

A Review on Conventional and Alternative Methods for Defluoridation of Water

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Abstract

Occurrence of fluoride in groundwater is due to anthropogenic influences on its natural formation and geological settings. Consuming fluoride has both beneficial and detrimental effects on dental and bone structures. This review article is aimed at facilitating precise information on the various methods applied to remove fluoride from water. The defluoridation techniques are divided into coprecipitation, adsorption ion exchange, contact precipitation, electro-coagulation and membrane process. The mechanism involved in each defluoridation technique is enumerated. The natural and synthetic materials employed by various researchers to remove fluoride are reviewed and tabulated in order to provide information on removal efficiency or capacity of the media.

Keywords: *Fluoride, adsorption, capacity, precipitation, electro-coagulation*

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INTRODUCTION

Fluoride is commonly observed in ground water due to natural and anthropogenic influences during its formation. Fluoride can get leached out and dissolved in groundwater during the natural movement of water in the soil substrata. High fluoride content is found mostly in calcium-deficient ground waters in many basement aquifers, such as granite and gneiss, geothermal waters and sedimentary basins [1]. Natural phenomenon includes mainly weathering of rocks, volcanoes and geothermal activities.

The geological settings and types of rock are the two main influencing factors for varying fluoride concentrations in groundwater. Igneous and volcanic rocks have a fluorine concentration from 100 mg/kg (ultramafic) to > 1000 mg/kg (alkalic); sedimentary rocks fluorine concentration ranges from 200 mg/kg (limestone) to 1000 mg/kg (shales); metamorphic rocks contain 100 mg/kg (regional metamorphism) to more than 5000 mg/kg (contact metamorphism) of fluorine [2]. Table 1 provides information on some of the fluoride-bearing minerals or rock with its chemical compositions. Ground water with high fluoride concentrations is observed in many areas of the globe including large

parts of Africa, China, the Middle East and Southern Asia (India, Sri Lanka, Bangladesh, and Pakistan). One of the best known high fluoride belts on land extends along the East African rift from Eritrea to Malawi and also from Turkey through Iraq, Iran, Afghanistan, India, Northern Thailand and China.

Even though aquifer mineral has high concentration of fluoride, contact time or reaction time plays major role in ultimate concentration of fluoride in source water. High fluoride concentrations can build up due to longer reaction time. These types of aquifers are commonly associated with deep aquifer systems and zones where groundwater flow velocity is low [3–6]. Shallow aquifers which contain recently infiltrated rainwater usually have low fluoride. Exceptions can occur in shallow aquifers situated near active volcanic areas which are affected by hydrothermal alteration. Under such conditions, the solubility of fluoride increases with increasing temperature and also by dissolution of HF gas [7]. Thus, groundwater with high fluoride concentration is associated with the geochemistry of the region having neutral to alkaline pH of 7.6–8.9, low Ca, and high Na and HCO₃ concentrations. Further, natural concentration of fluoride in groundwater depends on the geological and

physicochemical characteristics of the aquifer (temperature, porosity, acidity, and chemical composition), and depth of the aquifer and intensity of weathering [8].

Some of the anthropogenic activities like agriculture (use of phosphatic fertilizers) and industrial activities (clays used in ceramic industries or burning of coals) also greatly influence in increasing the groundwater fluoride concentration. Source includes liquid discharges from industries like glass, ceramic, brick, iron works, toothpaste, electroplating, etc. [9]. Fuel combustion byproduct fly ash

contains high fluoride similar to volcanic fly ash. More than 100 to 150 million tons of fly ash is produced worldwide annually due to combustion of coal especially from power plants [10, 11]. Inappropriate disposal of fly ash will result in the leaching of fluoride to groundwater. Atmospheric fluoride originates from the dusts of fluoride containing soils, from gaseous industrial wastes, coal fires and volcanic activity. At later stages, these atmospheric fluorides are deposited on ground and enter the hydrological cycle. Table 2 shows the concentration of fluoride in different environments.

Table 1: Natural Source of Fluoride [12, 13].

Source	Chemical formula	Fluorine content
Sellaite	Mg F ₂	61%
Villianmite	Na F	55%
Cryolite	Na ₃ Al F ₆	54%
Fluorite (Fluorspar)	Ca F ₂	49%
Topaz	Al ₂ SiO ₄ (F, OH) ₂	11%
Bastnaesite	(Ce, La) (CO ₃) F	9.0%
Lepidolite	K(Li, Al) ₃ (Si, Al) ₄ O ₁₀ (F, OH) ₂	4.9%
Phlogopite	KMg ₃ (Si ₃ AlO ₁₀) (F, OH) ₂	4.5%
Fluorapatite	Ca ₃ (PO ₄) ₃ F	4.0%
Biotite	K (Mg, Fe) ₃ (AlSiO ₃ O ₁₀) (F, OH) ₂	1.1%
Muscovite	KAl ₂ (Si ₃ Al) O ₁₀ (OH, F) ₂	1.0%

Fluoride route to humans is mainly through consumption of water, vegetables, fruit and milk. Water is considered to be the largest contributor for daily fluoride intake amounting to about 75–90%. Fluoride in drinking water has always been a double-edge sword with both beneficial and detrimental effects on human health depending upon its concentration (refer Table 3). It is beneficial for older people since it reduces hardening of arteries, stimulates bone formation, and helps in the treatment of osteoporosis [14]. The presence of fluoride above 1.5 mg/L is known to cause spotting and discoloration (mottling) of teeth. The long-term exposure may result in permanent grey to black discoloration of the enamel (dental fluorosis).

Children consuming water containing fluoride of 5 mg/L may develop pitting of the enamel. Further, consuming larger concentration of 30–50 mg/L may lead to deformation of bones and other skeletal abnormalities. Since fluoride affinity towards phosphate is high, 96–99% of consumed fluoride combines with bones. Optimum concentration of fluoride consumption (1–1.5 mg/L, according to Bureau of Indian Standards 10500:2003) helps to maintain dental health and appropriate bone density [15]. Non-skeletal fluorosis leads to gastrointestinal problems and neurological disorders. From the facts, it evident that fluoride has adverse impact on human health when it is consumed at higher concentration and for longer duration.

Table 2: Average Fluoride Concentration Ranges in Environment [16].

Environment	Range	Unit
Ambient air (non-industrial zone)	0.01–0.4	µg/m ³
Ambient air (industrial zone)	5–111	µg/m ³
Precipitation (non-industrial zone)	1–89	µg/L
Precipitation (industrial zone)	0.1–1	mg/L
Ocean (increases with depth)	0.3–1.4	mg/L
Soil	90–980	mg/L
River	0.1–0.2	mg/L

From the above facts, reducing fluoride concentration from excess to safe levels is observed to be very essential. Different physicochemical methods are proposed to be practiced and investigated for removal of fluoride from water using chemicals, bio-sorbents, ion exchange resins, etc., which are synthesized or are naturally available. The present review aims at providing information on various conventional and alternative methods developed for de-fluoridation.

DE-FLUORIDATION METHODS

It can be categorized into three main groups [17]

- Adsorption using bone char, activated alumina and clay as packed media in columns which are used for a period of operation. These processes result in

saturation of media which can be renewed or regenerated.

- Aluminum sulfate and lime in the Nalgonda technique, poly aluminum chloride, lime and similar compounds act as co-precipitation chemicals to be added daily and in batches. Precipitation techniques produce a certain amount of sludge every day.
- Calcium and phosphate compounds are the so-called contact precipitation chemicals to be added to the water upstream of a catalytic filter bed. In contact precipitation, there is no sludge and no saturation of the bed, only the accumulation of the precipitate in the bed.
- Other advanced treatment processes include reverse osmosis, electro-dialysis, electro-coagulation, distillation, etc.

Table 3: Health Significance of Consuming Fluoride [13, 18, 19].

Fluoride, mg/L	Impact
< 0.5	Dental caries
0.5–1.5	Optimum dental health, works against dental caries
1.5–3	Dental fluorosis, blackening and pitting of enamel and teeth from long-term exposure, mottled enamel, Roentgenographic bone changes, polydipsia
3–8	Skeletal fluorosis, damages fetus, increase in F-concentration in milk, infant mortality due to calcification of blood vessels, lack of intelligence quotient in children, osteosclerosis, renal diseases, elevated serum alkaline phosphatase, stiffness of knees and hips, increased bone mineral density, bone and joint pains.
10–100	Gastroenteritis, skin irritation, deformation of bones and other skeletal abnormalities, thyroid changes, growth retardation, kidney damage, crippling fluorosis.

Coprecipitation

It is the transfer of trace constituents to a precipitate simultaneously with the deposition of primary substances present in a solution. It occurs when a solution is supersaturated with a substance forming the precipitates.

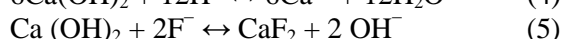
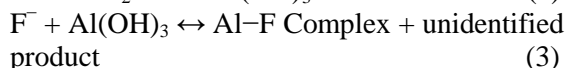
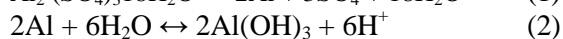
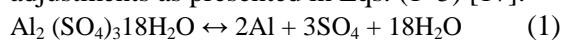
Nalgonda Technique

It involves sequential addition of an alkali, chlorine and aluminum sulfate or aluminum chloride or both by employing several unit operations and processes which include rapid mixing, chemical process, flocculation, sedimentation, filtration, disinfection and sludge concentration to recover water and aluminum salts. Depending upon sulfate and chloride content in raw water aluminum sulfate or aluminum chloride is selected in order to avoid unnecessary increase in sulfate or chloride concentration above permissible limits. This technique is a cost-effective

method which is extensively practiced in most of the developing countries. Though lime softening alone accomplishes fluoride removal, its high initial cost, dosage and alkaline pH of the treated water renders it unsuitable for field application as it requires pH adjustments for treated water and thereby increasing the overall treatment cost. The process is initiated by addition of lime to raw water and followed by rapid mixing. Alum is added and slowly mixed for 10 min. The flocs formed are settled out under quiescent condition.

The addition of aluminum sulfate to water results in the formation of insoluble positively charged flocs of aluminum hydroxide. These charged particles attract negatively charged ions by electrostatic force and are removed from subsequent settling [20]. The function of lime or sodium carbonate is to hydrolyze alum

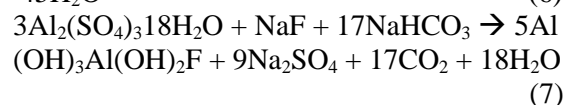
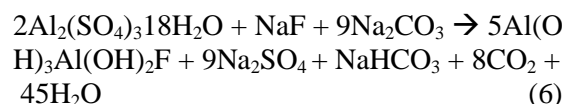
completely. In order to disinfect water, bleaching powder is also applied simultaneously prior to the addition of alum. The reaction mechanism involves (i) aluminum dissolution, (ii) aluminum precipitation, (iii) coprecipitation, and (iv) pH adjustments as presented in Eqs. (1–5) [17].



Addition of lime leads to pre-precipitation of fluoride as insoluble calcium fluoride and initial increase in the pH of water up to 11–12. Lime also facilitates in formation of dense flocs for rapid settling of insoluble fluoride salts. The dose of lime is empirically 1/20th of that of the dose of aluminum salt. Researchers recommend alum and lime dosage of 500 and 30 mg/L respectively to effectively reduce fluoride from water. The alum dosages required for different levels of alkalinity are presented in Table 4.

Alum, in the presence of sodium carbonate reacts with fluoride ions to give a complex, as indicated in Eqs. (6) and (7). Alkalinity supplemented by the addition of sodium carbonate or sodium bicarbonate, ensures

effective hydrolysis of aluminum salts leaving no residual aluminum in the treated water.



Suneetha *et al.* [15] performed experiments by modifying dosage of alum and lime in conventional Nalgonda technique for effective defluoridation of water. The results indicated that by doubling the concentrations of alum and lime, significant decrease in fluoride was observed compared to the existing Nalgonda technique. Other modifications for Nalgonda technique include using poly-aluminum chloride and poly aluminum hydroxy sulfate (PAHS) when higher concentrations of fluoride are present in water. The removal efficiency of fluoride is higher with poly-aluminum chloride (PAC) when compared with alum (89). A polymeric aluminum compound, poly-aluminum-hydroxy-sulfate (PAHS) is found to require less flocculation time and settling time. Detention time of 20 to 30 min will be adequate for complete settlement of all flocs. However, alum is more affordable and accessible than PAC and PAHS cost is said to be lesser than alum.

Table 4: Alum Dosages Required to Obtain Desired Fluoride Concentrations at Different Levels of Alkalinity [21].

Test water fluorides (mg/L)	Alkalinity (ppm)							
	125	200	300	400	500	600	800	1000
2	145	220	275	310	350	405	470	520
3	220	300	350	405	510	520	585	765
4	*	400	415	470	560	600	690	935
5	*	*	510	600	690	715	885	1010
6	*	*	610	715	780	935	1065	1210
8	*	*	*	*	990	1120	1300	1430
10	*	*	*	*	*	*	1510	1690

*To be treated after increasing the alkalinity with lime or sodium carbonate

Bone Char and Contact Precipitation

The degreased and alkali-treated bones were employed initially in home filters. Later the material was discontinued due to odor problems and imparting taste into treated water. Investigators suggested using of bones after converting to charcoal to avoid odor and taste in treated water. In practice, the bone char is prepared from the animal or bird bones and teeth, which comes out as a waste from

poultry or meat processing small to large scale industries. The bones before being charred are boiled, washed, dried and crushed to required size. The charring processes can be pyrolysis (without oxygen) or calcination (limited supply of oxygen).

The crushed bones are converted to char in an oven or furnace at a temperature of 300–800 °C for duration of 1–3 h [22, 23]. The

char obtained is further pulverized to required sieve sizes and used for defluoridation process. The process of charring results in formation of three fragments (white, grey and black) depending upon the applied temperature. Each fragment exhibits difference in fluoride adsorption capacity. The composition range of compounds present in bone charcoal is presented in Table 5 [17, 24].

Table 5: Major Components of Bone Charcoal.

Compounds	Range (%)
Calcium phosphate	57–80
Calcium carbonate	6–10
Carbon	7–10
Iron, aluminum	0.5–1
Magnesium	0.2–0.5
Nitrogen	0.8–1
Residue insoluble in acid	0.1–0.3

Mwaniki *et al.* (25) investigated on adsorption capacities of different forms of bone char produced at 350 °C (black), 450 °C (grey) and 600 °C (white). Bone char (black colored) showed the ability to take up fluoride from aqueous solution with a maximum adsorption capacity of 11.4 mg F⁻/g of bone char. White bone char exhibited less adsorption capacity of 0.3 mgF⁻/g of bone char (26). Phantumvanit and LeGeros [27] conducted a comparative study on fluoride removal performances of bone chars obtained by calcination of bone meal (i.e., cow and pig bones) and concluded that 30 min calcination time at temperature of 400, 600 and 800 °C highest fluoride uptake was observed was at 400 °C.

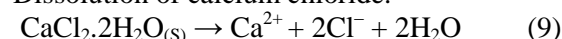
Pyrolysis temperature is a critical operating parameter for the synthesis of bone char and it has a major effect on the fluoride adsorption properties due to the dehydroxylation process of the hydroxy apatite present in the adsorbent [28]. The fluoride removal mechanism is predicted to be an ion exchange process in which complex carbonate radicals present in bone char are replaced by fluoride forming an insoluble fluorapatite as represented in Eq. (8).

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 2\text{F}^- \rightarrow \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 2\text{OH}^- \quad (8)$$

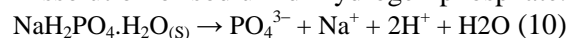
Contact precipitation is a method of defluoridation, in which fluoride is precipitated as fluorapatite Ca₁₀(PO₄)₆F₂, due

to chemical reaction with calcium and phosphate compounds applied to water in presence of catalyst which is a previously fluoride-saturated bone charcoal. The commonly used chemicals in contact precipitation are calcium chloride and sodium di-hydrogen-phosphate [29]. The reaction involved in the process is summarized in Eqs. (9–12). Fluoride-saturated bone char is prepared by packing the fresh bone char in a column circulating fluoride-rich water until the effluent concentration fetches high fluoride or equal to influent concentration or simply by suspending the fresh bone char medium in a fluoride solution with concentration of 1g/L [23].

Dissolution of calcium chloride:



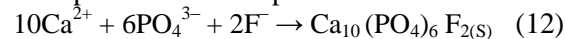
Dissolution of sodium di-hydrogen-phosphate:



Precipitation of calcium fluoride:



Precipitation of fluorapatite:



Contact precipitation has shown promising results of high efficiency (90–95%) with reliability, good water quality and cost effectiveness compared to other defluoridation methods. The method has been further developed by incorporating the combined use of calcium phosphate pellets and bone char as the defluoridation medium and has shown considerable potential for removing fluoride [30]. Studies have also revealed that degreased and alkali-treated bones are effective in reducing fluoride concentration > 3mg/L to < 0.2 mg/L.

Kawasaki *et al.* [87] concludes that fluoride ion exchanges not only hydroxyl ions but also phosphate ions present in bone char. The amount of phosphate ion eluted from bone char, which contained the calcium phosphate, with fluoride ions adsorption depends on the source species of animal biomass. And also remarks that fluoride adsorption increases with decrease in charring (carbonizing) temperature.

Adsorption and Ion Exchange

Fan *et al.* [31] enumerated the theoretical aspects of fluoride adsorption on to solid particles by three essential steps: (i) diffusion

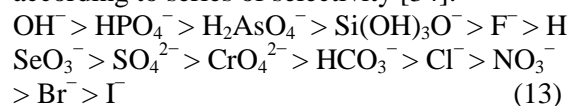
or transport of fluoride ions to the external surface of the adsorbent from bulk solution across the boundary layer surrounding the adsorbent particle, called external mass transfer; (ii) adsorption of fluoride ions on to particle surfaces; (iii) the adsorbed fluoride ions probably exchanged with the structural elements inside adsorbent particles depending on the chemistry of solids, or the adsorbed fluoride ions are transferred to the internal surfaces for porous materials (intra particle diffusion).

In adsorption method, use of activated alumina (AA) has been a method of choice in developed countries [32]. Activated alumina is an aluminum oxide that is highly porous and exhibits high surface area. It can be produced through different methods from aluminum salts. Onyango and Matsuda (33) state that the main activated alumina phase used as an adsorbent is gamma alumina ($\gamma\text{-Al}_2\text{O}_3$).

AA adsorption is a physicochemical process by which ions in water are removed by the available adsorption sites. AA is usually prepared through dehydration of precipitated $\text{Al}(\text{OH})_3$ at high temperatures (300–600 °C) which consists of amorphous and gamma alumina oxide. AA is generally used as packed beds to remove fluoride, arsenic, selenium, silica and natural organic matter (NOM). The process involves simply passing the water continuously through one or more AA beds. When the available adsorption sites are exhausted, the AA media may be regenerated with a strong base, NaOH, or simply disposed of. Removal efficiency is noted to be more than 90% with the optimum adsorbent dosage of 1.6 g/L, for water having initial fluoride concentration of 20 mg-F/L and has a wide range of working pH of 4–9. Shimelis *et al.* [88] determined fluoride adsorption capacity of untreated hydrated alumina (7 mg/g) and thermally treated hydrated alumina (23 mg/g), and observed that adsorption capacity was significantly higher compared to AA (1.8–1.9 mg/g).

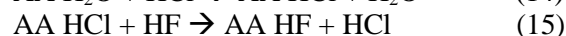
The crystal structure of alumina contains cation lattice with discontinuities giving rise to localized areas of positive charge and therefore alumina attracts various anionic species. As polymeric anion exchange resins, AA exhibits

high preference for fluoride ions (from Eq. (13)) compared to other anionic species according to series of selectivity [34].



When pH is less than 5, hydroxide, silicate and arsenic ions are competing ions for fluoride ions and AA easily dissolves in acidic environment leading to loss of adsorbing media. It has large internal surface in the range of 200–300 m²/g due to its crystalline structure [35]. The capacity of the activated alumina to adsorb fluoride depends on its crystalline form and its preparation, activation process and operation conditions.

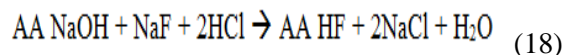
The adsorption capacity varies from 1–12 mg-F/g of alumina depending on available active adsorption site, ion preference and surface area [36, 37]. The AA process is pH sensitive and anions are best adsorbed at pH below 8.2, which is a typical zero point charge (ZPC) for AA. Below pH of ZPC, the AA surface has a net positive charge that can be balanced by adsorbing anions, such as hydroxide, fluoride, arsenate, etc. [34]. Maximum adsorption of fluoride on to AA takes place between pH of 5 and 7. When pH is above ZPC, AA is predominantly a cation exchanger which is having relatively rare application in water treatment [38, 39]. In practice, AA is first treated with HCl to make it acidic form. When AA is contacted with fluoride ions, it displaces the chloride ions and gets attached with the alumina. The series of reactions (14–17) is presented as a model of the adsorption and regeneration cycle that is useful for design purpose.



The exhausted AA is regenerated by treating it with dilute solution of 0.25 to 0.5N NaOH, resulting in AA in basic form (AA NaOH). Alumina is both a cation and an anion exchanger; Na^+ is exchanged for H^+ , which immediately combines with OH^- to form H_2O in the regenerant basic solution [40]. To restore the fluoride removal capacity, alumina in basic form is acidified by contacting it with an excess of dilute acid, typically 0.5N HCl or H_2SO_4 .



Alternatively, water can be acidified prior to contact with basic alumina, thereby combining acidification and adsorption as summarized in Eq. (18).



Srimurali and Karthikeyan [41] enumerated the effects of process contact time, pH, dosage and ionic environment in AA process. The discussion made by the author clearly indicates that fluoride removal increases with increase in contact time and dosage. At lower pH, maximum removal takes place and a drastic decrease in removal efficiency was noted as pH was increased beyond 7.5. Carbonate ions have strong influence on sorption capacity by decreasing the removal efficiency.

Lavecchia *et al.* [42] evaluated high alumina content bauxite as adsorbent having Al_2O_3 (81.5%), Fe_2O_3 (9.3 %) and SiO_2 (8.9 %). Considering maximum uptake capacity, author noted 3.125 mg/g which is higher than 1.45 mg/g reported with respect to activated alumina [43]. In order to enhance the adsorption efficacy, the surface of activated alumina can be modified by impregnation with alum which facilitates high fluoride adsorption [44]. The removal efficiency noted was more than 90%, i.e., greater than the conventional activated alumina process efficiency of 55% [45].

Natural materials such as red soil, untreated charcoal, local powdered brick, fly-ash and mineral serpentine also have affinity towards fluoride thereby reducing its concentration [46]. Among these materials, red soil is more effective in removing fluoride followed by fly-ash and brick. Red lateritic soil possesses intrinsic anion exchange properties and it contains very fine clays, organic matter, oxides of iron and aluminum. Dongre *et al.* [47] developed a novel, cheap and efficient porous chelating resin, through 80% deacetylation of chitin and 20% doping was made with zirconium oxychloride hexahydrate. Author noted that optimum pH for using zirconium dopes chitosan for fluoride removal was 6.5–7, above which efficiency reduced by 40–50%. Maximum

fluoride removal was 90% with 6 mg/L as initial concentration.

Hydrated cement particles are also found to have high affinity towards fluoride ions. The influencing parameter with respect to adsorbent dosage follows the similar trend as that of AA process. It is noted that this method of defluoridation can be applied over a wide range of pH. However, at highly alkaline pH, the defluoridation capacity drops sharply. The process showed negative effect in removal of fluoride due to counter ion carbonate and bicarbonate [48]. Several researchers have studied fluoride sorption process on to clay in its native and heat-treated form (fired clay). Clay having higher Al and Fe oxides has fluoride adsorption of about 85% [49]. When clay is heat treated (calcined) adsorption capacity increases with increase in temperature up to 550–600 °C above which the efficiency drops down due to change in mineral structure. Deshmukh *et al.* [50] investigated on adsorbent synthesized using rice husk and concluded that maximum fluoride removal efficiency achieved was 50% in acidic condition (i.e., at pH 2).

Haghigat *et al.* [45] showed that carbon nanotubes of both single and multi-walled configurations have the potential to defluoridate aqueous solution with efficiency of 58 and 54% respectively. Optimum pH range was 5–7 above which single-wall or multi-wall carbon nanotubes had no appreciable difference in removal efficiency. Different types of adsorbents or ion exchange media are being investigated and their adsorption capacities are determined. Table 6 provides the information on adsorption capacity of various natural minerals used for removal of fluoride from water. But the adsorption capacity varies with the factors such as pH, competitive ions present in the solution and stability of adsorbent. Adsorption capacity of synthetic material also varies on the calcination temperature applied for coating the media with metal oxide and also the composition of the resultant synthetic material (Table 7).

Table 6: Minerals Used in Defluoridation of Water.

Mineral	Adsorption capacity
Bentonite beads [55]	0.9 mg/g
Bauxite + gypsum + magnesite [19]	30 mg/g
Kaolinite [49, 56]	0.1 mg/g
Bauxite [42]	3.125 mg/g
Lateritic soil [57]	2.5 mg/g
Stilbite zeolite [58]	2.3 mg/g
Diatomaceous earth [59]	51.1 mg/g
Magnesia [60]	2.2 mg/g
Tourmaline [61]	15 mg/g
Polygorskitic clay [62]	95 mg/g
Illito clay [62]	69 mg/g
Smectic clay [62]	84 mg/g
Charcoal [63]	90–95%
Montmorillonite [64]	2 mg/g

Table 7: Synthetic and Natural Sorbents Used to Remove Fluoride from Water.

Material	Max capacity or efficiency	Reference
Moringa Oleifera [65]	65–78%	Parlikar et al. 2013
Chitosan Beads [55]	0.36 mg/g	Zang et al. 2013
Sonneratia Apetala [66]	2.2 mg/g	Patil et al. 2013
Terminalia Cattapa [66]	1.4 mg/g	Patil et al. 2013
Ananas Comosus [66]	1.3 mg/g	Patil et al. 2013
Manikara Zopata [66]	1.8 mg/g	Patil et al. 2013
Pisum Sativum [66]	2.2 mg/g	Patil et al. 2013
Cocos nucifera [66]	1.5 mg/g	Patil et al. 2013
Zr – Chitosan [47]	3.3 mg/g	Dongre et al. 2012
Iron Oxide Coated Sand [67]	90–97%	Togarepi 2012
Bagas [68]	1.4 mg/g	Mohammad et al. 2012
Modified Bagas [68]	6.8 mg/g	Mohammad et al. 2012
Acid Treated Laterite Mineral [59]	3–10 mg/g	Wambu et al. 2012
Aluminum Modified Bone Char [69]	85–97%	Zhu et al. 2011
Hydrotalcite [70]	175–238 mg/g	Hosni et al. 2011
Bi metal – polymeric adsorbent [71]	45 mg/g	Kumar et al. 2011
Basket Willow [72]	35–50%	Telesinski et al. 2011
Nano Magnesia [73]	21 mg/g	Maliyekkal, 2010
MgO-Chitosan [60]	4.4 mg/g	Sundaram et al. 2009
Ground nut shell carbon [74]	1.3 mg/g	Alagumuthu 2010
Nano Iron oxyhydroxide [75]	63 mg/g	Sujana and Mohanty 2010
Mesoporous alumina [76]	14.3 mg/g	Lee et al. 2010
Mg – Bentonite [77]	2.26 mg/g	Thakre et al. 2010
Ceramic [78]	2.16 mg/g	Chen et al. 2010
manganese-oxide coated alumina [79]	7 mg/g	Teng et al. 2009
Aluminum titanate [80]	0.85 mg/g	Karthikeyan et al. 2009
Bismuth aluminate [80]	1.55 mg/g	Karthikeyan et al. 2009
Bone char [61]	18 mg/g	Ma et al. 2008
Activated alumina [61]	12 mg/g	Ma et al. 2008
Crystalline Fe/Al oxides [81]	18 mg/g	Biswas et al. 2007
Al super paramagnetic adsorbent [82]	38 mg/g	Chang et al. 2006
Magnetic chitosan [83]	23 mg/g	Wei Ma et al. 2006
Alga spirogyra [84]	1.3 mg/g	Mohan et al. 2006
Pipal [63]	1.5 mg/g	Tembhurkar et al. 2006
Neem [63]	0.8 mg/g	Tembhurkar et al. 2006
Neem, pipal and khair (comp. ad.) [85]	85–90%	Jamode et al. 2004

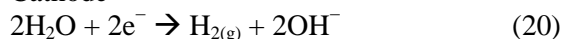
Electro-coagulation

The process involves application of electric current across electrodes generally made of iron or aluminum in a reactor tank. The anode sacrificial electrode generates the flocculating agent by undergoing electro-oxidation with gas bubbles. Flocculating agent is a metal ion coagulate with pollutant present in water, similar to the addition of coagulating chemicals such as alum and ferric chloride. The electrochemical process that occurs inside the reaction chamber is outlined below

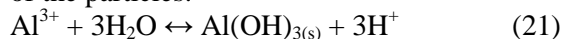
Anode



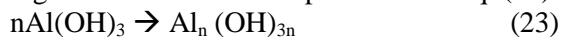
Cathode



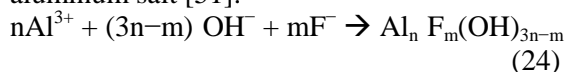
The hydrogen gas formed at cathode helps to drive floatation process. The Al^{3+} ions further react to form $\text{Al}(\text{OH})_3$ precipitates. These precipitates form flocs which attract and adsorb negatively charged ions like fluoride. Later they are removed by subsequent settling of the particles.



Polymerization of Al flocs occurs usually at high Al concentration as presented in Eq. (23).



Equations (24 and 25) are the overall generalized reaction of fluoride with aluminum salt [51].



Membrane Process

Membrane provides physical barrier that filters out the particles having size greater than the membrane pores. There are four cross flow, pressure driven membrane processes: ultra filtration (UF), reverse osmosis (RO), nano filtration (NF) and micro filtration (MF). Membranes are in variety of configurations including flat sheet and tubular shape (i.e., hollow fiber, spiral wound). Dialysis and electro-dialysis (ED) are also membrane processes, during which ions are transported through semi-permeable membrane under atmospheric pressure. Electro-dialysis includes the application of an electric potential to mobilize the ions and membranes used are cation- or anion-selective, which basically

means that either positive ions or negative ions will flow through depending on ionic charge.

Ndiaye *et al.* [52] investigated on fluoride removal using reverse osmosis technique and observed that the rejection of fluoride was higher than 98%. Elazhar *et al.* [86] evaluated the performance of nano-filtration and electro-dialysis through pilot plant study and concluded that both technologies confirm the performance in the fluoride reduction which is in compliance with the comments made from Tahaikt *et al.* [53]. About 70–75% reduction can be achieved through electro-dialysis at neutral pH [54].

Although membrane process has proved in rejecting fluoride from the water stream to acceptable levels, the construction, operation and maintenance are complex with advanced control equipment which render the process costly.

CONCLUSIONS

From the present review, following conclusions can be drawn:

- Excess fluoride concentration in water is commonly observed where the geological settings contain high levels of fluoride and deficit in competing ions like calcium.
- Fluoride consumption has both detrimental and beneficial effects on human health especially in young age.
- Various treatment methods have been adopted to reduce fluoride to safe limits which include media-based adsorption and ion exchange, electro-coagulation and dialysis, membrane separation technique and precipitation by adding chemicals.
- Precipitation is a cost-effective method having simple treatment steps and involves use of alum which is easily available. Since this process produces sludge rich in chemical composition which renders them hazardous in nature.
- Membrane process has also proved in reducing the fluoride concentration but the construction, operation and maintenance is a costly affair.
- Although precipitation and membrane processes have successfully reduced fluoride concentration to acceptable levels, adsorption process remains the most

preferred method in defluoridation research and practice because of greater accessibility and cost effectiveness.

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