Defluoridation-A review of water from aluminium and alumina based compound

M. Khichar and S. Kumbhat

Abstract
Fluoride contamination in drinking water due to natural and anthropogenic activities has been recognized as one of the major problems worldwide imposing a serious threat to human health. Up to a small level (1–1.5 mg/L) this strengthens the enamel. Concentrations in the range of 1.5–4 mg/L result in dental fluorosis whereas with prolonged exposure at still higher fluoride concentrations (4–10 mg/L) dental fluorosis progresses to skeletal fluorosis. Several materials including aluminium salts, calcined alumina, magnesia, lime, activated carbon sulphonated carbonaceous materials and ion exchange resins have been screened for their utility in defluoridation of water. Aluminium impregnated cation exchange resin and sulphonated carbonsaceous materials prepared from coconut shell, paddy husk have been found to have a significant defluoridation capacity. Aluminium sulphate (Filter alum) solution is also found efficacious. On the basis of results extensive investigations, different researchers have developed a simple and economical domestic defluoridation processes.

This paper represents the critical review of the past work on defluoridation studies by using conventional and unconventional materials and different methodologies.

Keywords: Defluoridation, ion exchange, precipitation, adsorption, and bone charcoal

1. Introduction
Fluorine is a naturally occurring element found in various minerals. However, release into groundwater from volcanic activity and weathering processes can cause elevated levels of fluoride in drinking water. Fluoride, although beneficial for the mineralization of hard tissues in the human body, can be toxic to humans with chronic exposure to elevated concentrations [1].

The standard level for fluoride in drinking water is 1.5 mg/L, according to the World Health Organization (WHO) [2]. Effects can range from mottling of teeth to severe skeletal deformations, known as skeletal fluorosis. The United Nations Environmental Program (UNEP) currently estimates that the number of individuals affected by fluorosis is in the tens of millions across at least 25 countries in both developed and developing nations [3]. Depending on the concentrations and the duration of fluoride intake, it could have a positive effect on dental caries [4]. On the contrary, long term consumption of water containing excessive amounts of fluoride can lead to fluorosis of the teeth and bones [9]. The excessive intake of fluoride may cause dental [9] and skeletal disorders [7]. Fluoride ion is attracted by positively charged calcium ion in teeth and bones due to its strong electronegativity which results in dental, skeletal and no skeletal forms of fluorosis i.e. high fluoride ingestion, in children as well as adults. Fluorosis in mild version can be evidenced by mottling of teeth and in high version by embrittlement of bones and neurological damage [8], in some of the cases it may even interfere with carbohydrates, proteins, vitamins and mineral metabolism and to DNA creation as well if intake excessively [10]. Studies have shown that the major of the Kidney diseases have a great inclination of the toxicity of fluoride. At high doses and short term exposure fluoride can exterminate the kidney function. Several research groups have also shown that fluoride can interfere with the function of pineal gland as well as of brain. Pineal gland is one of the major fluoride accrued site in body with concentration more than that of teeth and bones. Workers exposed to high fluoride concentration areas are diagnosed with bladder cancer [10]. Various diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer syndrome, and thyroid disorder can attack the human body on excessive intake of fluoride [11]. In Mexico alone, an estimated five million people are impacted by fluorosis, representing 6% of the population [12]. Therefore, it is crucial that effective fluoride removal methods are developed that can be used not only in developed
nations, but also in developing countries. Currently, a wide range of defluoridation methods exists. These methods can be divided into the following categories: sorption, chemical precipitation, removal by ion exchange, and membrane filtration [13]. The permissible limits of fluoride concentration in drinking water prescribed by various organizations are shown in Table 1 [14].

Table 1: Permissible limit of fluoride in drinking water prescribed by various organizations

<table>
<thead>
<tr>
<th>Name of organization</th>
<th>Permissible limit of fluoride ion (mg/L)</th>
</tr>
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<tbody>
<tr>
<td>World Health Organization (International standard for drinking water)</td>
<td>0.50</td>
</tr>
<tr>
<td>US Public Health Standard</td>
<td>0.8</td>
</tr>
<tr>
<td>The committee on public health engineering manual and code of practice, Government of India.</td>
<td>1.00</td>
</tr>
<tr>
<td>Indian Council of Medical Research Recommendations</td>
<td>1.00</td>
</tr>
<tr>
<td>ISI recommendations</td>
<td>1.50</td>
</tr>
</tbody>
</table>

2. Defluoridation methods:
Defluoridation is the process of removal of fluoride ion in drinking water. All the defluoridating method may broadly be classified in two categories, namely Additive methods and Adsorptive methods. In additive methods, certain reagents are added and optimum conditions for the defluoridation are maintained. A fluoride ion present in water reacts with the reagents added and forms an insoluble complex. In adsorptive methods, a bed of greater surface activity is chosen and water passes through the bed. Due to surface activity, the fluoride ion gets preferentially adsorbed on the bed surface, thereby causing a reduction of fluoride ion in the exit stream [15]. The different method so far tried for the removal of excess fluoride from water can be broadly classified in four categories viz.
- Ion Exchange method
- Precipitation method
- Miscellaneous methods [16]

The materials used in these methods are presented in Table 2.

Table 2: Defluoridation methods and required materials

<table>
<thead>
<tr>
<th>Adsorption</th>
<th>Ion Exchange</th>
<th>Precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon. Raw material for activated carbon</td>
<td>Fluoride Exchangers Raw materials was</td>
<td>Lime slurry Alum treatment (Nalgonda Technique)</td>
</tr>
<tr>
<td>i) Wood</td>
<td>i) Degreased and alkali treated bones</td>
<td>i) Fill and draw method</td>
</tr>
<tr>
<td>ii) Coal</td>
<td>ii) Bone charcoal</td>
<td>ii) Continuous flow method</td>
</tr>
<tr>
<td>iii) Lignite</td>
<td>iii) Inorganic ion exchangers</td>
<td>iii) Package treatment plant for the Hand pump installation</td>
</tr>
<tr>
<td>Iv) Bone</td>
<td>Iv) Tricalcium phosphate</td>
<td>iv) Alum floccidage blanket technique</td>
</tr>
<tr>
<td>v) Petroleum residue</td>
<td>V) Fluorex</td>
<td></td>
</tr>
<tr>
<td>vi) Nut shells</td>
<td>vi) Serpentine</td>
<td></td>
</tr>
<tr>
<td>vii) rice husk</td>
<td>vii) Anion exchanger resin</td>
<td></td>
</tr>
<tr>
<td>viii) Saw dust</td>
<td>viii) Activated alumina</td>
<td></td>
</tr>
</tbody>
</table>

In this paper reviewed defluoridation method based on aluminium and alumina compounds.

3. Alumina and aluminium
Alumina has been an effective adsorbent for defluoridation of water. For the fluoride removal from water Acidic alumina [17] Adsorbent react fluoride at pH range 3–8 with fluoride concentration 1.9 -19 mg/L., amorphous Al(OH)₃, gibbsite or alumina (Al₂O₃) [18] have been used. At pH 5.5-6.5, maximum fluoride uptake was observed 9 mol/kg. At lower pH, fluoride uptake decreased due to the preferential formation of AlF₆⁻ soluble species, but at higher pH, OH⁻ displaced F⁻ from the solid Al(OH)₃ so the amount of fluoride adsorbed to complexes declined towards zero between pH 6–8. At lower rates, same reaction was followed with gibbsite. At pH 5–7, maximum fluoride removal was found 16.5 mg/g. α- Al₂O₃ [19] was also investigated At 25 °C and pH 5–6, maximum fluoride removal was occurring. From the zeta potential measurement, it was achieved that fluoride adsorbed onto α-Al₂O₃ by replacing hydroxyl ions from positively charged surfaces and through hydrogen bond. Adsorption capacity of activated alumina (AA) [20] (grad OA –25) was also studied for defluoridation of aqueous solution. At pH 7, adsorption capacity was obtained 1450 mg/kg. Defluoridation increased at pH 4–7 but decreased thereafter. At pH >7, silicates and hydroxyl ions were considered to compete with F⁻ ions for alumina exchange sites, but at pH <7, alumina fluoro complexes were formed in the presence of aluminium ions in the treated water. Comparison between the adsorption capacities of the untreated hydrated alumina (UHA) and thermally treated hydrated alumina (THA) [21] were obtained from the hydrolysis of locally manufactured aluminium.
sulphate for defluoridation. The capacity was found to be 23.7 mg F⁻/g and 7.0 mg F⁻/g for THA and UHA, respectively, at pH 4–9. To improve the adsorption capacity of alumina, it has been modified. For the modification of it, it has been impregnated by La(III) and Y(III) [22]. Comparison was witnessed between La(III) and Y(III) impregnated alumina and original alumina [23] for the adsorption of fluoride. Lanthanum hydroxide supported on alumina has also been investigated for defluoridation. The adsorption capacity of alumina impregnated lanthanum hydroxide was 48 mg/g, which was higher than original alumina 23–25 mg/g. Defluoridation by impregnated alumina was explained by ion exchange process between anion and hydroxide groups in surface material. Adsorption was found to increase with decreasing of fluoride concentration from 130 mg/L to 0.57 mg/L at pH 5.7–8.0. The surface of alumina was also impregnated with alum [24] for defluoridation. At pH 6.5, the adsorption of fluoride was found 92.6% and then decreased with further increased in pH. To improve the efficiency of alumina for defluoridation of aqueous solution, it modified by coating of copper oxide. The adsorption capacity of copper oxide coated alumina [25] was mentioned which was higher than unmodified activated alumina. Fluoride removal by amorphous Fe/Al mixed hydroxides [26] was evaluated. At pH 7.5, mixed Fe/Al samples were prepared by the increase of Al content in Fe(OH)₃ matrix increase the surface area. Granulated mixture of Fe-Al-Ce nano [27] adsorbent for fluoride removal by spraying Fe-Al-Ce nano-adsorbent suspension onto glass beads in a fluidized bed was developed. It was found that fluoride adsorption capacity was 2.22 mg/g at pH 7 and initial fluoride concentration of 1 × 10⁻³ M using the coated granules as an adsorbent. Aluminium hydroxide impregnated limestone [28] as an adsorbent used for fluoride removal from water. At pH 2, the adsorption in case of modified lime stone was decreased. The maximum sorption capacities of the limestone and aluminium hydroxide impregnated limestone were found 43.10 mg/g and 84.03 mg/g, respectively. Al-Ce hybrid adsorbent [29] by co-precipitation method was prepared and used for fluoride removal. For fluoride, the adsorbent capacity of Al-Ce adsorbent was 91.4 mg/g at 25 °C. At pH 6, maximum adsorption capacity was achieved. Aluminium titanate (AT) and bismuth aluminate (BA) [30] as an adsorbent used by authors. The amounts of fluoride adsorbed by AT and BA were 0.85 and 1.55 mg/g, respectively at 30 °C from 4 mg/L initial concentration. Hybrid process was applied that combined the adsorption on conventional solid adsorbents such as aluminium and zirconium oxide along with specific donnan dialysis [31] for defluoridation of ground water. It was found that adsorption was not dependent on pH and ionic strength of water to be treated. Donnan dialysis pilot was equipped with specific anion exchange membranes to reduce electrolyte leakage and thus increased in mineralization of treated water.Micro/nano-hierarchical web consisting of activated carbon fibres and carbon nano fibres impregnated with Al used as an adsorbent [32] for fluoride removal from wastewater. At pH 5–8, Al-carbon nano fibres were used for treating the wastewater. The potential of nano alumina [33] for fluoride removal and was found to be 140 mg/g. Defluoridation studies were conducted under various experimental conditions such as pH, contact time, initial fluoride concentration, temperature and the presence of counter ions. It was noticed that the maximum fluoride removal occurred at pH 6.15 and increased with increase in time and initial fluoride concentration. Carbon nanotubes (CNTs) as support to deposit Al₂O₃ and explored the possibility of Al₂O₃/CNTs [34] for fluoride removal from drinking water. The fluoride removal was occurred on Al₂O₃/CNTs at pH 5.9–9.0. The adsorption capacity for Al₂O₃/CNTs was 13.5 times higher than AC-300 carbon and four times higher than that of γ-Al₂O₃ at an equilibrium fluoride concentration of 12 mg/L. The mass of fluoride adsorption for Al₂O₃/CNTs at pH 6 reached 28.7 mg/g at an equilibrium concentration of 50 mg/L. Effect of aluminium fluoride complexation on fluoride removal by Al salts coagulation [35] was investigated by a series of batch experiments. Transformation of fluoride species in coagulation was studied by simultaneous determination of free fluoride and total fluoride at different pH and fluoride concentrations. Results showed that aluminium fluoride complexes dominated at low pH and high fluoride concentrations, but more complexes did not represent higher fluoride removal. Comparison between coagulation with complexation and adsorption by Al(OH)₃ flocs was conducted and coagulation showed higher fluoride removal efficiency than adsorption in the pH range of 6.0–9.0. The calcination product of Mg-Al-Fe hydrotalcite compound [36] at 500 °C (HTlc500) was used as the adsorbent to remove fluoride ions from aqueous solution. Batch adsorption studies were conducted under various equilibration conditions, such as different pH, calcined temperature, adsorbent dose, co-existing anions, contact time and initial fluoride ions concentrations. It was found that the HTlc500 had the largest adsorption capacity of 14 mg/g at pH 6 with adsorbent dose of 0.2 g/L. Porous granular ceramic adsorbents containing dispersed aluminium and iron oxides [37] were synthesized by impregnating with salt solutions followed by precipitation at 600 °C. The adsorbents were spherical in shape, 2–3 mm in particle size, highly porous and showed specific surface area of 50.69 sq m/g. The fluoride adsorption capacity of prepared adsorbent was 1.79 mg/g, and the maximum fluoride removal was obtained at pH 6. A coating granulation technology comprising the spraying of a Fe–Al–Ce nano-adsorbent suspension onto glass beads in a fluidized bed [38] was developed. The optimal parameters for making high performance adsorbent granules were for the granules to be coated at 65 °C using a latex/Fe–Al–Ce ratio of 0.5:1 and a coating amount of 27.8%. These granules had a fluoride adsorption capacity of 2.77 mg/g (coated granules) for water with an initial fluoride concentration of 0.001 M that was treated at pH 7. Continuous flow experiments with monopolar aluminium electrodes [39] for fluoride removal were undertaken to investigate the effects of the different parameters such as: current density (12.5–50 A/m²), flow rate (150–400 mL/min), initial pH (4–8), and initial fluoride concentration (5–25 mg/L). The highest treatment efficiency was obtained for the largest current and the removal efficiency was found to be dependent on the current density, the flow rate and the initial fluoride concentration when the final pH ranged between 6 and 8. Two novel applied biocarbon-Mg/Al layered double hydroxides composites (CPLDH and CPLDH-Ca) [40] were successfully prepared. The fluoride removal efficiency (Rₚ) and protein recovery ratio (Rₚ) of the adsorbents were studied in protein systems of lysozyme (LSZ) and bovine serum albumin (BSA). The results showed that the CPLDH-Ca presented remarkable performance for selective fluoride removal from protein solution. It reached the maximum Rₚ of 92.1% and 94.8% at the CPLDH-Ca dose of 2.0 g/L in LSZ and BSA system, respectively. A rotating impeller aluminium cathode and a cylindrical aluminium anode [41] were used, and various operating parameters, such as the electrode material (aluminium and iron), the current density (in the range of 0.5–
2 mA/cm²), the duration of electrolysis, the supporting electrolyte dosage (in the range of 0.01–0.03 M Na₂SO₄), the initial pH (in the range of 4–8) and the presence of other ions (Ca²⁺, Mg²⁺, PO₄³⁻, SO₄²⁻), were examined to achieve optimal performance of the process. The experimental results revealed that the fluoride removal could be enhanced at pH 6, higher current density and higher electrocoagulation time using aluminium electrode.

Synthetic solutions [42] were employed to elucidate the effects of the initial fluoride concentration, the applied current and the initial acidity on the simulation results of the model. The proposed model successfully describes the fluoride removal reaction, except in a system in which the initial concentration of the acid is less than the initial fluoride concentration. With synthetic wastewater, competitive adsorption characteristics of fluoride and phosphate on calcined Mg-Al-CO₃ layered double hydroxides (CLDH) [43] were investigated. It was found that the optimal pH is around 6 and it took 24 h to attain equilibrium when fluoride and phosphate were simultaneously added. Simple aluminium (hydr)oxides and layered double hydroxides [44] were synthesized their adsorption capacities at dissolving fluoride concentrations close to the World Health Organization drinking water guideline of 1.5 mg L⁻¹ were much lower than those for the aluminium (hydr)oxides. The effect of the molar ratio of hydroxide and fluoride ions to Al(III) ions (ΟH⁻ and ΦF⁻) on coagulation and electrocoagulation (EC) [45] was studied to solve the problem of the over addition of acid or base. The efficiency of defluoridation was approximately 100% when the sum of ΟH⁻ and ΦF⁻ was close to 3. Electrocoagulation [46] is a method of applying direct current to sacrificial electrodes that are submerged in an aqueous solution. The defluoridation process was found to be efficient for a pH ranging from 6 to 8. The fluoride removal mechanisms are investigated based on the solution speciation (Al and Al–F complexes) and dried sludge characteristics in the electrocoagulator. Solid sorbents containing ettringite, Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O, were prepared from concrete sludge by adding various amounts of aluminum sulfate to enhance ettringite formation. For the same Ca/Al ratio, improved removal performance was observed for sorbents treated at higher temperatures. The highest removal capacity was found when the sorbent was prepared with a molar ratio of Ca/Al of 3.2 and heat treatment at 175 °C. The final concentrations of boron and fluoride were 6.3 mg-B/L, and less than 4 mg-F/L for initial concentrations of 100 mg-B/L and 300 mg-F/L. The optimal scheme for the design and operation of CEC [48] were obtained through experiments in the treatment of F⁻-containing groundwater. It was found, with OH⁻ being the only alkalinity of the raw water, that the highest efficiency would be obtained when the molar ratio of alkalinity and fluoride to Al(III) (ΟH⁻/ΦF⁻) was controlled at 3.0. Aluminium electrodes [49] have been studied. Electrocoagulation was investigated for applied potential (10–30 V), electrolysis time and supporting electrolyte (NaCl) concentration (0–100 mg/L). The results showed that with increasing applied potential and electrolysis time, the Al³⁺ dosage increases, and thereby favours the fluoride ions removal. It was also observed that defluoridation is dependent on the concentration of supporting electrolyte. Alumina/chitosan (AICs) composite [50] was prepared by incorporating alumina particles in the chitosan polymer matrix, which can be made into any desired form viz., beads, candles and membranes. AICs composite displayed a maximum DC of 3809 mg F⁻/kg than the alumina and chitosan (52 mg F⁻/kg). The fluoride removal studies were carried out in batch mode to optimize the equilibrium parameters viz., contact time, pH, co-ions and temperature. Batch experiments with bipolar aluminum electrodes and potentiodynamic polarization tests with monopolar systems were conducted [51] to investigate the effects of the type and concentration of co-existing anions on defluoridation in electrocoagulation (EC) process. The defluoridation efficiency was almost 100% and most of the fluoride removal reaction occurred on the surface of the anode in the solution without the co-existing anions, due to the electro-condensation effect. Mg-Al-CO₃ layered double hydroxides (LDHs) [52] have been employed to treat high fluoride concentration solution. The influences of solution pH, initial fluoride concentration and other anions in the solution were investigated by a series of batch experiments. A marked decrease in the amount of adsorbed fluoride by LDHs was observed with increasing pH. The extent of fluoride removal in the presence of other anions decreases in the order HCO₃⁻ > Cl⁻ > H₂PO₄⁻ > SO₄²⁻. Two effective types of superparamagnetic nano-scale adsorbents of bayerite/SiO₂/Fe₂O₃ [53] have been synthesized via three sequential steps: chemical precipitation of Fe₂O₃, coating of SiO₂ on Fe₂O₃ using acidifying method, and further coating of bayerite (Al(OH)₃) on SiO₂/Fe₂O₃ adopting sol–gel (MAGS) or homogeneous precipitation (MAHP) methods. Removal of fluoride from aqueous solution was evaluated to examine the adsorptive capacity of MAGS, MAHP, and commercial activated alumina (CA), and the effects of enclosure of Fe₂O₃ with SiO₂ for SiO₂/Fe₂O₃, MAGS, and MAHP particles. Among the adsorbents tested under the same experimental conditions, MAGS is the most effective adsorbent, of which the adsorption capacities are 38 g/kg (based on adsorbent mass) in adsorption in terms of equilibrium constant qL of Langmuir isotherm, and can compete with CA even at a high pH value. Aluminum sorbent (Al-sorbent) [54] was produced in a parallel-plate electrochemical reactor by anodic dissolution of aluminum electrodes in a dilute sodium chloride (NaCl) aqueous solution. The freshly generated Al-sorbent was able to reduce fluoride concentration from 16 to 2 mg/L at 2 min. The final concentration was further reduced to 0.1 mg/L by partial neutralization of the mixture to pH 6.3. The ability of waste residue, generated from the alum manufacturing process [55], to remove the fluoride ion from water has been investigated. Series of batch adsorption experiments were carried out to assess parameters that influence the adsorption process. Results showed that Adsorption of fluoride is fairly rapid in first 5 min and thereafter increases slowly to reach the equilibrium in about 1 h. The removal efficiency of fluoride was increased with adsorbent dosage. About 85% removal efficiency was obtained within 1 h at an optimum adsorbent dose of 16 g/L for initial fluoride concentration of 10 mg/L. The kinetics of fluoride removal from water by the adsorbent alumina cement granules (ALC) [56], exploring the mechanisms involved. ALC exhibited a biphasic kinetic profile of sorption with an initial rapid uptake phase followed by a slow and gradual phase. Effects of different operating conditions such as temperature, pH, voltage, hydraulic retention time (HRT) and number of aluminum plates between anode and cathode plates [57] on removal efficiency are investigated. Experimental results showed that by increasing HRT, removal efficiency increases, but after 5 min changes are negligible. Therefore, the total HRT required is only 5 min. The more HRT, the more electrical current is needed in order to achieve to constant voltage and temperature in system. In addition, it is found that pH value decreases from 6.91 to 4.6 during first 10 min but it increases up to 9.5 during 50 min. After treatment, the fluoride
concentration was reduced from initial 4.0–6.0 mg/L to lower than 0.5 mg/L.

Surface modification of rice husk ash (RHA) by coating aluminum hydroxide \[58\] RHA is obtained by burning rice/paddy husk which is an abundantly available and is an inexpensive raw material. The results showed excellent fluoride removal efficiency and the adsorption capacity was found to be between 9 and 10 mg/g. The adsorption characteristics of fluoride on activated alumina (AA) \[59\] were studied using batch methods. Kinetics data indicated that the fluoride adsorption process reached equilibrium within 10 h. In an experimental pH range of 5–10.5, fluoride uptake decreased with the increase of pH. Ionic strength did not impact fluoride adsorption in the entire experimental pH range. The objective of this work was to evaluate the capacity of steel slag filters \[60\] to treat a gypsum mining leachate containing 11–107 mg P/L ortho-phosphates, 9–37 mg/L fluoride, 0.24–0.83 mg/L manganese, 0.20–3.3 zinc and 1.7–8.2 mg/L aluminum. Column tests fed with reconstituted leachates were conducted for 145–222 days and sampled twice a week. The best removal efficiencies over a period of 179 days were obtained with sequential filters that were composed of Fort Smith EAF slag operated at a total HRT of 34 h which removed 99.9% of phosphorus, 85.3% of fluoride, 98.0% of manganese and 99.3% of zinc. The performance of Ti–Al binary metal oxide supported beads using chitosan template \[61\] was studied for fluoride removal from drinking water. Material works very effectively at all pH except at pH greater than 9. Alumina cement granules (ALC) \[62\] in removing fluoride from natural ground water, and synthetic water prepared using conditions and concentrations relevant to natural freshwater environments. The fluoride removal was concentration dependent on synthetic systems as the equilibrium adsorption capacity was found to be 4.75 and 3.91 mg g\(^{-1}\) corresponding to initial concentrations of 20 and 8.65 mg L\(^{-1}\) at optimal conditions. A novel Al–Ce hybrid adsorbent \[63\] with high sorption capacity for fluoride was prepared, it was very effective in fluoride removal from aqueous solution via electrostatic interaction. Especially, the adsorbent had the high sorption capacity up to 27.5 mg g\(^{-1}\) for fluoride at the equilibrium fluoride concentration of 1 mg L\(^{-1}\), much higher than that of the conventional adsorbents. The combined use of calcium salt and polymeric aluminum hydroxide \[64\], for treatment of fluoridated waste water has been described. F\(^{-}\) has been removed by activated carbon and ordinary quick lime \[65\]. The removal of fluoride was 80.6% and the final concentration was 9.7 mg/L at optimum condition from the synthetic solution having initial fluoride concentration of 50 mg/L. A continuous electrocoagulation–flotation (ECF) \[66\] system was employed to treat synthetic high fluoride-content wastewater following calcium precipitation. The aluminum form of each aminomethylphosphonic acid-type ion exchanger \[67\] was studied for fluoride uptake from tap water. Its fluoride uptake performance was studied under dynamic conditions by varying the F\(^{-}\) content of water, the flow-rate and the strength of the regenerant. The product developed showed a good capacity and selectivity for fluoride removal, and the uptake was found to be reversible and superior as compared with that of the commercially available strongly acidic cation exchanger Indion 225 and aminomethylphosphonic acid-type chelating ion exchanger Duolite ES 467. Due to the electrostatic repulsion in acidic solutions, adsorption of fluoride was retarded. At higher pH, fluoride adsorption on alum occurred due to electrostatic repulsion of fluoride ion to the negatively charged surface of alumina; competition for active sites by exclusive amount of hydroxide ion \[68\]. Defluoridation increased at pH 4–7 but decreased thereafter. At pH >7, silicates and hydroxyl ions were considered to compete with F\(^{-}\) ions for alumina exchange sites, but at pH <7, alumina fluoro complexes were formed in the presence of aluminium ions in the treated water. The potential of metallurgical grade alumina (MGA) for defluoridation was investigated at different condition \[69\]. The effect of temperature on zeta potential and fluoride adsorption was observed at α-Al\(_2\)O\(_3\)/aqueous solution interface \[70\]. The capacity was found 23.7 mg F\(^{-}\)/g and 7.0 mg F\(^{-}\)/g for THA and UHA, respectively at pH 4–9. The potential of alumina for fluoride removal from aqueous solution was explained by several other researchers \[71-74\]. HPLC–UVVIS method used in speciation analysis of aluminum form Al(II) ion, aluminum complexes with fluorides and iron in groundwater samples. Based on the obtained results of groundwater samples analysis, the separation of iron in the retention time ≈3.7, was obtained. The proposed method is selective for aluminum fluoride complexes and Al(III) in the pH conditions of their occurrence. The paper presents the possible types of transformation of aluminum hydroxyl forms and aluminum sulfate complexes by the reaction of the sample with mobile phase. An indirect method for the determination of aluminum in the form of aluminum sulfate was proposed \[75\]. Magnesia amended activated alumina \[76, 77\] and calcium oxide modified activated alumina \[78\] was also used for fluoride removal from water. The Langmuir sorption capacity of fluoride was found 7.22 m/g for copper oxide incorporated alumina. It was found that at same concentration Cao-AA works 5-10 times better than the MnO2-AA \[79\]. Activated alumina is an excellent adsorbent for the removal of fluoride from waters of various compositions and lowering the fluoride level to < 1 mg / 1 which maximum admissible concentration level for drinking water, is readily achieved by activated alumina. The adsorption capacity of activated alumina is very favourable for treatment of water contains less than 20 mg/1 of fluorides, provided interfering ions such as bicarbonate and silica are not present \[80\].

4. Conclusions

Studies for the removal of fluoride, using several aluminium and alumina based adsorbents have been summarized briefly in this review. The efficacy of each adsorbent has been examined and discussed. The following conclusions have been made on the basis of literature review:

- Aluminium and alumina based compounds are good adsorbents of fluoride.
- Although activated alumina adsorption technology shows higher uptake of fluoride, but it is expensive and its performance is affected by the presence of co-ions in water.
- Nano alumina- adsorbents have been attracted considerable attention in the recent years in fluoride removal and these materials have shown higher fluoride uptake capacity.
- The influence of pH, agitation time, initial fluoride concentration, temperature, particle size, surface area, presence and nature of counter ions and solvent dose were studied for defluoridation with various adsorbents.
- The sorption kinetics was pseudo-second order or pseudo-first order and the equilibrium data fitted well to the adsorption isotherms like Langmuir and Freundlich.

So, the future research should be concentrated on evaluating the efficacy of adsorbents in terms of cost and...
feasibility for removal of fluoride. It would be worthwhile to study the suitability of different chemicals to regenerate the spent adsorbents.

5. Acknowledgement
Financial support to Khichar M as NET-JRF from University Grants Commission, New Delhi is gratefully acknowledged.

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