

Fluoride Removal from Water by Aluminium Based Adsorption: A Review

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ABSTRACT: The present manuscript reviews on the research and exclusive development on defluoridation process about alumina based adsorbent. For the improvement of properties, enhancement in the capabilities to balance the tendency of reliability for alumina, the basic and fundamental technological advancement have been done by utilizing alumina base adsorbent for various application in treatment of waste water. In this content, the review related to recent progress on the modification of alumina based adsorbent to levy so as to improve the solubility and application. It present the underlying factor such as type and concentration of initiator, temperature and time are responsible for influencing the alumina based adsorbent. The alumina and its derivatives have lots of capabilities for the process of defluorination, so it is also predicted to good source for discarding pollutant from water and waste water as well. In the present review, the various aspect of alumina based adsorbent such as preparation, application, kinetic studies effects have been put forward for further view.

Keywords: Adsorbent; adsorption; entropy; enthalpy; Langmuir; aluminum hydroxide and kinetics.

INTRODUCTION: The worldwide hazardous effects of health regarding the fluoride in drinking water are well reported. Various defluoridation techniques have been accepted for providing safe drinking water to the people all over the world. Among these well-versed technologies, adsorption process is well established due to its varied properties such as cost effectiveness, ease of operation and eco-friendly in nature. Efforts have been under taken to review on defluoridation method using adsorption process based on a wide array of low-cost and specialized adsorbents to water for consumption having fluoride in desirable or permissible amounts prescribed by various national and international standards. The regeneration and safe disposal of adsorbents have been also reviewed for this chapter.

ALUMINA BASED ADSORBENTS:

Activated Alumina: Activated alumina (AA) is broadly studied adsorbent for removal of fluoride from drinking water. The different fluoride adsorption capacity for activated alumina has been suggested by various researchers. Fluoride removal capacity of activated alumina increases directly with fluoride concentration. It is inversely with pH of water as reported by Boruff (1934), Fink and Lindsay (1936),

Swope and Hess (1937), and Savinelli and Black (1958).¹⁻⁴

Bishop *et al.* (1978) also studied the fluoride removal from drinking water by using fluidized activated alumina as an adsorbent.⁵

Hao *et al.* (1986) were the one to suggest about the adsorption characteristics of fluoride on to hydrous alumina.⁶

Schoeman *et al.* (1987) gave the concept that the rate of fluoride adsorption of small particles was significantly more than the large-size particles. For the best absorption of fluoride, the favorable pH was 5 to 6, which is acidic in nature. Activated alumina can be regenerated by flushing it with a solution containing 4 % sodium hydroxide, which displaces fluoride from alumina surface. The chance of releasing toxic aluminium ions usually occurred by using some aluminium oxide/hydroxides.⁷

Farrah *et al.* (1987) investigated the interaction of fluoride ion with amorphous aluminium hydroxide, gibbsite which is naturally-occurring aluminium hydroxide and aluminium oxide over a wide range of pH values from 3 to 8 and fluoride concentrations from 0.1 – 1 mM (1.9 – 19 mg/l). It was remarkable that most of the aluminium hydroxide formed AlF complexes and dissolves at pH<6 and total F-Al ratio >

2.5. Maximum fluoride uptake occurred within the pH range of 5.5 – 6.5. The fluoride uptake varied in accordance with the Langmuir model at fixed pH between 5 and 7.5. The Gibbsite removal capacity was less as compared to other compounds by same reaction.⁸

Karthikeyan *et al.* (1997) studied the behavior of activated alumina by the batch calibration method. The minimum contact time for defluoridation was 30 minutes where the fluoride adsorption capacity was 3 mg/g and 20 mg/g in alkaline and acidic water respectively, while at neutral condition (pH=7), the fluoride capacity was 5.6 mg/g. The defluoridation capacity was not affected by the presence of chloride and sulfate ions were as with the increase in bicarbonate concentration the capacity got decreased. The regeneration studies were performed by 2 % hydrochloric acid, 2 % sodium hydroxide or 1 % sulfuric acid. The fluoride removal obeyed Langmuir's adsorption isotherm indicating that the forces of adsorption are governed by Chemi-sorption.⁹

Bahena *et al.* (2002) successfully studied the fluoride adsorption on to α - Al_2O_3 and its effect on the zeta potential at the alumina aqueous. Maximum fluoride removal was achieved between pH of 5 and 6 at 25 °C. The point of zero charges (pzc) of α - Al_2O_3 at 20 °C was found to occur at pH 9.2. Adsorption showed the Langmuir isotherm model. In the presence of fluoride, zeta potential is reversed towards the more acidic pH. Thus, fluoride ion replaces OH^- ions from the positively charged surfaces and gets adsorbed by H-bonding ($\text{pH} \geq \text{pzc}$). Regeneration studies have also been observed.¹⁰

Ku and Chiuo (2002) studied about the maximum fluoride at a pH range of 5 -7, which was 16.3 mg/g by using activated alumina as an adsorbent. They observed that adsorption of fluoride considerably retarded in acidic solutions because of the electrostatic repulsion between them. If the equilibrium solution pH was greater than 7.0, the fluoride adsorption is reduced by alumina. It was attributed to the electrostatic repulsion of fluoride ions to the negatively charged surface of alumina and it competes for active sites through excessive amounts of hydroxide ions. For neutral, the adsorption capacity of alumina for fluoride was found to be interfered due to the presence of sulphate.¹¹

Ghorai *et al.* (2004) investigated the removal of fluoride using activated alumina (Grade OA – 25) in batch and continuous operation and observed the adsorption

capacity to be as 1450 mg/kg at pH 7. It was noticed that there was a marginal decrease in the uptake capacity after each regeneration cycle. The regeneration procedure resulted in 85% efficiency with the grade of AA studied. However, later on, a loss of 5% in uptake capacity of AA was observed after five cycles.¹²

Pietrelli (2005) suggested about the fluoride adsorption of metallurgical grade alumina (MGA). According to them, the best removal was observed at pH 5-6 hence it was favourable to promote stable fluoro-alumina complex. The fluoride adsorption onto MGA sites decreased drastically at higher pH values, which was attributed to compete with hydroxide ions on the binding to the MGA surface. The fixed bed study resulted in the adsorption capacity of 12.21 mg/g.¹³

Shimelis *et al.* (2006) studied the adsorption capacities of untreated hydrated alumina (UHA) and thermally treated hydrated alumina (THA) obtained from hydrolysis of locally manufactured aluminium sulphate for fluoride removal from aqueous solution. The removal efficiency of fluoride increases with an adsorbent dosage. The increase in temperature treatment up to 200 °C was suitable for adsorption, but further increase in temperature lowered the fluoride removal. It was also foreseen that high defluoridation efficiency was achieved using both UHA and THA within a pH range of 4.0 to 9.0. The adsorption data fitted well to the Freundlich isotherm model with a minimum capacity of 23.7 mg F⁻/g and 7.0 mg F⁻/g for THA and UHA, respectively. Continuous packed bed column experiment using THA indicated that 4.5 g of THA could treat 6 L of water containing 20 mg/L fluoride before the breakthrough.¹⁴

Rao *et al.* (2008) investigated the fluoride adsorption capacity of gamma alumina for a fluoride solutions of 4 mg/l. They revealed that about 85 % to 95 % removal were achieved in the first 10 minutes after a sorbent dose of 8 g/l in pH 3 to 4 and remain fairly constant up to pH 7 where the adsorbent was used up to 10 cycles by cyclic regeneration with alum.¹⁵

Wang *et al.* (2008) suggested about the fluoride removal potential of nano-scale aluminium oxide hydroxide (nano- AlOOH). The maximum adsorption capacity of 3259 mg/ Kg of fluoride occurred at pH of around 7. The fluoride removal process obeyed the pseudo-second-order kinetic equation and the Langmuir adsorption model.¹⁶

Tang *et al.* (2009) studied the adsorption characteristic of fluoride on activated alumina. The fluoride adsorption study was carried out on a wide range of pH be-

tween 5 and 10.5. They observed that the fluoride uptake decreases for an increase in pH. The major anions reduce fluoride in the sequence following the order of $\text{HPO}_4^{2-} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$. Arsenic and selenium present in water are comparatively reducing fluoride adsorption showing competition for the same surface sites. A speciation-based model was developed for pH 5-10.5 and a wide surface loading range of 1–10 mg-F/g adsorbent was observed.¹⁷

Yadav *et al.* (2009) studied the performance of fluoride removal of soil pot made by soil with the different amount of $\text{Al}_2(\text{SO}_4)_3$ and observed remarkable decrease in 10 mg/l fluoride concentration into 0.61 mg/l with 2 gm/kg soil of $\text{Al}_2(\text{SO}_4)_3$ and contact time to 3 hours.¹⁸

George *et al.* (2010) investigated the modeling and simulation of remaining aluminium in water defluoridated using activated alumina adsorbent. An Activated Alumina Defluoridation Model Simulator (AAD) that has to be developed, predicted that the dissolution of aluminium fluoride and aluminium complexes is more favourable to high fluoride concentration with low alumina dosage in pH range of 6.5-7.5, which may lead to increase in residual aluminium in treated water. Thus, regeneration is essentially required before the complete exhaust of alumina to minimise residual aluminium concentration in treated water within a permissible limits.¹⁹

Sivasankari *et al.* (2010) remarked that 98 % removal of fluoride was achieved by 1.0 g of powdered activated alumina (PAA) and 1.4 g granular polymer-agglomerated alumina (GPAA) at pH 6 from 100ml of 10mg/l fluoride solution but fluoride uptake reduces drastically at pH greater than 7. The adsorption of GPAA was slightly faster than PAA. The adsorption capacity of 1.948 mg/g of fluoride was achieved by GPAA in column study of the flow rate of 10 mL/min.²⁰

Lee *et al.* (2010) studied meso porous alumina prepared by using aluminium tri-sect-butoxide in the presence of either cetyltrimethylammonium bromide (MA-1) or stearic acid (MA-2) as a structure directing agent has enhanced adsorption capacity and faster kinetic when compared with commercial activated alumina. The maximum adsorption capacities for the MA-1 and MA-2 adsorbents were estimated to be 7.51 and 14.26 mg/g, correspondingly, while the corresponding values for boehmite and gamma alumina were 6.13 mg/g and 6.36 mg/g, respectively. MA-2 prepared by using stearic acid, in particular, demon-

strated an adsorption capacity of 14.26 mg/g and initial adsorption rate of 14.6 mg/g min that were 2.2 and 45 times higher than those of a commercial gamma alumina.²¹

Kamble *et al.* (2010) studied the fluoride adsorption by alkoxide origin alumina. The maximum fluoride adsorption capacity occurred at pH 5 and 7, and pseudo-second order model fitted well as per kinetic data. The regeneration of adsorbent with sulphuric acid solution was carried out.²²

Kumar *et al.* (2011) studied the fluoride adsorption capacity of nano-alumina. The maximum fluoride removal capacity of 14 mg/g was occurred at pH 6.15 and 25 °C.²³

Li *et al.* (2011) reported the use of highly ordered meso porous alumina (Meso-Al-400) and calcium-doped alumina (Meso-Al-10Ca) for removal of fluoride and arsenic. The highest defluoridation capacity reached 300 mg/g and 450 mg/g at pH 6.5 and temperature of 298 K for 12 hours of contact time.²⁴

Biswas *et al.* (2012) investigated synthetic hydrous aluminium oxide (HAO) for fluoride adsorption. The maximum fluoride removal occurred at pH 6.5, and the reaction kinetic is a pseudo-second order type. Langmuir monolayer adsorption capacity was 14.79 mg/g at room temperature.²⁵

Gong *et al.* (2012) studied the adsorption of fluoride onto five unusual types of alumina synthesized at unusual pH and calcination temperatures. Langmuir and Freundlich isotherms were fitted best, and adsorption was spontaneous and endothermic as per thermodynamic study. The kinetic was well described by pseudo-second-order model and the weak acidic pH favoured fluoride adsorption. Acidic alumina has higher ion-exchange capacity than basic alumina without pH adjustment.²⁶

Goswami *et al.* (2012) investigated acidic alumina has BET surface area of 144.27 m²/g which removes maximum fluoride at pH4.4. The adsorption process followed the pseudo- second order kinetics and Langmuir isotherm showed the adsorption capacity of 8.4 mg/g. The study of thermodynamic parameters inferred that physical adsorption was dominant with activation energy of 95.13 kJ/mol and endothermic behavior during the process was revealed.²⁷

Gupta *et al.* (2013) studied the removal of fluoride with activated alumina in the presence of chloride. They observed that the percentage removal of fluoride increases without an increase as the dosage of acti-

vated alumina.²⁸ The studies show that the activated alumina was capable of remove approximately 60 to 70% of fluoride from water, but a slight decrease in fluoride removal capacity was observed due to the presence of chloride ions. The foremost disadvantage of fluoride removal by activated alumina is that the optimum fluoride removal capacity takes place only at a pH value to the solution below 6.0, which limits the practical applications of the AA heavily. Moreover, it has been also reported that alumina begins to leach below pH 6 and poses severe threats to human health since the aluminum and its fluoride complexes are known to cause Alzheimer's disease, which is a chronic neurodegenerative disease and the other health effects are well documented.²⁹⁻³²

MODIFIED ACTIVATED ALUMINA:

To enhance the adsorption efficacy of activated alumina, researchers have also modified alumina surface in the various forms as describe below:

Aluminium + Alum: Tripathy *et al.* (2006) investigated the fluoride adsorption by alum impregnated activated alumina that was capable enough to remove 92.6% of fluoride at pH 6.5 at the dose of 8 g/l and 3h contact time from water containing 25 mg/l and then regulated to decrease with a further increase in pH. In the acidic range, the fluoride removal decreases due to the formation of weak hydrofluoric acid or combined effect of both chemical and electrostatic interaction between the oxide surface and fluoride ion. At pH above 6.5, the fluoride removal decreases sharply due to strong competition with hydroxide ions on the adsorbent surface. The Langmuir sorption capacity of fluoride was found to be 40.68 mg/g at pH 6.5. Desorption of fluoride from the adsorbent was done by rinsing the fluoride-adsorbed AIAA with 0.1 M NaOH at pH 12.0 followed by the process of neutralization with 0.1 M HCl. However, the adsorbent can be used extensively for further removal of fluoride prior to impregnation with alum.³³

Aluminium + Calcium: Nawlakhe *et al.* (1975) reported the Nalgonda technique for fluoride removal from water in which two chemicals alum in the form of aluminium sulphate and potassium aluminium sulphate and lime as calcium oxide was rapidly mixed with fluoride contaminated water to formed focus of aluminium hydroxide. After gentle, stirring it was allowed to settle down to remove the maximum amount of dissolved fluoride. Nalgonda technique has been introduced into various countries such as India, Kenya, Senegal and Tanzania.³⁴

Dahi *et al.* (1996) implemented Nalgonda technique in Tanzania village of Ngurdoto at the community and household level. According to house hold version, 12.8 g of alum and 6.4 gm of lime was mixed in a bucket of 20 litre and allowed to settle down the sludge for one hour. The treated water was withdrawn through a tap that was 5 cm above the bottom of first bucket and store for many days as drinking in the second bucket. This technique could reduce the 8.8 to 12.5 mg/l initial concentration of fluoride into 0.7 to 2.1 mg/l of fluoride, which was still notice to be above the WHO standard.³⁵ Even if the Nalgonda process was recommended as an effective technique for fluoride removal, some critics highlighted its disadvantages as well. For example, Meenakshi and Maheshwari (2006) have listed the following drawbacks,³⁶

- (i) The process removes only a smaller portion of fluoride (18–33%) in the form of precipitates and converts a greater portion of ionic fluoride (67–82%) into soluble Al_3p-F_- complex ions which are themselves toxic in nature by Apparao and Kartikeyan, (1986).³⁷
- (ii) The concentration of the SO_4^{2-} ion from the aluminium sulphate coagulant reaches to the high levels, and in a few cases it crosses, the maximum authorized limit of 400 mg/L.
- (iii) The residual aluminium in excess of 200 ppb in treated water is believed to cause dementia, and it also affects musculoskeletal, respiratory and cardiovascular systems by Nayak, (2002).³⁸
- (iv) Many users do not like the taste of the treated water as it was appreciated earlier.
- (v) Regular analysis of feed and treated water is required for calculating the correct dose of chemicals to be added, because the water matrix fluctuates enormously with time and season.
- (vi) The maintenance cost of a community plant is high. On an average as experienced in the recent years, a plant of 10,000 L per day capacity requires Rs. 3000 every month which is quite expensive.
- (vii) The process is not automatic as it requires a regular attendant during the treatment process for regulating.
- (viii) Large space is required for drying of sludge.
- (ix) Silicates have adverse effect on defluoridation by Nalgonda technique. Temperature of an area also affects the defluoridation capacity.

Dayananda *et al.* (2014) investigated CaO loaded meso porous Al_2O_3 as adsorbent for defluoridation of

water. It was observed that 20 % by weight CaO loaded meso porous Al_2O_3 had the capacity to remove 90% fluoride from water within 15 minutes using 3 gm/l of dose whereas pure Al_2O_3 were capable of remove only 22% of fluoride after 1 h. The maximum fluoride adsorption capacity of Al_2O_3 and $\text{CaO}20@\text{Al}_2\text{O}_3$ were found to be 24.45 mg/g and 136.99 mg/g respectively. The maximum removal of fluoride in case of $\text{CaO}20@\text{Al}_2\text{O}_3$ were mainly due to impregnation of Ca which reacted with fluoride to form CaF_2 precipitates and had high value of zeta potential (pH_{pzc}). This composite adsorbent had lots of potential to remove fluoride at a wide range of pH.³⁹

Aluminium + Carbon: Lunge *et al.* (2012) studied the alumina supported carbon composite prepared by waste of egg shell for removing fluoride from water. The Langmuir adsorption capacity of composite adsorbent was 37mg/g at 303 K for a wide range of pH between 3 and 9. The adsorbent capacity of 15.15 mg/g and 71.43 mg/g was observed in the tested field water and waste water, which generally had initial concentration of 8.5 and 46.4 mg/l respectively.⁴⁰

Aluminium + Copper: Bansiwal *et al.* (2010) investigated copper oxide coated alumina (COCA) for removal of fluoride. COCA was synthesized by saturating alumina with copper sulphate solution followed by a calcination process in presence of air at 450°C. The adsorption capacity of COCA for fluoride obtained as the basis of the Langmuir model was 7.22 mg/g, which was three times higher than that of unmodified AA where value obtained was 2.232 mg/g. The adsorption kinetics followed the pseudo-second-order model to the results of pH studies, it is revealed that the COCA can be used for defluoridation of water in broad pH range between 4 and 9. The significant increase in adsorption capacity of COCA was described, which could be due to the increase in zeta potential referred to as more positive values resulting in elevating fluoride sorption. A slight variation in the fluoride removal was seen with variation in pH. Marginal decreases in sorption capacities were reported at pH above 8 which might be due to the competition by OH^- ions present in alkaline conditions. The assessment of water quality after treatment confirms that there is no leaching of metals namely aluminium or copper. The fluoride desorption by using NaOH solution (4 M) was regenerated to about 97% of saturated sorbent but adsorption capacity was found to decrease from 98 % to 91% with 10mg/l of fluoride.⁴¹

Aluminium + Iron: Chubar *et al.* (2005) studied a novel ion exchanger based on double hydrous oxide

($\text{Fe}_2\text{O}_3\text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$) for removal of fluoride, chloride, bromide and bromate ions. According to their studies, the Langmuir fluoride adsorption capacity was 90 mg/g at pH of 4. Kinetic data on fluoride and bromide sorption fitted well as the pseudo-second-order model. The adsorbent was effectively under pH range of 3-8.5 for removal of F^- , Cl^- , Br^- and BrO_3^- .⁴²

Biswas *et al.* (2007) studied the adsorption capacity of iron (III) – aluminium (III) mixed oxides made by co-precipitated aluminium and iron hydroxides from a chloride mixture in equimolar quantities using ammonia. Then the mixed oxides was aged, and it was found that resulted dried binary metal oxides was a better adsorbent for fluoride than either aluminum hydroxide or iron (III) hydroxide. The optimum pH for fluoride removal was 4-10 and equilibrium time required was 1.5h. The Langmuir monolayer adsorption capacity was 17.73 mg/g where the pseudo-second order was standard as per kinetic study, and the adsorption was endothermic in nature.⁴³ Dang Dan *et al.* (2011) studied fluoride adsorption from water by $\text{Fe}_2(\text{SO}_4)_3$ modified granular activated alumina (1- 2 mm). The adsorption study was carried out at a wide range of initial fluoride concentration (0.5 to 180 mg/l at pH \approx 7) under the adsorbent dose of 1.0 g/l. They concluded that both Langmuir and Freundlich isotherms were fitted for low equilibrium concentrations (0.1 to 5.0 mg/L) but the Freundlich isotherm model fitted only for high equilibrium concentration (5.0 to 150 mg/L).⁴⁴

Aluminium + Magnesia: Maliyekkal *et al.* (2008) developed magnesia amended activated alumina (MAAA) by calcination of magnesium hydroxide impregnated alumina at 450 °C. More than 95% of fluoride removal (10mg/l) was achieved within 3 h of contact time at neutral pH. The maximum sorption capacity of MAAA for fluoride deduced from Sips equation was found to be 10.12 mg/g. An optimum fluoride removal was detected at pH range of 5.0–7.5. The fluoride sorption capacity was reduced from higher concentrations of bicarbonate and sulphate. Adsorption kinetics followed the pseudo-second-order model, which indicates that F^- removal might be due to chemisorption process. It was noticed that the rate of sorption by MAAA was much more than that of AA and it was concluded that fluoride uptake by MAAA is a complex process. Both the surface sorption as well as intra-particle diffusion plays an outstanding role during the sorption process showing that the fluoride bearing MAAA regenerated with 2% sodium hydroxide solution as an eluent.⁴⁵

Aluminium + Manganese Oxide: Teng *et al.* (2009) used redox process to coat hydrous manganese oxide from the surface of activated alumina (HMOCA). The maximum removal of fluoride was found at pH between 4 and 6 where the Langmuir adsorption capacity was 7.09 at pH 5.2 ± 0.05 . Adsorption of fluoride took place mainly by the anion exchange between hydroxyl ion and fluoride at acidic pH range. Fluoride adsorption onto HMOCA followed the pseudo-second-order equation. The presence of co-ions greatly affected the fluoride removal capacity. HMOCA was used for carrying out the column study to reduce 5mg/l initial concentration to less than 1.0 mg/l at flow rate of $2.39 \text{ m}^3/\text{m}^2\text{h}$.⁴⁶

Aluminium + Manganese Dioxide: Tripathy *et al.* (2008) have investigated the fluoride removal ability of manganese dioxide coated with activated alumina and perceived the fluoride removal up to 0.2 mg/l at pH 7 in 3 h with 8g/l adsorbent dose when 10 mg/l of fluoride was present in 50 ml of water. The second-order rate kinetic was integrated as per kinetic study and found Langmuir fluoride adsorption capacity to be as 0.17 mg/g. The fluoride uptake was mainly governed by physical adsorption as well as the initial intra-particle diffusion at the porous surface.⁴⁷

Aluminium + Lanthanum: Wasay *et al.* (1996) have modified the alumina by impregnating it with La^{+3} and Y^{+3} for removal of fluoride along with other hazardous anions. The order of selective removal was observed as – fluoride >phosphate >arsenate >selenite.⁴⁸

Puri *et al.* (2000) reported about fluoride removal by Lanthanum hydroxide assisted on alumina. The adsorption capacity for alumina impregnated with Lanthanum hydroxide was found as 0.340-0.365 mM/g, whereas for the original alumina it was 0.170-0.190mM/g. The mechanism involves the exchange of ion between OH^- and anion. The adsorbent was effective when the fluoride concentration decreases from 7 mM to 0.003 mM in the pH range of 5.7–8.0 where the Langmuir adsorption capacity was 0.82 mM F⁻/g of the adsorbent. Fluoride removal was indiscriminately affected by the presence of phosphate and sulphate whereas chloride, bromide, iodide and nitrate ions had no show significant influence on the sorption of fluoride by the prepared sorbent. The sorbed fluoride ions were eluted from the adsorbent with 10 mL of 0.1 M NaOH and the column could be reused after being conditioned with 10 mL of 1 mM HCl.⁴⁹

Shi *et al.* (2013) reported about lanthanum oxide impregnated granular activated alumina (LAA) for fluoride removal. Five cycles of lanthanum impregnation on AA were carried out followed by the calcination at 573 K which was responsible for increasing the La content up to 19.1% and achieved the maximum fluoride adsorption at 16.9 mg/g. LAA could adsorb 70.5 – 77.2 % fluoride in the pH range of the actual groundwater between 3.9 and 9.6 that were about four times higher than AA and sustained the reduced Al release.⁵⁰

Aluminum + Polymer: Karthikeyan *et al.* (2009) studied the polyaniline/alumina (PANi-AIO) and polypyrrole/alumina (PPy-AIO) composites for the removal of fluoride. The maximum amount of adsorption was 6.6 mg/g and 8 mg/g for PANi-AIO and PPy-AIO respectively. The fluoride removal mechanism of these composite was based on formation of aluminium-fluoro complexes on the alumina surface and doping/dopant –exchange of fluoride ions in the polymer. The pH study was under taken over the range of 3 – 9, and it was found that the amount of fluoride ions adsorbed (Q_e) in this pH range varied from 3.96 to 2.64 mg/g for PANi-AIO and 4.7 to 3.16 mg/g for PPy-AIO. In acidic pH, adsorption was high due to availability of more positive charged polymer/alumina composite to attract fluoride ions electrostatically whereas in the alkaline range, the hydroxide ion could compete effectively with fluoride ions leading to a lower defluoridation.⁵¹

Others: Sequeira *et al.* (2012), investigated the modification effects of hematite with aluminium hydroxide on the removal of fluoride ion from water. The optimum pH range was between 2.34 to 6.26 and the maximum Langmuir adsorption capacity of modified adsorbent was 116.75 mg/g.⁵²

Rafique *et al.* (2013) studied the defluoridation of drinking water by using modified immobilized activated alumina (MIAA) prepared by adding the specific amount of alum during synthesis via Sol-gel method. Fluoride removal up to 95% at $20 \pm 1^\circ\text{C}$ was achieved by MIAA within 60 minutes of contact time. The fluoride adsorption capacity of MIAA was much higher to be as 0.76 mg/g when compared to activated charcoal which was 0.47mg/g at same concentration. Langmuir and Freundlich isotherms were fitted well with regression coefficient R^2 of 0.99 and 0.98 respectively. MIAA was regenerated thermally and chemically for the defluoridation process.⁵³

RECENT DEVELOPMENTS:

Du *et al.* (2014) has prepared the simple aluminium hydroxides and double layered hydroxides by varying its synthesis regarding temperature, concentration of extra sulfate, citrate and metal oxide amendments for defluoridation. They observed that higher temperature had the negative effect on fluoride adsorption. The addition of extra sulfate during the synthesis of aluminium hydroxides resulted in higher fluoride adsorption as compared to aluminium hydroxides prepared with extra citrate/ no extra ligands. Addition of extra sulfate liberated to form pseudo-Boehm and basaluminate at 200°C. Treatment of aluminium hydroxides with magnesium, manganese and iron oxides did not have any significant impact on fluoride adsorption. Double layered hydroxides exhibit higher fluoride adsorption capacity and found to be much more than aluminium hydroxides.⁵⁴

Nazari *et al.* (2014) has studied that nano-magnesia/alumina adsorbent by doping γ -Al₂O₃ with MgO nanoparticle through sonochemical approach for defluoridation of water. The optimum removal up to 85% and its adsorption capacity 5.6 mg/g was attained at neutral pH range of 6.3-7.3 in 140 min and adsorbent dose of 0.5 g/l. The presence of phosphate ions highly responsible for affecting adsorption capacity whereas presence of other ions such as Cl⁻, SO₄²⁻ and HCO₃⁻ had the slight effect of the defluoridation capacity. The experimental data fitted well with Langmuir adsorption isotherm and adsorption process followed the pseudo-second-order kinetic model.⁵⁵

Oladoja *et al.* (2014) used aluminium oxide infused with diatomaceous earth (AD) via co-precipitation method for defluoridation of water. The optimum calcination temperature for AD was 250°C. The experimental data was fitted well with Temkin isotherm model. The adsorption process followed pseudo-second-order kinetic model, and the value of the approaching equilibrium factor R_w was less than 0.01. The Langmuir adsorption capacity of AD was 13.141 mg/g at neutral pH. The presence of sulphate, chloride and nitrate ions in water had no effect of the defluoridation capacity whereas phosphate and carbonate ion was responsible for reducing the defluoridation capacity.⁵⁶

Mulugeta *et al.* (2014) studied about the defluoridation capability of aluminum hydroxide (AO) from water where the surface area and size of AO were 37.7 m²/g and 200-300 nm respectively. The fluoride uptake was not hindered due to the presence of so-

dium salts of chloride and sulphate in concentration up to 500mg/l., the reduction of fluoride efficiency with an increase in concentration of hydroxide and bicarbonate was dependent on pH of solution. The phosphate ions interrupt the fluoride adsorption. The fluoride uptake capacity of 26.2 mg/g was obtained in continuous packed bed column experimentation with deionized water at flow rate of 100 empty bed volumes (eBV) per day, resulting to bring down fluoride concentration to 1.5 mg/l (the WHO guideline value). The adsorption capacity of AO was six times greater than that of activated alumina (AA) (3.8-4.5 mg/g) under the same condition of pressure and volume. The pH of treated water was in between the range of 4.4-7.0. The fluoride uptake capacities of Ethiopian ground water at 100 and 10 eBV/day were 4.65 and 9.0 mg/g respectively. At pH less than 5, the aluminium released was between 0.6 and 2.0 mg/l. For avoiding the release of aluminium in treated water, the pH of water was maintained within the range of 7.5-8.5 by adding calcite (CaCO₃) post-treatment column that neutralizes the pH and is responsible for controlling both aluminium and sulphate concentration in treated water. It showed that AO was most promising adsorbent due to low-cost, ease of availability and simplicity in manufacturing process along with limitation in the presence of bicarbonate ion under the condition of untreated water and pH dependent process.⁵⁷

Liu *et al.* (2015) prepared fresh aluminium hydroxide for simultaneous removal of arsenic and fluoride from the groundwater. The removal of neutral As(III) was independent on the pH at a molar ratio between arsenic to aluminium $R_{As(III):Al}$ to be $\leq 0.70:1$ which was much lower than that of As(V). Fluoride at a molar ratio of fluoride to arsenic $R_{F:As(V)}$ was $> 35:1$ that significantly impair the removal of As(V) with more significant inhibition at an elevated pH. The negatively charge As(V) inhibits fluoride removal to a large extent than the neutral As(III) dose. The optimum As(V) removal was weak at pH of 5 and 6, which is acidic in nature whereas that of fluoride removal was at pH of 7 and 8. The adverse effect of fluoride on As(V) removal is mainly attributed to the lowered ζ -potential, which is controlled by the combined effects of pH and $R_{F:As(V)}$. In relative terms, the removal of fluoride is highly dependent on pH, although $R_{As(V):F}$ shows very minor effects. The oxidation of As(III) to As(V) and the adjustment of pH to a weak acidic range is well preferred for attaining the simultaneous removal of As and F by AlOxHy adsorption.⁵⁸

Jin *et al.* (2015) used alumina-modified expanded graphite ($\text{Al}_2\text{O}_3/\text{EG}$) composite via facile solution method at 450°C for 2 hours for the defluoridation of water. The fluoride removal at pH range between 3 and 7 was not readily affected by the pH of aqueous solution. The fluoride removal of 94.4% and adsorption capacity of 1.18 mg/g was observed by $\text{Al}_2\text{O}_3/\text{EG}$ composite adsorbent. This adsorbent was quite efficient enough for removing lower concentration of fluoride ions present in water below permissible standard. Therefore, the adsorption was a multi-molecular layer adsorption between the adsorbed molecules where the process was spontaneous and endothermic in nature.⁵⁹

CONCLUSIONS AND FUTURE PERSPECTIVES:

Water is an important natural-resource for maintaining environmental and life that we have constantly regarded as around in wealth and free present of nature.⁶⁰⁻⁶² Fluoride is a hard-to-eliminate leading groundwater impurity of global issue.⁶³⁻⁶⁵ By the way a small concentration of fluoride in drinking-water is valuable for bone and tooth, its surplus has the undesirable.⁶⁶ This review has attempted to cover a wide range of aluminium based adsorbents which have been used so far for the removal of fluoride from the water and wastewater. Different experimental parameter and methods were applied for the synthesis of alumina based adsorbents. Due to the synthesis of expected compound generally having high purity at comparatively low temperature, the sol-gel technique is prominent all over the world that are used extensively for defluoridation process. Another properties have been created due to the enhancement of new material which needs awareness for employing it in research studies and also for commercial uses. Therefore, alumina based adsorbent is on the trench to become one of the beneficial adsorbent for creating the surrounding free from pollution. The alumina based adsorbent and its vast uniqueness opportunities in near future that have been set by the nanotechnology is regarded for advancement in the present world.

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