Chapter

Carbon-Based Materials for De-Fluoridation of Water: Current Status and Challenges

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Abstract

World is facing scarcity of pure and safe drinkable water and third world war would be based on this issue. Recently ground water is excessively used to meet drinking water needs. Water is the principal source of fluoride in daily intake. Excessive fluoride content in ground water due to leaching from fluoride bearing rocks, pose a serious threat worldwide. Concentration of fluoride in drinking water beyond the recommended standards may lead to serious health problems such as skeletal problems, restricted movement, severe anemia and fluorosis. De-fluoridation of water is quite difficult and expensive. Various materials and technologies have been developed to solve this world wide problem. Ion-exchange, precipitation, electro-chemical, reverse osmosis and adsorption are most widely applied methods for de-fluoridation of water. The main highlight of this chapter is to identify and compare carbon-based materials for de-fluoridation of water on the basis of their efficiency, cost and availability. Challenges associated with the development and use of cost effective and environmental friendly materials for de-fluoridation of water have also been discussed.

Keywords: carbon-based materials, de-fluoridation, ground water purification, water contaminates, de-fluoridation techniques, environmental impacts

1. Introduction

Water is an important constituent of our body. It is not only essential for survival but also improves the quality of life. Water is polluted every day by various pollutants or industrial effluents. Fluoride is of the great environmental concern pollutant which contaminates ground water and affects human health. More than 260 million people around the world is affecting by the excess fluoride concentration in groundwater [1]. Only in India, more than 60 million people are at risk of developing fluorosis from fluoride contaminated drinking water [2, 3]. Water is the primary major source of fluoride in daily intake by human beings. The beneficial or detrimental effects of fluoride in water depend on the concentration of fluoride. As per the World Health Organization (WHO), the maximum acceptable limit of fluoride in water is 0.0015 g/L [4]. However, Bureau of India Standards (BIS) has set a limit between 0.0005 and 0.0010 g/L. The acceptable limit varies among countries and lower concentration is recommended for children [5].

Elemental fluoride is more toxic than its oxidized forms and has adverse health effects on human beings as well as on environment. Small concentrations of fluoride in water reduce the incidence of caries, stimulate bone formation and harden the enamel of teeth [6]. When the concentration is beyond the acceptable limit, it causes lesion of the liver, thyroid and endocrine glands, dental and skeletal fluorosis, arthritic symptoms and bone fracture well before the onset of crippling fluorosis, etc. [7–10].

Naturally fluoride originates in ground water due to leaching or dissolution from fluoride bearing rocks. Fluorspar, cryolite, fluorapatite and sellaite are the main fluoride rich rocks that contaminate the ground water after leaching or dissolution [2, 3]. Volcanic ash and rocks are often enriched in fluoride. Fertilizers such as superphosphate, NPK (nitrogen phosphorous potassium) and potash also contain remarkable quantity of fluoride to contaminate ground water [2, 3].

De-fluoridation of water is quite difficult and expensive. Various natural and synthetic materials have been applied to solve this world wide problem. Ion-exchange, precipitation, nano-filtration, electro-chemical, reverse osmosis and adsorption are most widely developed techniques methods for de-fluoridation of water [2, 3, 11]. Among them adsorption is quite effective method because it is easy to operate, needs less space, eco-friendly and cost effective method. Natural, natural modified and synthetic materials have been widely applied as adsorbents for removal of fluoride ions from water [2, 3].

Alumina, aluminum-based materials, manganese dioxide with coated alumina, bauxite, clay and soil, fired clay, carbon-based materials, synthetic resin and biopolymers have been extensively applied as adsorbents for removal of fluoride ions from water [2, 3]. Natural materials /plant waste materials such as rice husk, groundnut shell, saw dust are also most widely used materials used as natural adsorbents.

Carbon-based materials have shown great usefulness for water purification because they exhibit excellent adsorption characteristics and after modifications properties of these materials may be tailored as per requirement. The aim of this chapter is to identify and compare carbon-based materials for de-fluoridation of water on the basis of their efficiency, cost and availability. Challenges associated with the development and use of cost effective and environmental friendly materials and methods for de-fluoridation of water have also been discussed.

2. Background

2.1 Sources of fluoride in water

Groundwater without any physical or chemical treatment is the main source of drinking and other household purposes in most of the countries all over the world. United States, South America, Middle East of Asia, South-East of Africa, India and China are the fluoride affected regions (**Table 1**) [12–23]. However, India and China are the most affected countries worldwide by fluorosis [11]. Fluoride concentration in groundwater depends on the chemical, physical, geological properties of the aquifer. It also depends on the surrounding temperature, intensity of weathering, depth of the wells, porosity and acidity of the soil and rocks, interaction of other chemical elements present in the aquifer [24].

Soil and groundwater are contaminated with fluoride by natural or anthropogenic sources. Naturally soil and groundwater are contaminated by release of fluoride from weathering of the primary minerals fluorite, hydro-geothermal vents, and volcanic activities. However, the use of fluoride bearing fertilizers (fumigants,

Name of country	Sources of fluoride	Amount of fluoride in ground water (mg/L)	References
Brazil	Minerals, fertilizers	0.1–4.7	[16]
Canada	Minerals, fertilizers, rocks	0.1–15.0	[17]
China	Minerals, rocks	2.5–10.3	[18]
Ethiopia	Rocks	0.01–13.0	[19]
Ghana, Ketabasin	Mineral weathering	0–282.2	[20]
India	Geological, and chemical	0.1–16.5	[21]
Kenya	Geological, chemical, rocks	0.1–25.0	[22]
Korea	Geological, and chemical	0–48.8	[23]
Mexico	Geological, and chemical	0.5–7.5	[24]
Pakistan	Minerals, fertilizers, rocks	0.11–22.8	[25]
Sri Lanka	Minerals, fertilizers, rocks	0.1–4.3	[26]
USA, Wisconsin	Geological, and chemical	0.01–7.6	[2]

Table 1.
Fluoride concentration in groundwater in different country.

pesticides, aluminum phosphate fertilizer) and burning of coal increases the fluoride level in soil and groundwater in terms of anthropogenic ways.

The main primary source of fluoride is fluoride rich minerals or rocks. Ground water is contaminated from fluoride due to leaching from fluoride bearing minerals, cryolite (Na_3AlF_6), fluorspar (CaF_2), villiaumite (NaF), sellaite (MgF_2), topaz ($Al_2(SiO_4)F_2$), fluorapatite ($Ca_5(PO_4)_3F$) and fluoride bearing rocks, conglomerate, schist, killas, silexite, granite, sandstone, and gneiss [25]. Dissolution of fluorite mineral from the host rocks increases in alkaline medium. pH 7.6–8.6 is the most favorable range of dissolution of fluorite mineral [2]. Fluoride shows a constructive connection with sodium and bicarbonate while it shows inverse connection with calcium in water.

2.2 Health effects of fluoride

Exposure to fluoride more than the recommended value is associated with a number of health issues. Dental fluorosis, skeletal fluorosis, neurological problems, thyroid problems and other health problems are the main health issues associated with high exposure of fluoride [5, 8, 11].

Hypo-mineralization of tooth enamel due to excessive fluoride intake is known as dental fluorosis. Fluoride decreases the availability of free calcium ions in the mineralization environment. It is characterized by discoloration of the teeth or formation of pits in the teeth depending upon dose, age, and time of exposure. Faint white lines, white mottled patches, brown discoloration, brittle, pitted and rough enamel are the various stages of initial to severe fluorosis (**Figure 1**). The effects of dental fluorosis may not appear in case of already developed teeth [11, 18, 25]. It does not mean that fluoride intake in adults is within the safety limit. Only in India more than 60 million people are suffering from fluorosis. More than 85% children had dental fluorosis.

Bone and joint deformations is known as skeletal fluorosis due to excessive intake of fluoride (**Table 2**). The bones may become hardened, thicken and less elastic causes severe pain, impaired joint mobility and increasing the risk of fractures. Sporadic pain, stomach-ache, muscle weakness and stiffness of joints are the early symptoms of skeletal fluorosis. Hardening and calcifying of the bones (osteosclerosis) are the next stage and spine, muscles, nervous system and major joints damage are the final stage of

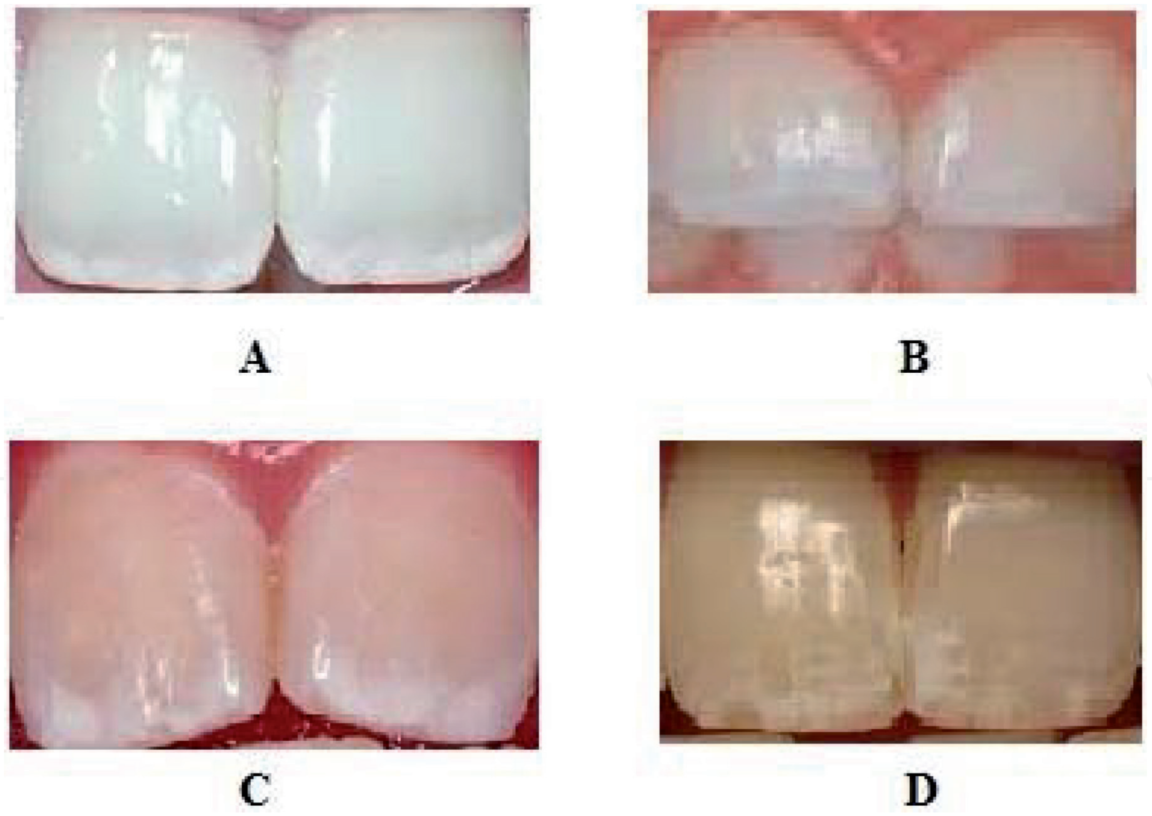

Figure 1.
Dental fluorosis: (A) normal, (B) mild, (C) moderate, (D) severe conditions.

S. No.	Name of standard agency	Permissible limit (mg/L)	Health effects
1	World Health Organization (WHO)	0.6–1.5	<0.5 = dental caries
2	Bureau of Indian Standards (BIS)	0.6–1.5	0.5–1.5 = optimum dental health
3	US Public Health Standards	0.8	1.5–4.0 = dental fluorosis
4	Indian Council of Medical Research (ICMR)	1.0	<4.0 = dental skeletal and crippling fluorosis

Table 2.
Permissible limit of fluoride in drinking water and associated effects on teeth.

skeletal fluorosis. More than 35% children had skeletal fluorosis. In both of the cases no treatment exists, thus prevention is better than cure. Long time exposure of fluoride also changes the DNA structure and may causes cancer [7].

Long time exposure of fluoride to pregnant women may affect cognitive ability for the child in the future. Excessive exposure to fluoride was associated with low intelligent quotient. Recently, fluoride was found as a neurotoxin affects the child development. Excessive exposure of fluoride may also causes high blood pressure, cardiovascular problems, cardiac insufficiency, heart failure, acne, skin problems, reproductive issues, thyroid dysfunction [7–10].

2.3 De-fluoridation techniques

Exposure of fluoride has various adverse effects. Therefore its monitoring and removal is very important. A number of techniques are available for the removal of fluoride from water. Physical, chemical and biological methods are applied for defluoridation of drinking water. Ion exchange, precipitation, membrane process,

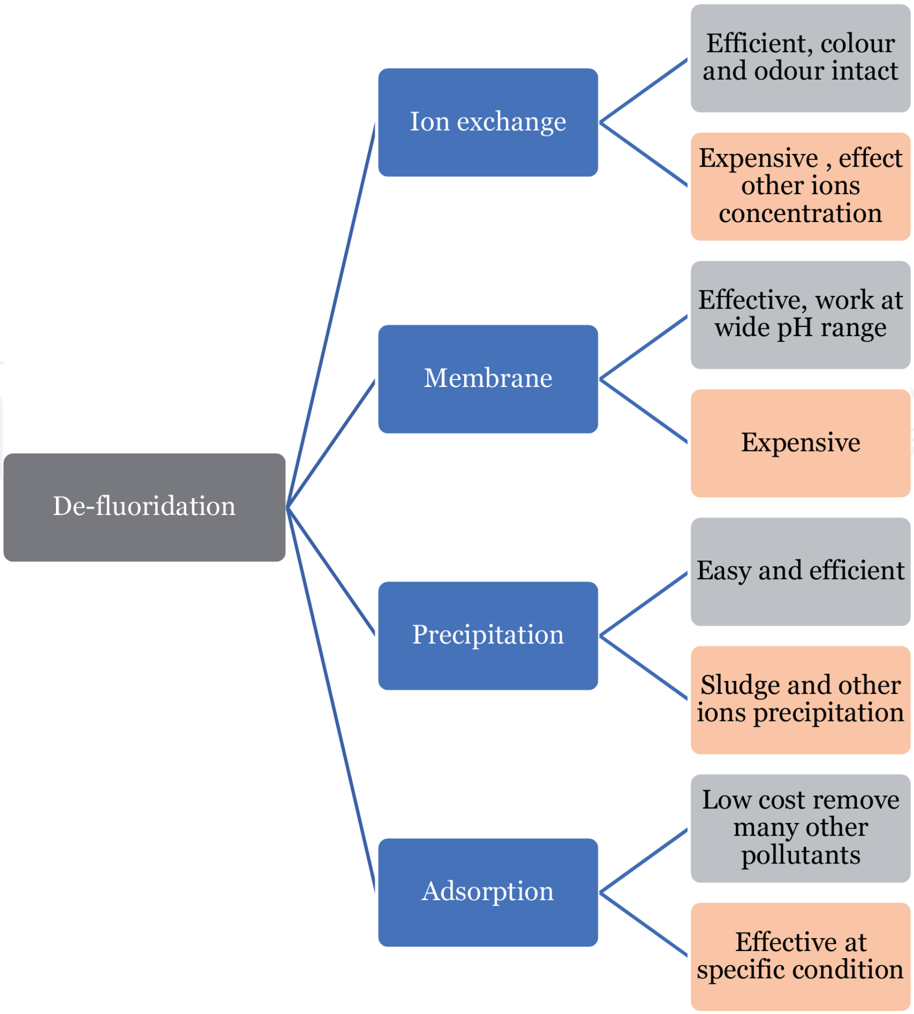

Figure 2.
Schematic diagram for some important defluoridation techniques.

adsorption and phyto- and bioremediation are most promising methods have been applied for defluoridation of drinking water (**Figure 2**) [2, 3, 11, 12].

In ion exchange method synthetic anionic and cationic exchanger resin are applied for defluoridation of water. Lewatit MIH59, Tulsion A-27, Ambalite TRA400, Deaceodite FFIP, Polyanion (NCL), anionic exchange resin and polystyrene resin, sulfonated saw-dust carbon, Wasoresin IR, cationic exchanger resins are most widely used ion exchangers for removal of fluoride from water.

In precipitation method fluoride in water gets precipitated out in the form of fluorapatite. The insoluble fluorapatite gets separated out from the aqueous phase. Nalgonda technique, contact precipitation and MgO, $Ca(OH)_2$ and $NaHSO_4$ mixtures are most widely used methods for precipitation of the fluoride from water.

Membrane process involves the compound specific permeability membrane with specific pore size. Reverse osmosis, electro-dialysis and nano-filtration are the method used for defluoridation of water using membranes [26].

Adsorption is one of the most promising methods widely applied for defluoridation of the water. It is cheap, needs less space and easy to handle method. Natural and synthetic materials are used as adsorbent for the removal of fluoride from water [26].

3. Discussion

Different adsorbent materials are reported in literature for effective removal of fluoride from water. Carbon-based adsorbents are often used for the removal of contaminants from water as their surface can be tailored as per the nature of contaminant.

3.1 Carbon-based materials as adsorbents for de-fluoridation

Carbon-based materials have unique properties such as high stability, large surface area, and high strength [2]. These materials can combine with other elements or materials to form strong covalent bond. Due to unique properties and versatile nature they have been widely used in different fields. Researchers have used different types of carbon-based materials for removal of fluorine from water. Various carbonaceous materials can be used to prepare activated carbon via chemical or physical activation. Carbon-based nanomaterials are also fast emerging materials for defluoridation of the water because of their very small size, high surface area, remarkable electrical conductivity, unique structural dimensions, high mechanical strength, and high efficiency [27]. In this chapter all the reported studies are reviewed and applicability of carbon-based adsorbents in different conditions are analyzed.

3.2 Natural and modified activated carbon/carbon-based waste

Abe et al. investigated the defluoridation of water by using various carbon-based charcoal in order to get the best adsorption capacity. The maximum adsorption capacity was found to be in following order bone char > coal charcoal > wood charcoal > carbon black > petroleum coke [28]. Defluoridation of water using activated carbon depends on various factors, such as pH, solubility, polarity, pore size distribution, molecular size of the adsorbate, surface area, surface functional groups, and other ions in solution. Microporous activated carbons have high surface areas shows high adsorption capacity for the adsorption of low molecular weight compounds [29]. Up to 85% of fluoride ions from water was removed by powdered activated charcoal at pH 2 adsorbent dose of 2.4 g/100 mL, stirring rate of 60 rpm and contact time of 120 min, which was very effective than the untreated charcoal [30]. Considering low pH vlaues, it is due to availability of the large number of H^+ ions. Up to 17, 10, and 82% defluoridation of water were achieved by using commercial activated carbon, carbon black, and bone char, respectively at 30°C at a fixed contact time of 3 h. Sreenivasulu et al. investigated defluoridation of water by using activated carbon prepared from Umbles of Prangos Pabularia Lindl [31]. In batch studies adsorption was completed within 90 min for 0.0028–0.0076 g/L fluoride concentration. Removal percentage increases up to 85% with increase in the concentration up to 7 g/1 at pH of 8.75 and temperature of 57°C. Singh et al. investigated defluoridation of water by using activated charcoal of wheat husk (AC) and alum treated fly ash (ATF) obtained from thermal power station in Agra city. About 68.6% defluoridation of water was achieved at 2 g AC/100 ml of ground water at pH 6.8 and temperature 25°C in 24 h [32]. Charcoal is produced by slow heating of wood, coal, bone, lignite, nutshells, and petroleum residues, low cost waste materials such as coconut shell, fruit waste, rice-husk, saw dust, tree bark, and cotton waste in the absence of oxygen. Arulanantham et al. were investigated defluoridation of water by using coconut shell carbon (CSC) and commercial activated carbon (CAC). Defluoridation of water from dilute aqueous solutions was very effective when coconut shell carbon impregnated with alum. Adsorption capacity of wet carbon was three times more than that the dry carbon. Coconut shell carbon has certain specific advantages over alumina for defluoridation of water at pH 5–8 [33]. Various animal bone char and its activated forms are widely used as adsorbent for defluoridation of water. Removal percentage depends on the initial fluoride concentration of solution, adsorbent dose, pH of the solution and contact time [34]. High defluoridation of water at pH 7.0 was observed by normal cow bone char and under different conditions such as CO_2 environment, NO_2 environment, Al doped cow bone char [35]. Maximum adsorption capacity was found to be 7.32–31 mg/g. Highest adsorption capacity was found to be for Al doped cow bone char (31 mg/g). Al doped cow bone char was prepared at 700°C temperature [36]. Adsorption capacity of bone chars are altered by the functional groups on the surface. Zuniga-Muro et al. were investigated defluoridation of water by doped two different cerium precursors (Ce^{3+} and Ce^{4+}) onto cattle bone char. The results showed that a significant enhancement in the adsorption capacity of fluoride on to the Ce^{4+} modified bone char composite from 5.47 to 13.6 mg/g at pH 7 [37]. Zhu et al. were investigated defluoridation of water by cattle bone char after modification with different aluminum salts ($AlCl_3$, $AlNO_3$, $NaAlO_2$, $Al_2(SO_4)_3$) [38]. About 97% removal was achieved onto $AlCl_3$ modified bone char at pH 7. Moreover, maximum adsorption capacity was found to be 6.8 mg/g by using bone char modification using $AlCl_3.6H_2O$ [39]. However, bone char pre-treatment with $Ca(OH)_2$, $FeCl_3$, $CaCl_2$ and $MgCl_2$ were less effective for defluoridation of water with maximum adsorption capacity 4.4, 1.56, 5.1 and 4.2 mg/g, respectively. Maximum adsorption capacity for unmodified bone char was found to be 7.32 mg/g. Rojas-Mayorga et al. were investigated defluoridation of water by doped aluminum sulfate onto bovine bone char (pyrolyzed at 700°C) on packed bed micro-columns [40]. Maximum adsorption capacity for bovine bone char (pyrolyzed at 700°C) at pH 7 was found to be 3.3–18.5 mg/g. The removal efficiency has significantly improved by doping bone char with different metals (Fe_xF_y, $Al(OH)_xF_y$, and CaF_2). The maximum adsorption capacity for aluminum sulfate doped bone char at pH 7 was found to be 31 mg/g. Chatterjee et al. were investigated defluoridation of water by aluminum sulfate with calcium oxide to chemically treat carbonized bone meal (a mixture of chicken and cattle bones). The maximum adsorption capacity increases for chemically treat carbonized bone meal from 14 to 150 mg/g [41].

Ma et al. were investigated defluoridation of water by using granular activated carbon coated with manganese oxides. Removal effieciency was three times higher than uncoated granular activated carbon at pH 3 [42]. Rao et al. were used activated carbon of bergera koenigh carbon (BKC), batavia orange carbon (BOC) and *Raphanus sativus* carbon (RSC) for defluoridation of carbon. 0.0040 g/L fluoride content was reduced to permissible level by using theses adsorbents at pH 6, 1 g/L adsorbent dose and at 30 min of contact time [43]. Roy and Das were investigated defluoridation of water by using activated carbon prepared from tea waste (ACTW). About 99.59% removal was achieved at adsorbent dose 1.0 g temperature of 60°C and contact time of 70 min [44].

Ramos et al. investigated defluoridation of water by using plain and alumina-impregnated activated carbons. Alumina-impregnated activated carbons were prepared by stirring with an aluminum nitrate solution at a fixed pH. Calcinations of the alumina-impregnated activated carbons were done under nitrogen at temperatures 300°C. Adsorption capacity of the adsorbent depends on the pH of the impregnating solution and the temperature of calcinations. Alumina-impregnated activated carbons showed 3–5 time's high adsorption capacity than the plain activated carbon [45]. Janardhana et al. investigated defluoridation of water by using zirconium impregnated activated charcoals. It also showed 3–5 time's high adsorption capacity than the plain activated carbon [46]. Dahiya and Kaur investigated defluoridation of water by using coconut coir pith carbon (CPC). The activated form of CPC was obtained by carbonization in presence of sulfuric acid without any chemical treatment as well as after impregnation with different alum dose. 78.8% defluoridation of water from standard fluoride solution of 0.0025 g/L after contact period of 12 h was achieved on 10 g/L CPC impregnated with 2% alum. Removal capacity of adsorbent decreased with increase in initial fluoride concentration and with decrease in dose of adsorbent [47].

Gupta et al. studied the defluoridation of water by using waste carbon slurries from fuel-oil energy generators. Solid was activated by heating in air at 450°C. Activated material was washed with sodium hydroxide solution and fluoride free water to remove ash and other contaminates. The final material which contains 92.0% carbon, 0.45% aluminum and 0.6% iron was dried at 100°C. Defluoridation of water and regeneration of material were pH-dependent with optimum pH 7.6 [48]. Thermally activated biosorbents prepared from banana (*Musa paradisiaca*) peel and coffee (*Coffea arabica*) husk were used as adsorbents for defluoridation of water [49]. Maximum adsorption capacity was achieved at pH of 2, 24 g/250 mL at 13 h contact time for banana peel and 18 g/250 mL at 3 h contact time for coffee husk. The real water samples were collected in consultation with WRDA (water resource development authority) office at Hawassa city, Ethiopia. The concentrations of fluoride in flour factory, poultry, and Lake Hawassa sites were found to be 0.0012, 0.0011 and 0.0067 g/L, respectively. The prepared adsorbents were used for the same water. The removal percentage was from 80 to 84% [49]. Karuga et al. investigated defluoridation of water by using activated fish swim bladder-derived porous carbon (FBPC). Maximum adsorption capacity was achieved at pH of 6, adsorbent dose of 5.0 g/L and contact time of 50 min. It follows pseudo second-order kinetic and Langmuir isotherm models for adsorption process [50].

3.3 Carbon-based pristine and functionalized nanomaterials

Carbon-based nanomaterials have also attracted considerable attention in the recent years for defluoridation of water with higher uptake capacity. Li et al. were investigated defluoridation of water by using graphene a single flat two-dimensional (2D) atomic sheet of carbon. Maximum adsorption capacity (17.65 mg/g) was obtained at 0.0025 g/L initial fluoride concentration and 25°C temperature [51]. Dongre was investigated defluoridation of water by using fabricated chitosan doped graphite novel composite (FCDGNC). Langmuir maximum adsorption capacity was found to be 37.9 mg/g at pH 6.5. It follows pseudo second order model. FCDGNC was regenerated and reused better upon five cycles [52]. Roy et al. were investigated defluoridation of water by using reduced graphene oxide. Chemical reduced graphene oxide (CRGO) can be prepared from 400 mg of graphene oxide dispersed in 400 mL deionized water by means of 30 min ultra sonication with ammonium hydroxide and hydrazine hydrate. Biochemical synthesis of graphene oxide can be done by tea polyphenol. Tea polyphenol reduced graphene oxide (TPGO) can be prepared by 50 mg graphene oxide powder added in the tea solution and sonicated for 30 min at 363 K in a nitrogen atmosphere. The removal percentage was 94.22% by TPGO whereas it was 87.4% in case of CRGO. Langmuir adsorption isotherm was the best fitted model for both of the adsorbents. The kinetic follows pseudo second order model. TPGO can be regenerated by using 1% sodium hydroxide solution and reused for defluoridation of water [53]. Aligned carbon nanotubes (ACNT) were prepared by decomposition of xylene, catalyzed by ferrocene [54]. ACNT adsorbs 4.5 mg/g fluoride from 0.0015 g/L fluoride at pH 7. Adsorption capacity increases with increasing the acidity or positive charge on the surface of ACNT. Adsorption capacity under the similar conditions for carbon nanotubes, typical soil, g-Al_2O_3 and activated carbon increase in following manner activated carbon < g-Al_2O_3 < soil < CNT. Haghighat et al. were investigated defluoridation of water using single and multi-wall carbon nanotubes (SWCNs and MWCNs) [55]. The study showed that 58% removal efficiency in 70 min was obtained at pH 5, 0.0010 g/L fluoride initial concentration by using 0.5 g/L single-wall carbon nanotube. However, 54% removal efficiency in 70 min was obtained at pH 5, 0.0010 g/L fluoride initial concentration by using 0.5 g/L multi-wall carbon nanotube. In acidic condition adsorption capacity was increased. SWCNs showed high removal efficiency in comparison to two types of fine powder and 150 mesh activated alumina in optimum conditions.

Tang et al. investigated the defluoridation of water by using novel hydroxyapatite decorated with carbon nanotube composite (CNT-HAP) [56]. Maximum adsorption capacity using CNT-HAP composite for removal of fluoride was found to be 11.05 mg/g at pH 6. Freundlich model showed the best fitted isotherm model. Regression coefficient showed that it follows pseudo-second-order kinetic model. Defluoridation of water was also investigated by using alumina-impregnated carbon nanotubes [57, 58]. Carbon nanotubes were synthesized by the pyrolysis of a propylene hydrogen mixture with Ni particles as the catalyst. The product was ball-milled and then stirred with aluminum nitrate solution at 500°C under nitrogen for 2 h. A sponge-like alumina supported on carbon nanotubes was obtained which was ground and sieved to appropriate particle size. The adsorption capacity of the alumina-impregnated carbon nanotubes was found to be very high (13.5 times) compared to AIC-300 (4 times) g-Al_2O_3 and IRA-410 polymeric resin. Li et al. were investigated defluoridation of water by using carbon nanotubes supported on alumina. Maximum adsorption capacity 9.6 mg/g was achieved at pH of 6 at alumina loading of 30 wt%. The adsorption follows Freundlich isotherm model. It follows second order rate equation [59]. Gupta et al. were investigated defluoridation of water by using a micronanohierarchal web (MiNaHiWe) consisting of activated carbon fibers (ACF) and carbon nanofibers (CNF), impregnated with Al. Aluminum carbon nanofibers (CNF) was applied for treating the wastewater at pH 5–8 [60].

3.4 Comparison of carbon-based materials for defluoridation of water in pH range 6.0–7.5

Carbon-based materials such as aligned carbon nanotubes (ACNT), single and multi-wall carbon nanotubes (SWCNs and MWCNs), hydroxyapatite decorated with carbon nanotube composite (CNT-HAP), alumina-impregnated carbon nanotubes (Al-CNT), charcoal, activated charcoal of various materials, bone char of various animals, graphene, chemical and bio-reduced i.e. chemical reduced graphene oxide (CRGO), tea polyphenol reduced graphene oxide (TPGO) and fabricated chitosan doped graphite novel composite (FCDGNC) are used for defluoridation of water. Maximum adsorption capacity of these materials depends on the pH of the solution, adsorbent dose, contact time, initial fluoride concentration and temperature. It is very difficult to identify the best adsorbent among the following for defluoridation of the water because the removal conditions are different (**Table 3**). However, the studies reveal that chemically treated carbonized bone meal is the best adsorbent for defluoridation of water. The maximum adsorption capacity of chemically treated (CT-CBM) is very high compared to other used adsorbents under the slightly different conditions. The maximum adsorption capacity of the used adsorbents at pH 6.0–7.5 follows the following order (**Figure 3**):

CT-CBM (150) > FCDGNC (37.9) > Al-S-BC (31.0) > TPGO (28.72) > CRGO (18.22) > CBM (14.0) > CNT-HAP (11.05) > Al-CNT (9.6) > CBC (7.32) > ACNT (4.5) > activated charcoal of materials (ACM) (~2.0) > charcoal of materials (CM) (~1.0).

Comparison of maximum adsorption capacity of different materials was also studied by various groups under the similar conditions. Adsorption capacity of

Carbon-based materials	Max adsorption capacity (mg/g)	pH	Isotherm/kinetics	Reference
ACNT	4.5	7.0	Langmuir/ pseudo-second-order	[54]
CNT-HAP	11.05	6.0	Langmuir/ pseudo-second-order	[56]
Al-CNT	9.6	6.0	Langmuir/ pseudo-second-order	[59]
FCDGNC	37.9	6.5	Langmuir/ pseudo-second-order	[52]
CRGO	18.22	7.1	Langmuir/ pseudo-second-order	[53]
TPGO	28.72	7.1	Langmuir/ pseudo-second-order	[53]
Activated banana peel	0.39	6.3	Langmuir/ pseudo-second-order	[49]
Activated coffee husk	0.41	6.3	Langmuir/ pseudo-second-order	[49]
Bagasse AC	1.15	6.0	Langmuir/ pseudo-second-order	[61]
Saw dust AC	1.73	6.0	Langmuir/ pseudo-second-order	[61]
Wheat straw AC	1.93	6.0	Langmuir/ pseudo-second-order	[61]
Fish swim bladder carbon	1.43	6.0	Langmuir/ pseudo-second-order	[50]
Cow bone char (CBC)	7.32	7.0	Langmuir/ pseudo-second-order	[36]
Cow bone char under CO_2 environment	5.92	7.0	Langmuir/ pseudo-second-order	[36]
Al sulfate doped (Al-S-BC)	31.0	7.0	Langmuir/ pseudo-second-order	[37]
Carbonized bone meal (CBM)	14.0	6.1	Langmuir/ pseudo-second-order	[41]
Chemically treated (CT-CBM)	150.0	6.1	Langmuir/ pseudo-second-order	[48]

Table 3.
Maximum adsorption capacity of carbon-based materials for defluoridation of water.

carbon nanotubes, typical soil, g-Al_2O_3 and activated carbon follows following order CNT > soil > g-Al_2O_3 > activated carbon under the similar conditions.

However, SWCNs showed high removal efficiency of fluoride in comparison to MWCNs which was also very high to two types of fine powder and 150 mesh activated alumina in optimum conditions.

The adsorption capacity of the alumina-impregnated carbon nanotubes was found to be very high (13.5 times) compared to AIC-300 (4 times) g-Al_2O_3 and IRA-410 polymeric resin under similar conditions.

In similar manners the maximum adsorption capacity of charcoals was found to be in following order bone char > coal charcoal > wood charcoal > carbon black > petroleum coke under optimum conditions.

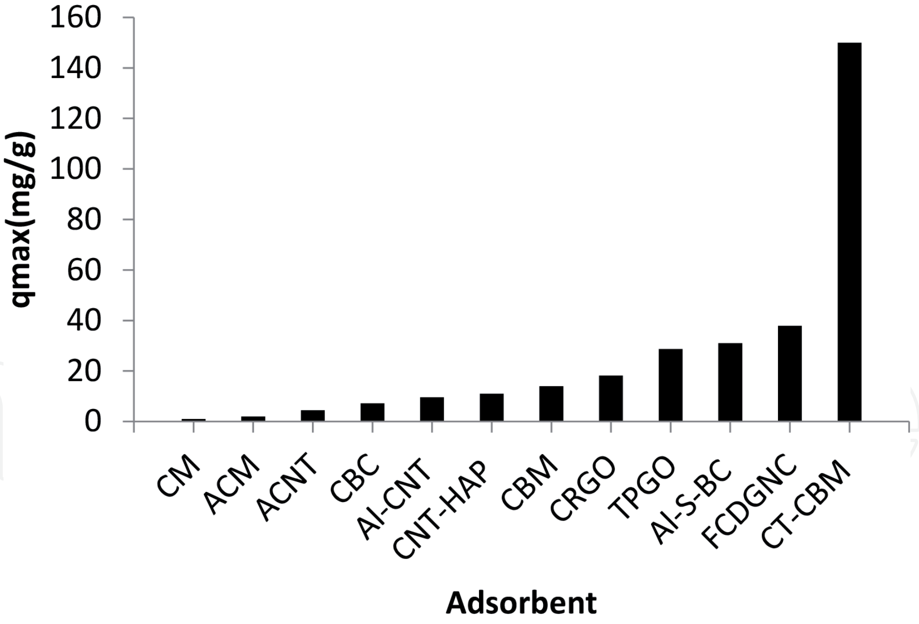

Figure 3.
Comparison of maximum adsorption capacity of carbon-based materials for defluoridation of water.

4. Conclusions

More than 260 million people around the world are exposed to excess fluoride concentration in groundwater which is the prime reason of dental and skeletal fluorosis. There is need to identify the feasible cost effective and eco-friendly materials for defluoridation of water at community level. Various natural and synthetic materials have been explored for defluoridation of water. The adsorption capacity was found to be very poor for pristine natural alternatives. However, they are cost effective, easily disposable and environmental friendly. Chemically treated carbonized bone meal is found to be best adsorbent for defluoridation of water. The maximum adsorption capacity of chemically treated (CT-CBM) was found very high when compared with other used adsorbents under the slightly different conditions. Carbon-based nanomaterials like graphene and its fabricated forms are also most widely used adsorbents for the defluoridation of water. Cost and disposal of graphene and nanomaterials is a very crucial issue while proposing these materials for defluoridation of water. Future studies should be focused to explore more low cost and eco-friendly materials that promise good adsorption capacity for fluorine and can be used to treat drinking water in normal conditions.

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