of fluoride levels in water samples, and resolve the issue with feasible alternatives. The team is comprised health experts who work to raise awareness among the general public.

**10.1.3 National rural drinking water program.** The Government of India initiated this initiative on April 1, 2009, intending to provide enough clean water to all rural residents for drinking, cooking, and other basic requirements. It has been implemented in all states and the Andaman and Nicobar Islands and Pondicherry, which are both union territories. In 2017, the program was restructured to be more result-oriented and outcome-specific. By 2030, the program's objective is to provide universal and equal access to clean and inexpensive drinking water.

### 10.2 Indian scenario

The Indian government has established many nationwide programs to provide the population with clean drinking water and to tackle the issue of fluorosis, including Project SARITA and Sachetana Plus. Various government and non-governmental organizations have worked to combat fluorosis during the past several decades. Table S5† gives a quick summary of the fluorosis mitigation programs in India.<sup>439</sup>

## 11. Role of the dentist in fluorosis mitigation

The role of dentists in fluorosis prevention, particularly public health dentists, is because they are uniquely qualified to address the root of this problem. Dentists may teach and urge patients to adopt safe drinking water habits as part of their usual clinical practice. Public health dentists may use their experience and numerous educational resources to educate people about the dangers of fluorosis, highlighting the necessity of drinking clean water *via* regular surveys or at dental camps. Public health dentists may play a critical role in policy development and implementation, such as the NRHM, NRDWP, and other initiatives.<sup>441</sup>

Combating skeletal fluorosis on a large scale remains a severe challenge due to the lack of awareness and costly therapy. Thus, research should focus on developing cost-effective and straightforward methods for treating skeletal fluorosis or removing this element from drinking water.



Not only does public knowledge play an essential role in the containment of this huge hazard, but also government and non-governmental organizations. As part of their curriculum, pupils are taught fluorosis mitigation measures, as an effort of the Rajasthan Government in India to raise awareness among young people. During regular surveys, public health officials should come across afflicted patients. It is necessary to organize camps and programs to educate the public and raise awareness about the dangers of fluorosis and the need to drink healthy water. In locations where water seems to be the primary cause of skeletal fluorosis, and there is no alternative water supply and health insurance, and thus the medical community should be educated to handle this issue and limit its effects. The National Rural Health Insurance Program is one such insurance scheme (under NRHM). Besides the steps mentioned above, healthcare staff should be well trained to diagnose fluorosis and prevent preventative actions accurately.

## 12. Perspective and future research direction

Here, we provide perspectives for fluoride removal and suggest water management and future research-based directions, as follows:

(1) There is little literature study on the data on fluoride levels in the environment and the monitoring of it. Furthermore, there is no recent literature study.

(2) Water contamination with fluoride ions is a significant health-related problem in arid and semi-arid areas. The fluoride concentration in groundwater is  $20 \text{ mg L}^{-1}$  and even more in some regions of China, India, and North Africa. This level is considerably more than the limit set by WHO, which is  $1.5 \text{ mg L}^{-1}$ .

(3) The contaminants in drinking water lead to various disease and health-based issues such as skeletal, dental, and non-skeletal fluorosis, which is caused by fluoride in groundwater. Because of its effect, WHO has limited the concentration of fluoride to  $1.5 \text{ mg L}^{-1}$ , and the BIS has determined it to be less than  $1 \text{ mg L}^{-1}$ .

(4) Various methods for fluoride ion removal have been proposed for reducing its acuity towards damage to human health and the environmental risk. However, due to the high variability of fluoride in drinking water, the conventional methods are expensive and inadequate. Hence, there is an urgent need to develop efficient and cheap strategies for fluoride water treatment.

(5) Many technologies are shown on the laboratory scale. However, wastewater with a high fluoride concentration has a critical effect on the environment and human health. This is later worsened by the inter-connection of the water-based ecosystem, which causes the toxic fluoride to be consumed in food and during recreational activities.

(6) Developing highly efficient and enhanced methods is required to generate more sanitation and treatment abilities. The developing techniques show higher potential for the 6th UNSDG.

(7) According to the literature, there is not enough data for interpolating or extrapolating the information based on

different methods. The literature collected from various sources states fluoride removal by employing adsorption. However, there is very little specified about it and limited discussion on the cost-effective adsorbents.

(8) The bioremediation technique is recognized for the indirect use of fluoride-containing effluent in WWT as the organisms have certain requirements and limited fluoride resistance. Bioremediation is integrated with water management by trapping free fluoride on the surface of water, avoiding the leaching of fluoride into the soil. The recent studies suggest the feasibility and sustaining material recovery of fluoride by the process of phytoremediation.

(9) The toxicity of fluoride is minimized through early diagnosis and reduced intake, generating enhanced nutrition in terms of calcium and vitamin D in the diet. Special attention is given to individuals living with painful and vulnerable conditions, resulting in physical, cultural, and social downfall.

(10) Highly developed research studies are needed for developing and implementing cost-effective, hybrid technology and sustaining features to eliminate the problems based on fluoride. Specific knowledge on fluoride disposal from groundwater is lacking, but it is observed that an innovative encapsulation method for fluoride isolation shows minimum risk and has a practical solution, which needs to be developed worldwide.

(11) Defluoridation needs various features to be followed, such as low-cost, highly advanced systems, with low waste, low procedure wastage, and high use of available waste on a large-scale basis.

(12) The content of fluoride arises from the food chain, and hence the nutritional status of most Indians is inferior. According to the facts listed, it is observed that fluoride contamination in India needs to be minimized to avoid hazardous health issues.

## 13. Conclusion

Fluoride-contaminated water is a severe concern affecting human health, requiring highly effective environmental protection and water management. Given that anthropogenic factors release fluoride in the environment, it is a severe health issue, and most of the problems result from ingesting fluoride from natural resources. The guide of the UNSDG for clean drinking water shows a cost-effective, efficient, viable method to remove fluoride and is mandatory. This method avoids the fundamental drawbacks. It is noticed that it is hard to provide precise and substantial criteria due to a lack of adequate data. Few researchers cannot focus on developing specified methods given that they combine various techniques to create synergistic methods for removing fluoride. This is responsible for bringing about growth and development in water engineering by employing the present and suitable methods, surpassing most minor efforts for practical use. Together with the literature, the narrative of this study is limited to fluoride removal method from aqueous solution, which cannot transcend the investigation on its recovery and re-use, and disposal of secondary polluting agents. The fluoride removal effectiveness varies



depending on site-specific chemical, topographical, and economic factors; therefore, real applications may differ from the assumptions suggested. Any acceptable procedure in one location may not fulfil the standards in another. Consequently, all techniques should be evaluated using natural water treatment. Thus, local authorities and communities need to concentrate on community-based treatment methods. Local communities should be notified and informed to assist in developing appropriate and low-cost curative technologies. Defluoridation of water and minimizing fluoride consumption are also necessary for the integrated mitigation of fluorosis. There is a need to raise awareness in fluorosis-prone regions about the need to eat foods with a low fluoride content and avoid meals with high fluoride concentrations. It is recognized that a comprehensive approach to fluorosis mitigation is necessary and that an appropriate strategy for water defluoridation, fluoride consumption reduction *via* foodstuffs and consumable products, and nutritional supplementation may be required. Using an electrolytic defluoridation system for integrated fluorosis mitigation may be helpful in the long run. With adequate planning, monitoring, and continuous reinforcement, a public-private partnership project should be implemented based on the need. If any of these aspects fails, the initiative will only operate on paper and will not reach the intended recipients. Due to the lack of communication, initiatives and public awareness, combatting fluorosis on a large scale has remained a dream. Mass media and social media may aid in fluorosis prevention and control. A comprehensive strategy is required to address the threat posed by fluoride. However, the principle of “prevention is better than treatment” remains the ultimate answer to the fluoride problem. Furthermore, narratives from the reviewed literature are restricted in their assessment of possible fluoride recovery, re-use, and/or disposal of secondary pollutants created. Consequently, we advise future researchers to take a more thoughtful and comprehensive approach to future studies. Finally, by using a comprehensive approach to examine the complex challenges of F<sup>-</sup> pollution, our study indisputably proves the importance of diverse exposure pathways and human health hazards. Therefore, it is suggested to the upcoming researchers that they should have a more conscientious and holistic method to investigate the fluoride concentration.

## Abbreviations

WHO	World Health Organization
BIS	Bureau of Indian Standards
ISI	Indian Standard Institution
ICMR	Indian Council of Medical Research
F <sub>2</sub>	Fluorine
F <sup>-</sup>	Fluoride ion
HF <sub>2</sub> <sup>-</sup>	Bi-fluoride ion
<sup>19</sup> F NMR	Fluorine-19 nuclear magnetic resonance spectroscopy
ppm	Parts per million
LOAEL	Lowest observed-adverse-effect level

NOAEL	No-observed-adverse-effect limit
UNICEF	United Nations International Children's Emergency Fund
PO <sub>4</sub> <sup>3-</sup>	Phosphate ion
IQ	Intelligence quotient
LH	Luteinizing hormone
FSH	Follicle-stimulating hormone
TH	Thyroid hormone
EL	Estrogen level
ER/AR	Estrogen receptor to androgen receptor
NaF	Sodium fluoride
CKD	Chronic kidney disease
GPx3	Serum glutathione peroxidase
MDA	Malondialdehyde
ROS	Reactive oxygen species
EGCG	Epigallocatechin gallate
Mip 2	Macrophage inflammatory protein 2
US	United States
UK	United Kingdom
HF	Hydrofluoric acid
DNA	Deoxyribonucleic acid
CER	Ceralite IRA 400
IND	Resin FR 10
AIAA	Alum-impregnated activated alumina
EDAX or EDS or EDX	Energy-dispersive analysis of X-rays
MAAA	Magnesia-amended activated alumina
XRD	X-ray powder diffraction
SEM	Scanning electron microscopy
BET	Brunauer–Emmett–Teller
TEM	Transmission electron microscope
FTIR	Fourier transform infrared spectroscopy
ATR-FTIR	Fourier transform infrared-attenuated total reflectance
HRTEM	High-resolution transmission electron microscopy
TGA	Thermogravimetric analysis
EXAFS	Extended X-ray-absorption fine-structure
MMS	Microfluidic modulation spectroscopy
GAPA	Gas adsorption porosimetry analysis
XPS	X-ray photoelectron spectroscopy
IRS	Infrared spectra
UV-Vis	Ultraviolet-visible spectroscopy
XRF	X-ray fluorescence
ASAP	Atmospheric solids analysis probe
TG-DTA	Thermogravimetric analysis-differential thermal analysis
IC	Ion chromatography
DFT	Density-functional theory
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
FESEM	Field emission scanning electron microscopy
SAA	Surface area analyzer
ZPC	Zero point of charge
BJH	Barrett–Joyner–Halenda
PZC	Point of zero charge
CEC	Cation exchange capacity
ICP-AES	Inductively coupled plasma-atomic emission spectrometry





NAD	Nicotinamide adenine dinucleotide
DSC	Differential scanning calorimetry
HAP	Hydroxyapatite
GFH	Granular ferric hydroxide

## Author contributions

Shaz Ahmad: conceptualization, investigation, data analysis, visualization, writing – original draft; Reena Singh: supervision, project administration, writing – review & editing; Tanvir Arfin: writing – review & editing; Krishna Neeti: investigation, data analysis, visualization, writing – original draft.

## Conflicts of interest

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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