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REVIEW

Treatment of fluoride-contaminated water. A review

P. Senthil Kumar¹ · S. Suganya¹ · S. Srinivas¹ · S. Priyadharshini¹ · M. Karthika¹ · R. Karishma Sri¹ · V. Swetha¹ · Mu. Naushad²  · Eric Lichtfouse³ 

Abstract

Delivering the right amount of fluoride to drinking water protects the teeth from decay and reduces the risk of cavities. Nonetheless, fluorosis has been diagnosed as the result of excessive exposure of fluoride, which induces brain impairment, muscle disorders and hyperactivity. Fluoride ingestion during the formation of the tooth enamel is the main reason for fluorosis, which is characterized by hypomineralization. Dissolution of fluoride-containing rock minerals contributes to naturally occurring fluoride contamination in water. The intentional addition of fluoride to water in dental care is alarming in growing countries such as India. This article reviews the origin of fluoride, the analysis of fluoride derivatives and the technologies to remove fluoride from water. The manuscript presents adsorption techniques for fluoride removal, using different types of adsorbents. The adsorption capacities of adsorbents under various conditions, such as contaminant concentration, adsorbent dosage, time, pH and temperature, are presented. Adsorbent types include alumina, zeolites, organic waste, shell-based and carbon-based including graphite and carbon nanotubes. Defluoridation of water using clays and muds, modified activated alumina, chitosan derivatives and composites are also discussed.

Keywords Defluoridation · Zeolite · Adsorption · Reverse osmosis · Activated carbon

Introduction

Water is an essential natural resource for sustaining life and environment, which we have always thought to be an abundant source and hence taken for granted (Ahamad et al. 2017; Naushad et al. 2017; Alqadami et al. 2017a). However, the chemical composition of surface or subsurface is one of the key factors on which the appropriateness of water for industrial, domestic or agricultural purpose depends (Adhikari et al. 1989). Low concentration of fluoride in drinking water has been considered beneficial to prevent dental caries. Fluoride occurrence in the environment, e.g. air, water and

soil, is well explained by Singh et al. (2018), demonstrating that some natural and anthropogenic sources are the main contributory factors. Significantly, soil contains more than 5000 mg F/kg approximately, caused by ejected ash volcanic ash and other fertilizers (Singh et al. 2018). Scientists have evidenced the effective health benefits of fluoride at low concentrations. However, it has been known for long time that extreme intake of fluoride, at concentrations higher than 1 mg/L, can lead to severe dental and skeletal fluorosis as shown in Fig. 1 (Vithanage and Bhattacharya 2015). Dental and skeletal fluorosis, a disease can cause mottling of the teeth due to the excess fluoride and calcification of ligaments. Similarly, long-term exposure may lead to crippling bone deformities, cancer and decreased cognitive ability (Newsletter, Medical News Today 2018). Noteworthy, the population residing in tropical belt are highly exposed to ground fluoride. A such geochemical anomaly should be taken into account.

Consumption of water containing fluoride 1.5 mg/L causes diseases such as fluorosis, arthritis, hip fractures, infertility, osteoporosis and polydipsia. It affects the teeth and skeleton, and the accumulation of fluoride over a long period of time can even lead to changes in the DNA structure

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Fig. 1 Dental fluorosis-affected child in Anuradhapura, Sri Lanka (Reproduced from (Vithanage and Bhattacharya 2015) with permission from Springer, Nature)



(Ahmad and Kumar 2010). Elemental fluorine is slightly basic when it reacts with water. This is the natural phenomena for fluoride transfers between water, soils and rocks (Alfredo et al. 2014). Hence, there is a need to reduce the fluoride content in water using various removal techniques in order to prevent health hazards.

Precipitation (Amalraj and Pius 2017) and adsorption (American Public Health Association 1992) are the two major methods to remove fluoride from water, whereas calcium and aluminum salts have been used in precipitation. Adsorption using a solid carbonaceous material to remove a soluble fluorine substance from water takes place through several mechanisms including chemisorption by ion exchange, complexation, coordination, chelation, physical adsorption and micro-precipitation (Ayoob et al. 2008). The efficiency of the adsorption technique depends mainly on the nature of adsorbent (Naushad et al. 2016; Mittal et al. 2016), ease of availability and accessibility, high-loading capacity and a strong affinity toward fluoride ions.

Removal of fluoride from drinking water can also be attained by membrane processes and ion exchange (Banasiak et al. 2007). Nonetheless, membrane processes and ion exchange are not very common due to the high cost for installation and maintenance. Alternatively, adsorption is very economical and can remove ions over a broad pH range, even to a lower residual concentration in comparison with the precipitation (Bansiwal et al. 2010). Activated alumina is one of the best available and generally used sorbent for the removal of fluoride from drinking water (Barathi et al. 2013). However, the slow rate of adsorption of commercially available activated alumina restricts its use for treating large quantities of water. Graphite-based materials are attracting increasing interest due to their large surface area, flexibility, high mechanical strength and significant thermal and electrical conductivities which make them potentially applicable for a wide range of applications such as water purification (Barbier et al. 2010). Other natural materials like red mud (Bertolacini and Barney 1958) and clay (Bhargava and Kille-dar 1991) have also been tested for the removal of pollutants. Thereby, defluoridation has been established using zeolites

(Bhaumik et al. 2017). The porous nature of zeolites (Bia et al. 2012) is one of the major factors that makes zeolites unique adsorbents (Biswas et al. 2007).

Recently, new adsorbents loaded with metal ions have been designed for the progressive removal of fluoride. For instance, the adsorption capacity of fluoride on aluminum-impregnated carbon is found to be three to five times higher than that of plain activated carbon (Bouhidel and Rumeau 2000). The removal of fluoride ion by zirconium (IV)-impregnated collagen fiber reaches 97.4% at pH 5.5 from an initial concentration of 5 mmol/L (Brownley and Howle 1960). In addition, some adsorbents loaded with rare earth ion (Zhu et al. 2015a) gain more attention. This article reviews the literature about excess fluoride concentration in water, fluoride toxicity and health hazards. It summarizes an expedient analytical technique for fluoride determination followed by defluoridation technique using novel sorbents. Authors also conclude the current debate between traditional (Nalgonda) and conventional techniques for the effective removal of fluoride.

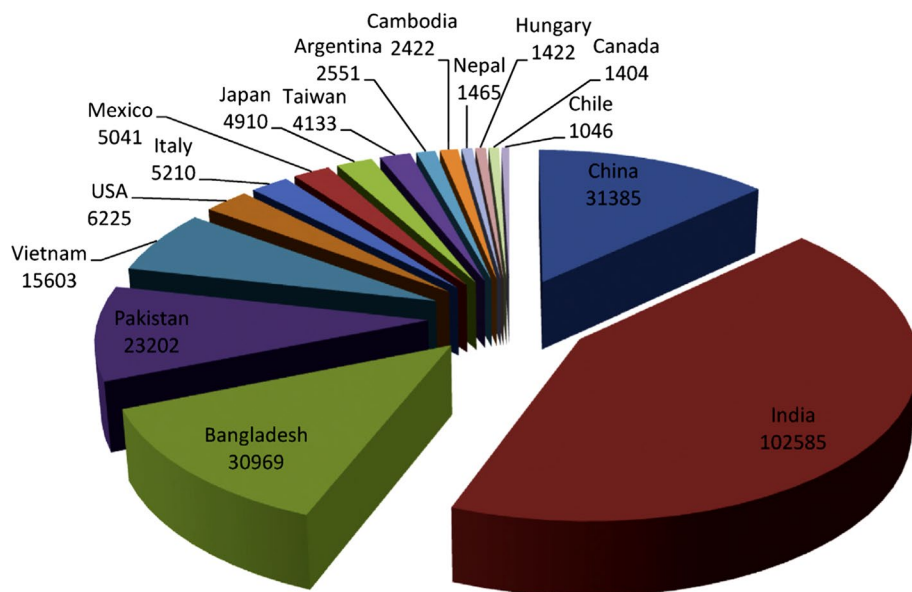
Fluoride presence in water

Health hazards

Fluorine is the most electronegative and reactive element that occurs naturally in soil, water, plants and animals in trace quantities. The countries like India, China and parts of Africa have seen a widespread problem with fluoride-rich drinking water. The highest fluoride contamination in the selected countries (India, Mexico, Pakistan, Egypt, Ethiopia, Saudi Arabia, Niger, USA, Senegal and China) is presented in Fig. 2 at concentrations above 1.5 mg/L which is considered as dangerous to human health (Ravenscroft 2007).

The fluorine is ingested by plants and animals, and some are taken up by their body tissues with long-term deposition in teeth and bones. The ingestion of fluorine is beneficial if it is not exceeding 0.10 mg/kg that provokes fluorosis (Bucher et al. 1991). The dental and skeletal fluorosis might postulate

Fig. 2 Estimated population exposed to fluoride contamination in selected countries. Reproduced from Jadhav et al. (2015) with permission from Elsevier



detrimental effects including immune toxicity, carcinogenicity, genotoxicity, reproductive toxicity, teratogenicity, renal toxicity, gastrointestinal tract toxicity and endemic dental mottling (Bulusu et al. 1979). Notably, young children are the most affected by dental caries in the primary dentition due to imbalanced diet and over usage of fluorinated dental care products like toothpaste. Dental fluorosis is a common disorder, also called as mottled enamel that is often characterized by hypomineralization of tooth enamel induced by ingestion of excessive fluoride during enamel formation (Taylor and Taylor 1965). Toothache, inflammation and dental extractions are some of the symptoms of dental fluorosis. This dental fluorosis can be treated by few techniques, mainly tooth whitening and other procedures to remove surface stains (Cao 2014). Concurrently, bleaching teeth may temporarily worsen the appearance of dental fluorosis. Dental veneers is fine option, looks alike custom-made shells that cover the front part of the teeth to improve their appearance, used at severe stage of dental fluorosis.

Fluorinated drinking water might be evidencing for the risk of osteosarcoma (a type of bone cancer), experimented in male rats (Chaturvedi et al. 2001). However, no evidence of cancer-causing potential in female rats was observed. In spite of expert's disagreement with the couple of animal studies that fluoride in drinking water causes cancer, it has been taken to next level investigations like mutations and chromosome aberrations in rodents and human cells (Chen et al. 1990), because fluoride can also cause mutagenic effect on osteoblasts, which could increase the risk of osteosarcoma, i.e., the primary stage of bone cancer. Indeed, adverse effects on reproduction in animals are associated with high levels of fluoride intake. The apparent threshold concentration for inducing

reproductive effects is 100 mg/L in mice, rats, foxes and cattle; 100–200 mg/L in minks, owls and kestrels and over 500 mg/L in hens (Chen et al. 2016). These experimental fluoride concentrations are far higher than those encountered in drinking water, i.e., 10 mg/L. In consequence, ingestion of fluoride at current concentration (120 mL for children and 240 mL of adults) should have no adversative effects on human reproduction (Chen et al. 2010).

Another serious issue is renal excretion, which is the major path to eliminate inorganic fluoride from the body. The effect of fluoride on the renal system results in exposure of kidney cells as a potential site for acute fluoride toxicity. Fluoride concentration of 100–380 mg/L can lead to necrosis of proximal and renal tubules, renal nephritis and dilation of renal tubules (Chen et al. 2011). In actual fact, human epidemiological studies revealed that no increase in renal disease was observed in a population with long-standing exposure of fluoride concentration within 8 mg/L in drinking water. In context, consumption of fluoride at presently commended concentration is not likely to produce kidney toxicity in humans (Chiba et al. 1982).

A further issue of high concentration of fluoride in the gastrointestinal system is irritation to the mucous membranes of the stomach lining by combining fluoride and hydrogen ions, resulting in the formation of hydrogen fluoride. It is evidenced by dose-dependent bad effects in animal species such as prolonged gastritis and other injuries of the stomach at a fluoride concentration of 190 mg/L (Chubar 2010). It is possible that individuals who have an existing stomach disorder may be vulnerable to irritation due to the ingestion of fluoridated water, but there are no published results for this. Owing to increased uptake of

fluoride by the human body can influence health through other mechanisms too (Dahi et al. 1996).

Analytical techniques for the determination of fluoride

Fluoride ions are colorless and difficult to determine in the solution by naked eyes. Hence, determination of fluoride requires minimal sample preparation with specific agents. A microdiffusion technique, such as the acid hexamethyldisiloxane (HMDS) diffusion method (Taves 1968), is expected to be more accurate. This method allows for the liberation of the fluoride from organic or inorganic matrices but free from sample contamination and losses due to volatilization. On the other hand, spectroscopic determination of fluoride using thorium as reagent has been attempted (Brownley and Howle 1960) by eliminating interfering cations using ion exchange column. Similarly, lanthanum chloranilate as an efficient reagent was investigated (Keihei et al. 1960) for the spectroscopic measurement of fluoride using calibration curves and interfering ions.

Beside spectrometry, other techniques like colorimetry, determination using electrode, chromatography, thermometric and conductometric titrations (Kubota and Surak 1959) are effective in the analysis of fluoride. New and efficient modifications in the existing technologies for various water sources have been developed. The rapid colorimetric determination using zirconium–alizarin reagent acidified with sulfuric acid has been attempted (Lamar 1982). The interference of sulfate, chloride and unneutralized bicarbonate in the determination of fluoride is reported in this study. However,

colorimetric methods are nowadays less extensively used as it is more time-consuming.

Table 1 presents the detailed account of the diverse technologies and methods investigated previously by several researchers for the analysis of fluoride with the appropriate references.

Chromatographic analysis has been used in small-scale analysis of fluoride. For instance, in 1982, Koichi et al. (1982) designed a combined system of GC-MIP gas chromatography microwave-induced plasma (GC-MIP) for the determination of fluoride in water samples. They designed a system involving a gas chromatograph of dual-column type equipped with a thermal conductivity detector (TCD) combined with a microwave cavity, generator and a photomultiplier. The lowest concentration of polar fluoride in water systems was successfully determined using a developed system. Volatile inorganic fluorides, especially uranium hexafluoride, chlorine trifluoride, chlorine, hydrogen fluoride and many more reactive components, are determined using gas–liquid chromatography with a special apparatus made of brass and copper protected by electroless nickel plating (Hamlin et al. 1963).

Polarographic measurement of fluoride (Guanghan et al. 1991) determines the reduction of fluoride using solochrome violet (pontachrome violet). Polarographic step in height is reduced while adding the fluoride compounds in the dye solution and further appeared second step. The sum of the height of these two steps becomes equal to the height of the original step, and the size of the second step is proportional to the concentration of fluoride present. This method is found to be more sensitive for its ion selectivity compared

Table 1 Various analytical methods for determining the concentration of fluoride

Compounds	Source of water sample	Analytical methods	Reagents/reaction enhancers	References
Fluoride	Aqueous solution	UV spectrophotometry	Chloranilic acid	Díaz-Nava et al. (2002)
Fluoride	Aqueous solution	Spectrophotometry	Cerium–alizarin	Ekka et al. (2017)
Fluoride	Natural waters	Spectrophotometry	Magnetic iron oxide nanoparticles	Ekka et al. (2017)
Fluoride	Natural waters	Spectrophotometry	Zirconium–xylenol orange	El Jaoudi et al. (2012)
Fluoride	Industrial effluents	Anion exclusion chromatography	–	Eom et al. (2009)
Fluoride	Rain water	Flow injection analysis	–	Fan et al. (2003)
Fluoride	Natural and fluoridated water	Rapid photometric method	Aluminum hematoxylin	Fucsko et al. (1987)
Fluoride	Tap water	Direct potentiometry (ISE)	–	Ganvir and Das (2011)
Fluoride	Drinking water	Potentiometry (F-ISE)	–	Gao et al. (2011)
Fluoride	Aqueous solution	Rapid spectrophotometry	Zirconium–eriochrome cyanine R	García-Sánchez et al. (2013)
Fluoride	Natural waters	Colorimetry	Resacetophenone	Gärtner et al. (2005)
Fluoride	Aqueous solution	Colorimetry	Monofluorophosphate	Genç-Fuhrman et al. (2004)
Fluoride	Aqueous solution	Reversed-phase HPLC	F ⁻ -La ³⁺ -alizarin complexone ternary complex	Ghorai and Pant (2004)
Fluoride	Aqueous solution	Spectrophotometric determination	Thorium–chrome azurol S	Ghorai and Pant (2005)

to the potentiometric selective determination. Likely, direct electrochemical ion selective method using selective electrode combined with Ag/AgCl reference electrode for tap water determination was effectively proved (El Jaoudi et al. 2012). It is been used for the determination of ultra-trace amounts of fluoride in tap water.

The evolution of reliable sensors such as optical sensors, absorption sensors and potentiometric sensor for measuring few nanograms per milliliter concentration of fluoride has been the dynamic field of a query. For instance, Zhou et al. (2004) contributed the development of a colorimetric chemo-sensor for fluoride ion detection. This study covered the interaction-based sensors, reaction-based sensors and many more.

Conventional technologies for fluoride removal

Nalgonda technique

The Nalgonda technique is one of the oldest defluoridation techniques, originated in a village in Andhra Pradesh, India (Fig. 3). It is available and used in developing nations like India due to its ease of handling, low cost and suitability to either community or household usage. It is based on the adsorption of fluoride on flocs of aluminum hydroxide in solution. This technique is a combination of several operations which includes flash mixing, chemical interaction, flocculation, sedimentation, filtration, disinfection and sludge concentration (Nawlakhe and Paramasivam 1993).

In the late 1990s, Dahi et al. (1996) investigated the defluoridation of water by employing the Nalgonda technique. In this technique, alum and lime were added to the fluoridated water with constant mixing in a two-bucket defluoridator. Alum and lime were added instantaneously

to the bucket containing raw water where it gets dissolved thoroughly with alum and lime mixture by stirring with a wooden paddle quickly for a moment followed by slow stirring for 5 min. The dose of lime was empirically 1/20th of that of the dose of aluminum salt. Bleaching powder was added to the raw water at a minimal rate of 3 mg/L for the purpose of disinfection. This defluoridation had been conducted for 1 ½ year having 76 families. Notably, built-in limitations of the current system exist, not allowing to treat lower fluoride concentrations unless excessive amounts of alum are used.

The Nalgonda technique involves the addition of alkali, chlorine and aluminum sulfate or aluminum chloride or both in a sequential order (García-Sánchez et al. 2013). This method seems efficient in larger quantities, simplicity of design, ease of construction and operation, ease of maintenance, less requirement of highly skilled workers, non-regeneration of media, low wastage of water, least mechanical and electrical equipment, minimum disposal problems, uniform quality defluoridated water and the reuse of alum from the generated sludge (Suneetha et al. 2015). Indeed, demerits of the Nalgonda technique are yet to be modified as following time-consuming, difficulty in controlling pH of treated water and regulation of pH with the help of lime, excess usage of alum and improper dosage of chemicals to remove low concentration fluoride. The above-mentioned advantages and limitations have been compiled (Renuka and Pushpanji 2013).

Reverse osmosis

In the late 1980s, reverse osmosis (RO) was considered as an alternative to conventional waste treatments due to its high removal capacities (Prihasto et al. 2009). In reverse osmosis, at one side of the semipermeable membrane, the hydraulic pressure is exerted which forces water across the membrane,

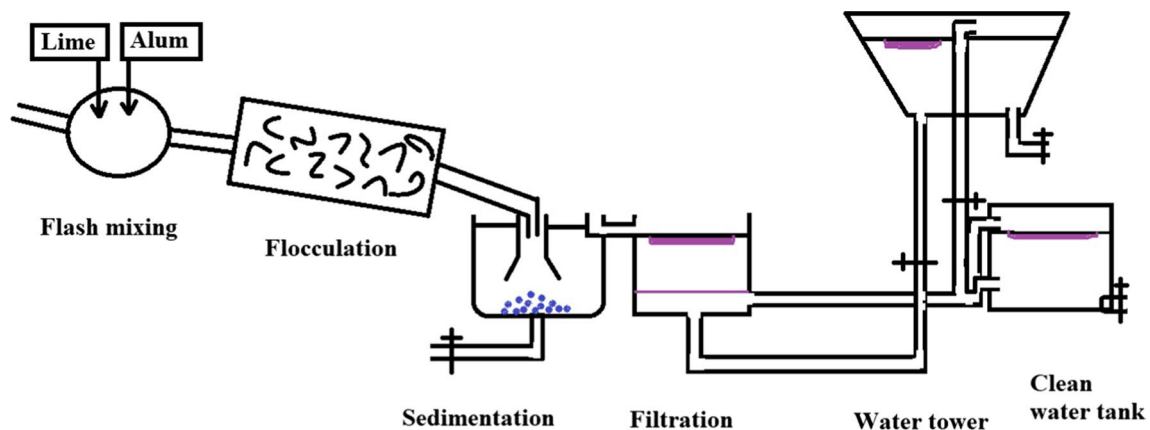


Fig. 3 A conventional Nalgonda technique first time implemented in Andhra Pradesh, India

thus leaving the wastes behind. Reverse osmosis involves in the inorganic removal using diffusion, size exclusion, charge repulsion and adsorption. Porosity of the membrane ensures nanofiltration. In contrast, nonporous membrane used in reverse osmosis follows the transport mechanism by the solution–diffusion model wherein solutes dissolve in dense material and then diffuses through the membrane down by the concentration gradient (Richards et al. 2010). Though reverse osmosis is a tedious process, it requires high pressure for the process to take place and permeability is also low as compared to specific nanofiltration. Low permeability is thus a major drawback of reverse osmosis technique. To overcome, nanofiltration thus performs better for the desalination for brackish water (Tahaikt et al. 2008). The removal of fluoride by reverse osmosis varies from 45 to 90% as the pH of the water is increased from 5.5 to 7 because the membranes are very sensitive to pH and temperature. Reverse osmosis can completely demineralize water with very low or practically no selectivity for monovalent ions, but it suffers from high operating pressure, low permeate flux and high energy requirements (Schneider and Middlebrooks 1983).

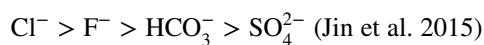
In addition, electronic industry strongly believes in reverse osmosis retaining all the effluent fluoride ions, with retention factor over 98% (Ndiaye et al. 2005). The retention factor is totally pH dependent. Having said, fluoride retention seems higher in the background solution than in the purified water in the single-feed solutions at pH 3–5. Working over a wide pH range, treating surface water, long-lasting membrane and minimal maintenance are the superior characteristics of reverse osmosis. This process might be expensive than others, but flow capability drops off for coagulant particles smaller than 10–15 microns (Joshi et al. 1992).

Electrodialysis

Dialysis is a process that separates solutes by transporting the solutes through a membrane rather than using a membrane to hold the solutes while passing water through it. The membrane pores are much less restrictive; hence, the solute can be driven by the Donnan effect (Hichour et al. 1999) or an applied electric field. Electrodialysis is a process used to remove ionic components from aqueous solutions through ion exchange membranes under the driving force of an electric field. Annouar et al. 2004 investigated both defluoridation and electrodialysis using natural chitosan as an adsorbent. Interestingly, both the approaches brought the fluoride level within 0.05–0.4 mg/L as per World Health Organization guidelines (Fawell et al. 2004). The utilization of permselective membranes in electrodialysis permits the control of fluoride concentration at various pH conditions (<https://www.bibliotecapleyades.net/>). Electrodialysis is a simple and reasonable process with no defects, minimizing

the precipitation risks of the bivalent salts present in the water during pre-treatment with low energy consumption (Inglezakis and Zorpas 2012), exhibiting removal of fluoride from brackish water.

On the other hand, an electric field as a driving force is applied through ion exchange membranes in order to remove ionic components from aqueous solution (Jadhav et al. 2015). This happens by applying a direct current potential between two electrodes where the negatively charged ions are retained by the positively charged anion exchange membrane and positively charged ions move toward cathode (Jain et al. 1999). Similarly, the negatively charged anions move toward anode and positively charged ion is retained by the negatively charged cation exchange membrane. At the end, the ion concentration increases in alternate compartments with a concurrent decrease in ions in other compartments. The membranes can be damaged by scaling and fouling (Jha et al. 2013). To avoid such risks, the electrodialysis operation is carried out in dual ways, i.e., with and without a chemical pre-treatment compliance. In specific, ACS-CMX membranes are used without pre-treatment stopping the transport of bivalent anions, in order to avoid the possible precipitation of bivalent salts. The transport of anions in ACS membrane is in the following order:



Defluoridation of water by adsorption

Adsorption is a process (Fig. 4) which is widely used for the defluoridation purpose in which materials like alumina, activated carbon, ion exchange resins, silica gel, natural materials like clay, mud and low-cost alternative adsorbents like fly ash, bone charcoal, etc., are employed (Johnston and Heijnen 2002; Joshi et al. 1992; Kalló 2001; Kamble et al. 2007). An overview of adsorption techniques and various adsorbents is presented in Table 2.

Alumina and aluminum-based adsorbents

Activated alumina is a porous, solid form of aluminum oxide (Al_2O_3). Shu et al. (1991) studied the interaction of fluoride ions with nanoscale aluminum oxide hydroxide (nano- AlOOH) over a broad range of pH from 3 to 12, with a varying fluoride concentration from 3 to 35 mg/L and adsorbent dose from 0.5 to 20 g/L. They found that the fluoride sorption reaches a maximum of approximately 96.7% at pH 6.8, indicating that fluoride adsorption increases in response to the increase in pH. In this study, fluoride sorption occurred in 30 min and reached pseudo-equilibrium in 6 h. In order to examine the interaction between fluoride ion and the nano- AlOOH , authors conducted X-ray photoelectron spectroscopic analysis before and after F^- sorption at pH

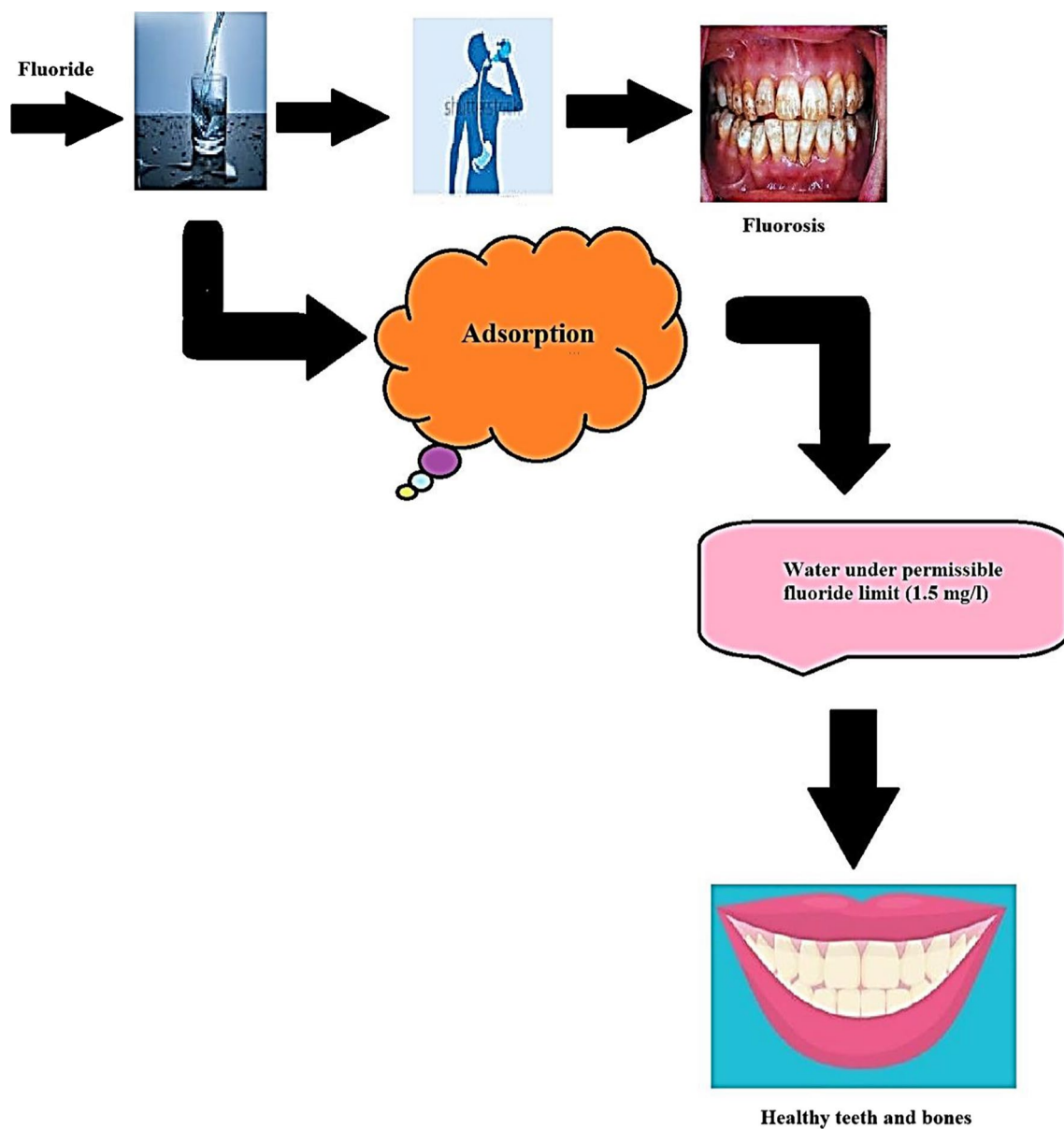


Fig. 4 Adsorption—a simple technique for effective fluoride removal

5.5. The competency of other anions (Cl^- , NO_3^- , HCO_3^- , SO_4^{2-} and PO_4^{3-}) with fluoride for active sorption sites was determined. In the presence of Cl^- and NO_3^- , no significant influence on the sorption mechanisms was observed, but the efficiency of the defluoridation is decreased roughly by 30%.

Sujana et al. (2009) also demonstrated the effects of various operational factors influencing the fluoride removal from aqueous medium by using amorphous iron- and aluminum-mixed hydroxides. The effect of solution pH studied over a wide range of 2.5–10 on fluoride removal by different synthetic materials and subsequently the temperature dependency of the process were studied in the range of 30–60 °C. The various concentrations of the solutions with different Fe/

Al ratio resulted in optimum pH. For instance, samples 1:0, 3:1 and 2:1 had an optimum pH range of 4–5, whereas for solutions 1:1 and 0:1, the pH was found to be 4–7.5 roughly. The equilibrium behaviors of the adsorption processes were well described by the Langmuir and Freundlich isotherm models. In conclusion, the fluoride sorption on these materials for all the samples obeyed first-order kinetics and was governed by intra-particle diffusion model.

The potential two kinds of mesoporous alumina were subjected to remove fluoride ions by Grace et al. (2010). Being aluminum alkoxide as precursor, the initial concentration of fluoride ions was from 20 to 250 mg/L with initial pH at 6.0. The concentration of fluoride in the filtrate was measured

Table 2 Adsorbents investigated for the removal of fluoride ions using various parameters at optimum conditions

S. no.	Adsorbent	Water source	pH	Adsorbent dosage	Time	Temp. (°C)	Adsorption capacity (mg/g)	References
1	Brick powder	Groundwater	6–8	0.2–2.0 g/100 ml	60 min	25 ± 3	0.789	Ahamad et al. (2019)
2	Bael (Aegle Marmelos) shell-activated carbon	Aqueous solution	6	2 g/L	60 min	30	48.8	Singh et al. (2017)
3	Chitosan-coated silica	Drinking water	4	10–20 mg/L	180 min	Room temp.	4.660	Prabhu and Meenakshi (2014)
4	Lightweight expanded clay aggregate	Aqueous solution	2–10	2–10 g/L	120 min	10–50	5.51	Tanvir and Waghmare (2015)
5	Nanostructured diatom–ZrO ₂ composite from algal biomass	Ground water	6	0.01–0.15 g	24 h	Room temp.	11.32	Thakkar et al. (2015)
6	Lightweight concrete	Aqueous solution	6.9	40 g/L	60 min	60	5.15	Oguz (2007)
7	NaP/HAp nano-composite	Aqueous solution	4–11	1.0–3.0 g	60 min	25–55	4.2	Zendehdel et al. (2017)
8	Ionic liquid-functionalized alumina	Synthetic and fluoride-contaminated solution	7	0.2 g	50 min	30–60	25.0	Ekka et al. (2017)
9	Ca-Zn(OH) ₂ CO ₃	Drinking water	7	0.14 g/L	40 min	30–50	14.56	Dhillon et al. (2017)
10	Chitosan–praseodymium complex	Synthetic solution	7	0.1–0.4 g/L	5–100 min	27	15.87	Kusrini et al. (2015)
11	Aluminum-impregnated chitosan biopolymer	Aqueous solution	2–12	0.7 g	60 min	25 ± 2	0.7919	Swain et al. (2009)
12	Artocarpus hirsutus-based adsorbent	Groundwater	6–8	–	–	30	6.19	Dhanasekaran et al. (2017)
13	Carboxymethyl cellulose loaded with zirconium	Aqueous solution	1–11	0.2–1.0 g	5 to 600 min	15–55	47	Wang et al. (2014)
14	Neodymium-modified chitosan	Aqueous solution	5–9	0.2–2.0 g/L	50 min	10–50	2.67	Yao et al. (2009)
15	CeO ₂ –ZrO ₂ nanocages	Aqueous solution	3.5–4.5	0.2 g/L	60 min	25	146.59	Wang et al. (2013)
16	Natroalunite micro-tubes and spheres	Synthetic solution	7	1 g/L	24 h	25	85.84	Zhu et al. (2015a, b)
17	Sulfate-doped hydroxyapatite hierarchical hollow microspheres	Aqueous solution	7	0.5 g/L	24 h	25	31.3	Chen et al. (2016)
18	Hydroxyapatite (HAP) nanowires	Synthetic solution	7	1.0 g/L	180 min	25	40.65	He et al. (2016)
19	Al-HAP adsorption membrane	Drinking water	3–12	–	24 h	25	93.84	He et al. (2017)
20	Porous granular ceramic	Aqueous solution	6	10–30 g/L	48 h	25	1.79	Chen et al. (2010)
21	Granular ceramic	Aqueous solution	5–8	–	72 h	20	2.157	Chen et al. (2011)

using ion chromatography. Notably, the mesoporous alumina prepared by anionic surfactant (MA-2) depicted superior adsorption performances in comparison with commercial gamma alumina in terms of sorption capacity as well as sorption rates. In this order, Li et al. (2011) analyzed the performance of mesoporous alumina corresponding to fluoride ion removal. The synthesis of highly ordered mesoporous alumina and calcium-doped alumina was performed and characterized. The sorption characteristic of prepared material was examined with the effect of pH, temperature, initial ion concentration and competency of anions, respectively. As reported earlier, fluoride-contaminated water almost contains other anions which may compete with fluoride for the active sorption sites. In conclusion, HCO_3^- had a positive effect on the fluoride adsorption, whereas SO_4^{2-} had a relatively greater negative effect on the fluoride adsorption. The highest fluoride removal capacity was 450 mg/g. Thus, this procedure has shown to be a proficient method for the removal of fluoride from water.

The adsorption performance of alumina-untreated hydrated alumina (UHA) and thermally treated hydrated alumina (THA) was compared by Shimelis et al. (2006). Aforesaid process influencing parameters revealed that the removal efficiency of fluoride was increased with the increasing adsorbent dosage. Interestingly, increase in temperature resulted in the reduction in removal efficiency. The defluoridation efficiency for both UHA and THA was within the pH range between 4.0 and 9.0. The kinetic of UHA followed pseudo-second-order. The optimum temperature of 300 °C was maintained in continuous packed bed column. The experimental data were well fit to the Freundlich isotherm model with a minimum loading capacity of 23.7 mg F⁻/g and 7.0 mg F⁻/g for THA and UHA, respectively.

Adsorption of fluoride into alum-impregnated activated alumina (AIAA) was studied by Tripathy et al. (2006). The pH from 2 to 8, adsorbent dose of 0.5–16 g/L, initial fluoride concentration (1–35 mg/L), contact time and temperature are the parameters used to determine the adsorption capacity of AIAA. Adsorption kinetics of the process indicates that the fluoride removal was rapid during the initial phases of the experiment. The 90% removal was done in 3 h which is significant. The regeneration of the spent AIAA was achieved by rinsing it with 0.1 M NaOH at pH 12 by neutralizing with 0.1 M HCl. In context, AIAA is efficient than unmodified activated alumina to remove fluoride (up to 0.2 mg/L) from water containing 20 mg/L fluoride.

Teng et al. (2009) attempted modifying activated alumina using manganese oxide to produce hydrous manganese oxide-coated alumina (HMOCA). Batch adsorption study of fluoride by HMOCA and ion exchange capacity with effect to process influencing parameters are well explained. The adsorption system obeyed Langmuir equilibrium model.

This study revealed that HMOCA is able to adsorb fluoride (adsorption capacity q_e 7.09 mg/g) at pH of 5.2 ± 0.05 . Bansawal et al. (2010) synthesized copper oxide-coated alumina (COCA) by impregnating mesoporous alumina in copper sulfate solution followed by calcination in the presence of air. Batch adsorption data revealed that the pH of solution plays a major part in the defluoridation of drinking water as the adsorption capacity was high while reducing the pH from 9 to 4. The adsorption isotherms were best explained by Langmuir equilibrium model, and the adsorption capacity of COCA is 7.220 mg/g which was found to be three times higher than unmodified alumina.

Activated alumina system is merged with other technologies. A new technique by combining activated alumina column and an electrochemical system for defluoridation of water was investigated by Lounici et al. (2004). The electrosorption technique was used in the present study to enhance the adsorbent capacity of the sorbent. It was found that at a concentration of 800 mg/dm³ of NaCl, the fluoride adsorption capacity of the electro-activated alumina was about 55% which was larger than that of the conventional alumina. The electric field effect on the mechanism and the execution of the intake were tested under various experimental conditions by varying initial fluoride concentrations, volumetric flow rates, pH, temperature and hardness of the sample water (Long et al. 2009). On the experimental basis, authors concluded that the performance of the electrosorption process in all experimental conditions appeared more efficient and presented higher adsorption capacities. Several other researchers also examined the potential of alumina-based adsorbents for defluoridation of water (Lee et al. 2010; Leyva et al. 1999; Li et al. 2011, 2013, 2016).

Carbon-based adsorbents

Activated carbon

Activated carbon (AC) is considered as a universal adsorbent for removing contaminants from water because of its high porosity, large surface area and also due to its versatile surface chemistry (Al-Othman et al. 2012). Activated carbon, also called activated charcoal which is a form of carbon, has low-volume pores that increase the surface areas available for adsorption or chemical reactions (Li et al. 2017). A manufacturing of activated carbon is gaining prominence due to the need of developing an affinity for certain contaminants toward carbon molecules to cater for their removal from wastewater. Recently, it has been noted that fluoride removal can also be done by biomass-based chemically modified activated carbon due to their low cost and availability (Li and Zhang 2011). Those chemically modified activated carbons are

zirconium-impregnated coconut shell (Liao and Shi 2005; Liu et al. 2015; Megregian 1954), aluminum hydroxide-coated rice husk (Yang et al. 2015) and tamarind fruit shell carbon (Ma et al. 2009).

Electrosorption is a process in trend using micropore-dominant activated carbon as the electrode material is used for fluoride removal. However, there had been only a few reports on the removal of fluorides by electrosorption process (Lupo et al. 2012). Electrosorption is a fine desalination process where ions are attracted and concentrated in the electrical double layers of electrodes on applying the electrical potential. Hence, fluoride-contaminated wastewater has experimented with the aid of activated carbons, derived from plant materials belonging to a different variety of kingdoms. Upon investigation, it has been found that there is a strong affinity between fluoride and activated carbon obtained from barks of *Vitex negundo* plant. The result shows that the maximum fluoride adsorption takes place at the optimum pH of 7.0 and adsorbent dosage of 0.4 g/L.

On the other hand, rice straw-derived activated carbon through steam pyrolysis helps in the reduction of fluoride from wastewater at harsh experimental conditions. Since a biomass of rice straw is not so denser, the activation process is facilitated and occurs faster with other carbon precursors. In spite of adhesion property, rice straw being a soft precursor limits the development of large surface areas (Macejunas 1969). In order to enhance the surface morphology, potassium hydroxide and potassium permanganate were engaged as an activating agent, while nitric acid resulted in the reduction in surface area. The effect of parameters like adsorbent dosage increases the percentage removal of fluoride as dose increases, hence reflected in increased adsorption capacity (Maier 1947). In the case of agglomeration, sorbent particles at higher doses would lead to a decrease in the surface area and an increase in the diffusion path length. Therefore, in conclusion, fluoride adsorption better occurs at lower concentration (Mattevi et al. 2009; Medellin-Castillo et al. 2007).

Likely, a study obtaining carbon from the barks of *ficus racemosa* reveals the greatest affinity of carbon precursor toward fluoride ions, also called "Active carbon derived from the barks of *Ficusracemosa*" (ACBFR) (Ravulapalli and Kunta 2017). The optimum pH for the fluoride removal was 7.0; beyond, a fall in the removal was observed, because a negative adsorption was featured by the lesser concentration of fluoride ions than that present in the bulk. Therefore, a higher pH features negative adsorption sites causing electrostatic repulsion for fluoride ions. This has been practically applicable, conducted in the most fluoride-affected ground area in Andhra Pradesh, exhibiting a successful removal percentage of fluoride ions than estimated. In extension, the spent activated carbon had regenerated while treating with 1.0 N of nitric acid or 0.1 N sodium hydroxide (Gupta

et al. 2007a, b). It discloses the regaining of sorption ability of activated carbon from both acidic and basic conditions. Thus, ACBER can be an effective and eco-friendly sorbent.

Activated carbon derived from bael shell (ACBS) was investigated on adsorption of fluoride ions, resulting in faster adsorption rate. At an initial batch sorption experiment, around 52% of removal was achieved (Singh et al. 2017). This has been extended to treat Congo red dye-contaminated aqueous solution (Ahmad and Kumar 2010). Similarly, titanium dioxide-loaded activated carbon (Ti-AC) was found to be efficient for defluoridation through electrosorption. The titanium dioxide-loaded activated carbon achieved two times defluoridation than the original AC electrode. It indicates that electrosorption with Ti-AC can act as a potential electrode as for removing fluoride ions from water. The pH study showed that the adsorption capacity of Ti-AC was optimum in the pH range 7–9 (Misaelides 2011). Thus, several other researchers also proved the efficiency of active carbon-based adsorbents for defluoridation in water (Mohan et al. 2012; Mumtaz et al. 2015; Murugan and Subramanian 2006).

Graphite

There are many research works being carried out on the removal of fluoride ions from water using carbon-based adsorbents like active carbon, graphite and carbon nanotubes. However, the utilization of graphite as an adsorbent is less but emerging with a featured porous structure, high surface area and the presence of more surface-active groups. An exclusive availability, practical insolubility in water and also non-toxicity in nature make graphite a great market demand. But attritional loss of graphite during regeneration makes it less wanted than that of other adsorbents holding crystalline nature.

Recently, it has gained much scientific attention since its discovery due to its unique electronic properties (Jin et al. 2015), mechanical properties, excellent mobility of charge carriers and electromagnetism ((Meenakshi 1992). Graphite has great potential application in adsorption of a different substance such as methylene blue, oil and Cr. Moreover, graphite has a good application as a matrix because of its excellent property such as chemical inertness, stability under high temperature and corrosion resistivity (Oguz 2017). Research work on removal of fluoride in aqueous medium by modified alumina-expanded graphite has resulted with successful output saying that alumina-modified expanded graphite composites have shown higher adsorption capacity which was due to surface charge of the sorbent and the generation of excess hydroxyl ions according to the effect of pH and FTIR analysis (Jin et al. 2015). Similarly, Wan et al. (2015) synthesized tea waste-assisted hydrous aluminum oxide nanoparticles which were mediated through anionic polyacrylamide (Tea-APAM-Al) that helps in aluminum assembly.

Graphite focuses on being positive for technological aspects such as sensors, solar cells, field effect transistors and also as adsorbents for heavy metal removal. The fluoride removal by graphite was conducted across the world researchers by demonstrating batch adsorption of fluoride and determining the adsorption equilibrium and kinetic properties of graphene. The surface morphology of graphene is customarily studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The new breakthrough in graphene functionalization is found that phenol, epoxide, carboxyl and other groups can be an additive to functionalize graphene through oxidation treatment. In addition, manganese oxide, an insoluble and non-toxic adsorbent, is found to be effective for the removal of fluoride, considering the various parameters like temperature, adsorbent dosage, contact time and pH. The pH is a significant factor that defines electrostatic interactions between fluoride and the surface of adsorbent (Roy et al. 2017). When the pH ranges from 2.3 to 8.0, the maximum adsorption capacity was observed at pH 5.5 and no obvious variation was found in the pH till 7.5 (Li et al. 2017). Besides, a rapid decrease in fluoride adsorption capacity was found above the pH 7.5. Hence, the optimum solution pH for fluoride removal ranges between 3.8 and 7.5. Similarly, the removal percentage increases with an increase in the adsorbent dose, while adsorption capacity showed a decreasing trend. Synthesis of graphene is in the first place, whereas tea solution was attempted to produce bio-reduced graphene oxide (TPGO), being used for defluoridation. As the maximum fluoride removal capacity is observed, efficacy of TPGO paid more attention and can be comparable with the available alternatives.

Natural materials

Many parts of the world are frightened by fluoride-related health hazards caused by excessive exposure of fluoride in water. Though the reports of risks of high fluoride dosing are alarming, benefits of minimal exposure of fluoride are hidden in scientific fact. The WHO recommends 1.5 mg/L for fluoride concentration in drinking water (Petersen and Lennon 2004). Defluoridation technologies comprise the principle of precipitation, ion exchange, adsorption and other electrochemical methods (Bulusu et al. 1979). Among them, adsorption is considered as a most suitable technique for the removal of fluoride and other pollutants also (Daneshvar et al. 2017; Sharma et al. 2015). Other technologies require a high cost of processing being unfit for developing countries. Therefore, there is a great need for low-cost, easy and environmental friendly technologies.

Numerous natural inorganic materials such as clays, soils, minerals and building materials have been utilized in the defluoridation of water. Bio adsorbents have various

functional groups such as imidazole, carboxyl, amide, carbonyl, sulfhydryl, phenol, thioether, amino and hydroxyl moieties which are capable of adsorbing various types of pollutants, especially the metal cations (Nichols and Condo 1954). Over the last few years, various studies have been performed to assess the low-cost adsorbent for fluoride removals such as titanium-rich bauxite (Liu et al. 2015), activated alumina, manganese oxide-coated alumina (Teng et al. 2009) and carbon nanotubes. Moreover, plant materials like tamarind seed, serpentine and tamarind gel, duck weed, Royale plants (Shrike and Chandra 1991) have also been testified to accumulate fluoride and hence used as defluoridation agents. The application of agricultural waste biomass is becoming an important concern because such unused means in many cases cause a severe disposal problem. Various waste biomass sources are accessible in different parts of the world. Based on their production and processing, experimental conditions and adsorption properties, for instance egg shell, corn cobs, tea and coffee waste, rice husk and its ash, peanut shells, coir dust, saw dust, dry tree leaves and barks, wheat and rice bran and sea weeds have been reported successfully.

Moringa oleifera is a native tree of the sub-Himalayan parts of Northwest India, Afghanistan and Pakistan. Previous studies have shown that *M. oleifera* is non-toxic and used as a coagulant. *Moringa oleifera* is edible and used for the chemical treatment of water (Sapana et al. 2012). The coagulation properties of *M. oleifera* being a coagulant protein are utilized for adsorption, charge neutralization and inter-particle bridging. Owing to the flocculation by inter-particle bridging, *M. oleifera* has the specific trait for being high molecular weight polyelectrolyte. Among all the plant materials tested so far, the seeds of *M. oleifera* are evidenced as the most effective primary coagulant for the treatment of water and comparable to alum, a conventional chemical coagulant. In view of all these, *M. oleifera* is termed as a “multipurpose tree.”

Aluminum and iron oxides are major components of red mud, and this mixed adsorbent has been studied extensively for anionic pollutants, especially anions from arsenic(III) and arsenic(V). As recovered from the Bayer's process, red mud is highly alkaline (pH 10–12) for the use as an adsorbent for anions (Teutli-Sequeira et al. 2013). The alkalinity could be decreased by washing with seawater. On laboratory level, the pH can be set with strong acid or base. A series of procedure like washing, acid activation followed by drying can let red mud to be an essential adsorbent that would escape the requirement for bulk acidification of water gets to be defluoridated.

Chitin and chitosan are natural polymers showing potential functional groups that must be constituted in any broad-adsorbents for removing various types of aquatic pollutants. Chitin is a polysaccharide containing amino and hydroxyl

functional groups (Miretzky and Cirelli 2011) which can be extracted from crustacean shells. It is commonly available as shellfish-processed waste, whereas chitosan is a copolymer of glucosamines derived from chitin in hot alkaline solution by deacetylation (Prabhu and Meenakshi 2014). It was reported that the adsorption of F^- from synthetic water samples using chitosan was very fast and reached a maximum within 5 min. The adsorption was increased with increasing the pH from 2 to 6 followed by a decrease up to pH 10 (Prabhu et al. 2014).

Fly ash is a crucial by-product, obtained on the combustion of coal in power stations. It seems a fine, powdery mass with a size of 1.0 to 100 μm , mainly made up of a mixture of amorphous and crystalline alumina silicates and numerous compounds of Al, Si, Fe, Mg and Ca. Fly ash is indeed a potential candidate for F^- adsorption from the water. Adsorption of F^- by fly ash contains 25.9% Al_2O_3 , 56.0% SiO_2 , 2.22% CaO and 1.26% Fe_2O_3 with a maximum adsorption capacity of 20 mg/g at the pH 6.5 (Chaturvedi et al. 2001). The adsorption of F^- was raised from 79 to 94% when the pH of the F^- solution (10 mg/L) was increased from 2.0 to 6.5 and then reduced with further increase in pH up to 9.5. The decrease in pH from 2.0 to 12 has resulted in the F^- adsorption by a fly ash reported by others. The effect of pH in the fly ash is owing to the difference in chemical features of the fly ashes including experimental conditions. A column study revealed an alkaline fly ash (pH \geq 10, 9.1% CaO) removed F^- (1–100 mg F^- /L) from aqueous solution when the solution was passed through a column (400 mm length) having 450 g fly ash at a flow rate of \leq 2 mL/h. A complete F^- adsorption was occurred after 120 h. In context, the F^- adsorption mechanism is proposed owing to chemical binding of F^- onto $\text{Ca}(\text{OH})_2$ and physical adsorption onto the residual carbon particles in the fly ash.

The removal of fluoride using natural materials as biosorbents has shown that the appropriate surface characteristics, metal binding properties, functional groups like amino, amide, carboxyl, alkene and sulfhydryl were found to be responsible for the adsorption of fluoride, because considerably calcium and magnesium are feasible owing to great affinity for fluoride ions. Therefore, recent research on biosorbents is further expandable with regeneration modeling and immobilization to treat the fluoride-polluted water.

Zeolites

Lack of clean drinking water is unavoidable nowadays as a result of pollution and improper discharge of waste from industries (Alqadami et al. 2016, 2017b, Naushad 2014). Such waste ordinarily contains anionic and cationic pollutants, oily substances which threaten aquatic ecosystem. In order to remove pollutants, natural zeolites as an adsorbent have found a variety of applications in adsorption, catalysis,

building industry, agriculture, soil remediation and energy (Tanvir and Waghmare 2015). Since fluoride is an essential micronutrient present in drinking water, excess concentration of fluoride ($>$ 1.5 mg/L) is removed by zeolites for its availability, a specific and strong affinity toward fluoride, low in cost, structurally stable resulted in spatial arrangement and stabilization of individual atoms, molecules and clusters (Serrano et al. 2011).

Notable in China, ammonium fluoride is used extensively as a surface treatment agent in the aluminum industry. The wastewater usually contains fluoride as high as 80–90 mg/L, a threat to human and ecosystem. CaCl_2 -modified natural zeolite (CZ) had been tested to treat fluoride-containing effluents from synthetic and aluminum industry-discharged wastewater (Samatya et al. 2007). Various operating conditions such as sorbent dosage, initial pH value, temperature and contact time were optimized. Consumption of this water troubled and altered many lives from mild dental to crippling skeletal fluorosis. The presence or absence of fluoride is associated with clinical dental fluorosis, losing enamel, particularly categorized by staining and pitting of the teeth. In severe cases, fluoride stores in the bones leading to toughness and pain in the joints and changes in bones structure. Considerably damage to non-skeletal tissues as kidneys, liver, brain, digestive and reproductive systems, etc., is due to the chronic ingestion of fluoride. Based on their cationic exchange properties, zeolites are found mainly appropriate for fluoride removal in the treatment of water but not for the adsorption of anionic species (Zhang et al. 2011).

Many reports show that natural zeolite (clinoptilolite) is able to treat fluoride-containing effluents through ion exchange and precipitation with La^{3+} , Al^{3+} or ZrO_2^+ and adsorption ordered as: $\text{CLI-ZrO} > \text{CLI-La} > \text{CLI-Al}$ reported by Samatya et al. 2007. An electrochemical method was engaged to modify clinoptilolite–mordenite-rich tuff with Al^{3+} or La^{3+} by refluxing, resulted in the opposite order of the fluoride removal efficacy. The adsorption capacity of aluminum-modified zeolite was observed about ten times more than the lanthanum-modified material.

Correspondingly, a natural Mexican zeolite (heulandite–clinoptilolite) was modified using Ca^{2+} , Na^+ , La^{3+} or Eu^{3+} . Their adsorption efficiency was found around 60% for the initial concentration of 5 mg/L. A natural Chinese stilbite was modified with iron, posing a maximum adsorption capacity for fluoride of 2.31 mg/g (Sun et al. 2011). Furthermore, a chabazite was modified with MgSO_4 solution in 2014 exhibiting 95% removal from 3 mg/L fluoride solution. In this trend, other modifications are encouraged for defluoridation of water. A calcium-modified zeolite-rich tuff was reported by Zhang et al. (2011) which showed the maximum capacity 1.76 mg F^- /g, while Zhou et al. used a zirconium-modified zeolite with the fluoride removal efficiency of 97% from a 10 mg/L fluoride solution. Adsorption

efficiency of each modified zeolite is determined by the type of zeolite, preparation methods, metal modification along with the experimental conditions such as temperature, pH, initial concentration of fluoride and water composition.

In note, zirconium-based materials were found interesting for defluoridation of water owing to their affinity to fluoride ions (He et al. 2014). It is important to indicate that the zeolite-rich tuffs did not show any fluoride removal capacity (He et al. 2017). Adsorption isotherms were examined through linear and Freundlich isotherm models using non-linear regression analysis (He et al. 2016). Fluoride adsorption capacity of zirconium-modified (ZM-FeZr) seems better than other zeolite-rich tuffs. However, it is well known that pH affects the adsorption phenomena of fluoride at the solid–water interface, as it influences on the chemical speciation and properties of the water pollutants. On the basis of fluoride speciation, hydrogen fluoride was predominant in the solution at pH < 3.18. Subsequently, fluoride ions were not accessible to be adsorbed. Similarly, when fluoride adsorption capacity was decreased at pH values above 7, the hydroxyl ions had competed with F⁻ ions for the active sites on the adsorbent (Özacar and Sengil 2005). Even in adsorption mechanism, thermodynamic data suggested physical interaction between the fluoride ion and iron. Hence, zirconium-modified zeolites acted as the activation energy magnitude and standard enthalpy values were lower than approximately 40 kJ/mol and 20.9 kJ/mol (Renuka and Pushpanji 2011). Another effect depends on the adsorbent dosage level; the efficiency of the fluoride removal takes place because of increase in surface area as more active sites were available for adsorption with increased dosages (Rajkumar et al. 2015).

Above all, Van der Waals force could be the possible reason for fluoride removal mechanism, as the positively charged ions might be attracted toward the negatively charged ions of the solution. In context, zeolite may be a probable adsorbent for removal of fluoride ions from the polluted water.

Ion exchange resins

Fluoride removal by means of ion exchange technology using anion exchange resins is difficult, since the order of selectivity for anionic species by anion exchange resins (Raju et al. 2012) is as follows:

citrate > SO₄²⁻, oxalate > I⁻ > NO₃⁻ > CrO₄²⁻
> Br⁻ > SCN⁻ > Cl⁻ > formate > acetate > F⁻.

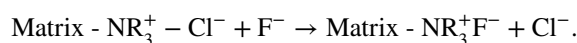
Consequently, the type of cation/chelating resins is equally employed for fluoride sorption. In addition, metal-loaded cation exchangers comprising inorganic cation exchangers like silica gel, alumina gel or other chelating resins (Runaska et al. 1951) loaded by high-valence metals such

as lanthanum(III), iron(III), cerium(IV) and zirconium(IV) are paid attention by researchers. The principle works here as the anionic sites of the resin are replaced by the fluoride ions. Such replacement continues until all the sites on the resin were occupied. Later, resin is backwashed with water as supersaturation takes place with the help of dissolved salt from the anionic element. Hence, new anions are welcome to replace the fluoride ions that lead to recharge resin and starting of the process all over again. Driving force for the replacement of ions from the resin is the stronger electronegativity of the fluoride ions (Zhou et al. 2004). In line, Xie et al. (2017) developed composite using lanthanum-modified bone waste (LBW) for fluoride removal from groundwater. For which, discarded bone waste was processed to improve the surface characteristic like porous structure and removal efficiency.

The ions were adsorbed physically by completely retaining their inner hydration shell wherein the adsorption was owing to coulombic or electrostatic attraction (Su et al. 2013). This process is rapid and reversible. Ion exchange tends to prefer counterions of higher valency, higher concentration and ions of smaller hydrated equivalent volume (Sepehr et al. 2014). Using ion exchangers, a selective fluoride removal process can be developed. However, the ion exchange process can only be effective if the fluoride concentration is less than 10 mg/L (Sepehr et al. 2013).

Amberlite resin is used in Japan for chemical modification by the incorporation of trivalent metal ions including cerium(III), lanthanum(III), iron(III), yttrium(III) and aluminum(III) for the removal of fluoride from hot spring water. The optimum conditions maintained for loading metal ions on Amb200CT resin were: the effect of initial concentration of fluoride solution, pH and adsorbent doses. Amberlite 200 CTNa resin is abbreviated after 200 CT, a strong acidic cation exchange resin of sodium salts. The functional group present in Amb200CT is –SO₃Na, and diameter ranges from 0.50 to 0.65 mm. Followed by, density is 785 + 25 g/L, a nontransparent ball with gray color (Suzuki et al. 1989).

A strong basic anion exchange resin comprising quaternary ammonium functional groups can be efficient to remove fluoride ions. The removal takes place according to the following reaction:



The commercial ion exchange resins (IERS) such as Indion FR 10, a chelating resin supplied by Ion Exchange (India) Ltd., Mumbai, and Ceralite IRA 400, an anion exchanger in Cl⁻ form (Wang et al. 2014) are implemented to replace the chloride ions of the resin by the fluoride ions. The removal was found to be between 90 and 95%, retaining the taste and color of water intact (143). The demerits are the presence of sulfate, phosphate, bicarbonate, etc., resulting

in ionic competition, relatively higher cost and low pH of treated water and high levels of chloride.

Miscellaneous adsorbents

The previous sections have summarized the different categories of adsorbents for the defluoridation of water. In an additional fact, Srimurali et al. (1998) investigated the utilization of low-cost materials like kaolinite, bentonite, charfines, lignite and nirmali seeds for the defluoridation of water. Among them, charfines and bentonite exhibited the highest adsorption capacity of roughly 40% toward F^- ions under optimum system conditions. The removal percentage increases with an increase in time but falls with an increase in the pH. The main aspect of the study revealed that chemical pre-treatment of the sorbents does not have any substantial effect on the adsorption efficiency. The order of the adsorption capacity of these five low-cost materials toward the fluoride ions is given as follows:

Bentonite > charfines > kaolinite > lignite > nirmali seeds.

Chitosan, a natural polymer, has been investigated for the wastewater treatment (Albadarin et al. 2016; Sharma et al. 2017). A study conducted by Guanghan et al. (1991) on the removal of fluoride from aqueous solution using Ce(III)-incorporated cross-linked chitosan (Ce-CCS) determines the adsorption capacity of Ce-CCS for the initial concentration of 0.15 g. The removal efficiency was found to be increased enormously with an increase in adsorbent dosage (100, 200 and 300 mg/L). However, a further increase in Ce-CCS dosage also had a significant effect resulting in the reduction in the adsorption capacity, thereby indicating the saturation of the adsorption studies.

The similar course of study was conducted by Zhu et al. (2017) using cross-linked chitosan composite. A cerium-immobilized cross-linked chitosan (CTS-Ce) was employed as an adsorbent to investigate fluoride removal over a broad range of pH (2–11), initial fluoride concentrations (5.0–100 mg/L), contact time and temperature (10–40 °C). The experimental data were well described by pseudo-second-order kinetic model and Langmuir equilibrium model. The effect of competing anions on fluoride adsorption by CTS-Ce was well explained that Cl^- had no significant effect, whereas SO_4^{2-} , NO_3^- and HCO_3^- affected the fluoride sorption when present in high concentrations.

Several other research activities are being carried out in the application of chitosan and its derivatives for the removal of fluoride from contaminated water (Swain et al. 2009). Miretzky and Cirelli (2011) reviewed on various chitosan derivatives and composites for the removal of fluoride from various sources of contaminated water. The removal process using electropositive multivalent metals-incorporated

chitosan beads was well studied and compared with other chitosan derivatives.

Other research team developed a composite from naturally available cow dung and calcium and iron salts-impregnated cow dung. These materials were dried up and further carbonized, resulting in the formation of cow dung carbon (CDC) or Ca-Fe-impregnated cow dung carbon (ICDC) (Rajkumar et al. 2015). Batch adsorption parameters for both CDC and ICDC were pH, contact time, adsorbent dosage, initial fluoride concentration, temperature and competence of other anions. Comparably, CDC exhibits better adsorption efficiency toward F^- ions under the optimum condition. The experimental data obeyed pseudo-second-order kinetic, thereby indicating that the defluoridation may be a chemisorption. Regeneration of CDC and ICDC adsorbents takes place by washing the F^- -loaded adsorbent using NaOH solution.

Gupta et al. (2007a, b) performed defluoridation using waste carbon slurry through batch adsorption experiments. The maximum fluoride uptake by the waste carbon slurry was found to occur at contact time of 1 h and pH of 7.58. Langmuir isotherm model produced the best fit. The enthalpy, entropy and free energy values for the adsorption studies were found to be 7.348 kJ mol⁻¹, 0.109 kJ mol⁻¹ K⁻¹ and -25.410 kJ mol⁻¹, respectively, depicting the feasibility of adsorption process. The percentage removal of fluoride was about 21% for the adsorbent dose of 0.5 g/L. While increasing the adsorbent dosage (up to 3.0 g/L), the removal percentage at a rapid rate to about 88.2% was perceived. The entropy change was positive, revealing the increased randomness of the solid-solution interface during the adsorption of fluoride ions on the active sites of the sorbent. The adsorption capacity of 4.861 mg/g at 15.0 mg/L exhibits that this system can successively be employed for the defluoridation of wastewater.

A descriptive summary of the application of various adsorbents for the defluoridation of water under different experimental conditions is presented in Table 2 with the appropriate references. It is to perceive that those miscellaneous adsorbents are great deal better than traditionally employed adsorbents.

Islam and Patel (2007) worked on the removal of excess fluoride from the aqueous solution by potential activated and ordinary quick lime. Defluoridation took place by chemisorption process and marginally by precipitation. The preparation of quick lime follows thermal treatment at 450 °C for about 4 h in order to enhance porosity, surface functional groups and adsorption capacity. Batch adsorption studies were experimented for both the presence and absence of competing anions such as phosphate (PO_4^{3-}), sulfate (SO_4^{2-}) and nitrate (NO_3^-) at room temperature (25 ± 2 °C). Pseudo-first-order kinetic was observed. The progress of experiment revealed that an increase in temperature (20–50 °C)

can also increase the percentage removal from 8.9 to 32.0% for 10 mg/L solution and from 71.6 to 80.9% for 50 mg/L solution. The experimental data fit with linearly transformed Langmuir isotherm. In context, the presence of the mentioned anions can reduce the adsorption of fluoride appreciably with an increase in the initial concentration. However, this method cannot be adopted for domestic water treatment, since it is not possible to bring the fluoride within the permissible limit and also because it increases the pH of water.

Suet al. 2013 tested the efficiency of Fe–Al–Ce nano-adsorbent for defluoridation after its granulation with an inorganic binder. Granulation with organic binder was avoided purposefully as it results in the great loss of adsorption capacity. In this experiment, aluminum, zirconium, titanium and silica sol were employed as binders for the granulation purpose. The adsorption capacity of these granulated adsorbents was observed to be relatively high and appeared to be still higher after calcination at 500 °C reaching over 90% roughly.

The evolution of an unconventional adsorbent for the defluoridation of aqueous solutions was studied (Parham and Rahbar 2009). They employed the scale of a major South Asian freshwater fish for the removal of F⁻ ions from aqueous synthetic solutions. A software model “Response Surface Methodology (RSM) based on Box–Behnken design (BBD)” was applied by this team to assess the fluoride sorption studies. Langmuir model was found to be the best fitting which suggested the homogenous mode of F⁻ sorption onto the fish scale. The pH during sorption experiment was set between 4 and 10, exhibiting the increase in adsorption efficiency at pH 6.0. And the maximum fluoride removal was 93.85% for uptake capacity of 4.69 mg/g. The solution temperature of 313 K was favorable for the adsorption process. The authors stated that the interaction between the adsorbent and the adsorbate remains exothermic in nature. This research seems to be unparalleled in several ways, yet successfully produced adsorbent can be an alternate source.

The potential miscellaneous adsorbents such as agglomerated nanoparticles of hydrous Ce(IV) + Zr(IV) mixed oxide (Richards et al. 2010), novel Al–Zr-impregnated cellulose adsorbent prepared using microwave irradiation (Ruiz-Payan et al. 2005), Al(III)–Zr(IV) binary oxide adsorbent (Gerente et al. 2007), eco-friendly conducting polymer/biopolymer composites (Sharma and Forster 1993), aluminum-modified iron oxides (Subremanian 2006), CaO-loaded mesoporous Al₂O₃ (Dayananda et al. 2014), zirconium-based nanoparticles (Zhu et al. 2015a; Wasay et al. 1996), metal ion-loaded silica gel/chitosan bio-composite (Viswanathan et al. 2009), chitosan-assisted ethylenediamine-functionalized synthetic polymeric blends (Price and Walker 1952; Revinson and Harley 1953; Tahaikt et al. 2008) and Zr(IV)-immobilized cross-linked chitosan (Tang et al. 2009, 2015; Thakkar et al.

2010, 2015; Tian et al. 2017; Zhou et al. 2014; Wang et al. 2013) for removal of excessive fluoride were investigated.

Conclusion

Water fluoridation was initiated by few countries in order to prevent dental fluorosis caused by tooth decay. Ultimately, it ends with the abundance of fluoride in drinking water which develops health hazards to the community. Hence, researchers recommended that fluoride in drinking water is not safe. Consequently, defluoridation has been tested using various types of adsorbents.

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