

# Fluoride Removal by Clays, Geomaterials, Minerals, Low Cost Materials and Zeolites by Adsorption: A Review

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**Abstract**— Defluoridation from ground water for drinking purpose and fluoride expulsion from wastewater is the one most significant problem throughout the world. Fluorosis is epidemic in more than 25 nations across the globe. The most severely affected countries are India, China, Sri Lanka and South Africa and found in trace amounts in rural and semi-urban regions of the United States of America, Central Argentina, Central Europe and North Mexico. The various resources that contaminated groundwater are fluoride bearing soft rocks and industrial effluents with rich in fluoride concentration. The permissible fluoride limit established by the World Health Organization (WHO) for drinking water is 1.0 mg/l and 1.5 mg/l for India. The fluoride concentration in the range of 1 to 1.5 mg/l strengthen the enamel. The excess gathering of fluoride in groundwater beyond 1.5 mg/l causes dental fluorosis, skeletal fluorosis besides non-skeletal fluorosis. In India, Nalgonda technique is mostly adopted for removing fluoride from water based on precipitation method. A couple of techniques are available for defluoridation yet adsorption approach was mostly upheld worldwide because of cost effective, simple in design, simplicity in operation, comfortable, effective and environment reason. The adsorbent materials, including clays, Geomaterials, minerals, low cost materials and zeolites for the most of the part receives practically speaking about uprooting of fluoride by adsorption in a decade ago because of the enormous accessibility in the world's covering, ease and high effectiveness. This paper signifies the critical review of past work on defluoridation by utilizing locally accessible materials such as clays, geomaterials, minerals, low cost materials and zeolites.

**Index Terms**— Adsorption, Defluoridation, Fluorosis, Kinetic.

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## I. INTRODUCTION

The purity of water is scared and gets always contaminated by several pollutants. Fluorine is one of such contaminants that contaminate water all place around the universes. The primary wellsprings of disintegration of fluoride in the ground water are delicate rocks that contain fluoride, for example, fluorspar, fluorapatite, cryolite and hydroxylapatite. The industrial effluents from aluminum, phosphate, semiconductor, glass and ceramic, fertilizer, uranium, electroplating, toothpaste manufacturing units and coal plant adds fluoride to the ground water [1]. The other source of fluoride intake for human beings are water, air, food, cosmetic and medicine. The permissible limit of fluoride was 1.5 mg/l and 1.0 mg/l for India as set by the World Health Organization (WHO). Fluoride is beneficial for the development of enamel when found in small concentration about 0.7 mg/l and causes severe health problems when found above 1.5 mg/l in ground water like dental fluorosis, skeletal fluorosis, non-skeletal fluorosis. Apart from fluorosis, excess fluoride in water causes diseases like cancer, damage kidney-liver-nervous systems, thyroids, respirator problems, Alzheimer, reduce pregnancy. The fluorosis were pervasive among the 200 million people groups from more than 30 nations over the globe [2]. In India alone 66 million people are under threat due to excess amount of fluoride present in water [3]. The most fluoride prone states in India includes Assam, Andhra Pradesh, Gujarat and Rajasthan [4-6]. Adsorption method is more popular than chemical precipitation, ion exchange, membrane separation and electro-deposition techniques due to economical, efficient, environmentally beneficial with ease of operation, simplicity in design and high selectivity technology [7]. Defluoridation of water and wastewater were tried by a variety of adsorbent such as alumina based adsorbents, carbon based adsorbents, agricultural and industrial wastes, metal oxides and hydroxides, calcium based adsorbents, clay based adsorbents, biopolymers and nano-materials based adsorbents. The present study described the overview of various clays, Geomaterials, minerals, low cost materials and zeolites as adsorbents for effective removal of fluoride from drinking and wastewater to meet national and international standards.

## II. CLAYS

Bower and Hatcher (1967) studied the defluoridation of water by minerals and soils by the release of OH<sup>-</sup> ions. The equilibrium information fitted well with the Langmuir isotherm model. The adsorption of fluoride at an equilibrium concentration of 16 mg/l for various soils and minerals were alkaline soils (59 to 120 mg/g); acid Aiken soil (1060mg/g); gibbsite and kaolinites (190 to 295 mg/g); dehydrated halloysite (1400 mg/g); hydrated (expanded) halloysite (1777 mg/g) and Al(OH)<sub>3</sub> (32600 mg/g). Goethite, bentonite and vermiculite adsorbed only traces of fluorides [8].

Omueti and Jones (1977) used Illinois soils for the removal of fluoride from water. It was reported that at low concentration of fluoride both Langmuir and Freundlich isotherm models described adsorption on soils. The optimum pH range for the maximum fluoride removal was between 5.5 and 6.5. The presence of amorphous aluminium oxyhydroxides was responsible for the removal of fluoride [9].

Chaturvedi *et al.* (1988) used china clay for fluoride removal from water. The optimal condition suitable for defluoridation consists of low fluoride concentration, high temperature and acidic pH. The maximum fluoride adsorption was mainly occurred due to the presence of alumina in china clay [10].

Hauge *et al.* (1994) studied the defluoridation of drinking water using pottery. The clay fired at 600°C temperature was found most effective for removal of fluoride [11].

Bjorvatn and Bardsen (1995) studied the defluoridation capacity of calcined red soil (laterite) at 570°C mainly consists of silicon, aluminium and iron from water. The defluoridation capacity of red soil from Balang in Adamoua province, North Cameroon was more as compared to that of N'Gaoundere. The fluoride removal was high initially in few hours and reached to steady state within 48 hours. The calcined red soil could reduce the fluoride from 12.2 to 0.26 mg/l in 12 hours and reduced fluoride from 132 to 4.58 mg/l in one week. The taste and odour of water was not changed by using red soil [12].

Zevenbergen *et al.* (1996) used local Kenyan soil derived from volcanic ash (i.e. ando soil) for fluoride removal from drinking water. The adsorption capacity of ando soil was 5.51 mg/g at pH 4.5. The fluoride adsorption by ando soil was done mostly due to the presence of high active aluminium content and the acidic property of soil. This soil adsorbent was mostly used for treatment of drinking water at village level in Kenya and other rural areas along the Rift Zone of East Africa [13].

Moges *et al.* (1996) used fire clay chip obtained from a region in Ethiopia for removal of fluoride from water. The defluoridation capacity of 200 mg/kg and 76 mg/kg was obtained by the adsorbent dose of 30 and 240g respectively. A packed column with same ground clay pot treated 6 litres of tap water containing 10 ppm fluoride to below 1.5 mg/l, whereas 20 litres of 10 ppm F-water showed removal efficiency of 285 mg/Kg at saturation point [14].

Bjorvatn *et al.* (1997) used laterite from North Cameroon, soils from Addis Ababa and top soils (red, laterite) from Ethiopian Rift valley for defluoridation of water. The soil samples from Addis Ababa could reduce the fluoride in water from 15 mg/l to 1 mg/l with dose of about 100g/l whereas the laterite from Northern Cameroon reduced 15 mg/l of fluoride concentration to 0.5 mg/l with the same dose. The soils from Ethiopian Rift Valley calcined at 250°C for 3 hours and its dose of 100g/l has very low or negative removal of fluoride. The average removal efficiency under the selected sequential conditions was about 58% and gets reduced by 90% in 30<sup>th</sup> runs [15].

Srimurli *et al.* (1998) used low cost materials such as kaolinite, bentonite, charfines, lignite and nirmali seeds for removal of fluoride from water in batch study. The defluoridation capacity of low cost materials at optimum conditions was found in order of bentonite (46%) > charfines (38%) > kaolinite clay (18.2%) > nirmali seeds and lignite (6 to 8%). The chemical modification of charfines did not show enhanced removal of fluoride [16].

Kau *et al.* (1998) investigated the adsorption of fluoride by kaolinite and bentonite. The results show that bentonite has a higher fluoride adsorption capacity than kaolinite [17].

Wang and Reardon (2001) have investigated the heavily-weathered tertiary soil from Xinzhou, Shanxi, China for defluoridation of drinking water in batch and column modes. The soil was composed of quartz, feldspar, illite and goethite with 6.75% of iron oxide. The presence of co-anions like chloride, sulphate and bicarbonates ions have shown little or no effects on fluoride removal in batch study. The soil could be regenerated by acid rising and directly passing through the treatment column. The experimental data followed Freundlich isotherm model. The activation of soil with heat treatment of 400-500°C for 2 hours produced granular and permeable adsorbent. The fluoride removal capacity of soil in the column was observed to be 0.23 mg/g at pH 5-7. The adsorption mechanism was mainly due to Fe(III) oxyhydroxides [18].

Wang *et al.* (2002) studied the defluoridation capacity and leaching of fluoride by using various soils of China. The fluoride adsorption capacity of soil was ranked as Black soils > Purplish soil > Red earth > Dark brown earth > Drab soil > Sierozen. The Leaching amount from different soils was Drab soil > Sierozen > Black soil > Purplish soil > Red earth > Dark brown earth. The fluoride predominantly occurred in shallow groundwater in northern China due to presence of alkaline soils from temperate arid and semi-arid areas that leach more fluoride whereas less fluoride leach from acid soil in tropical humid areas (Southern China) and in temperate semi-humid areas (North-Eastern China) and in turn prevents from fluorosis [19].

Agarwal *et al.* (2002) used acidified montmorillonite, montmorillonite and kaolinite for defluoridation of water. The optimum pH for montmorillonite and kaolinite as well as acidified montmorillonite was 4 and 6 respectively. The fluoride removal of 99% was achieved by acidified montmorillonite in the pH range of 5-7 [20].

Agarwal *et al.* (2003) used the vessels (pot) made from a locally derived sample of silty clay I for defluoridation of water. The silty clay with 50mg/g of Al (activated  $\text{Al}_2\text{O}_3$ ), Fe ( $\text{FeCl}_3$ ) and Ca ( $\text{CaCO}_3$ ) enhanced the removal of fluoride from water at pH of 6.0. The adsorption reaction was very fast and considerable fluoride was removed within 5 minutes of shaking time. The pots made with these materials were connected in series with rubber tubes and treated fluoride water below the permissible limit which provided economical way of defluoridation of water [21].

Coetzee *et al.* (2003) investigated the defluoridation capacity of South African clay for natural water. Various clay types such as bauxite, laterite, palygorskite, bentonite and kaolinite were used for defluoridation of water. Clays consisting of substantial amounts of gibbsite or aluminium oxides showed best removal of fluoride. The optimum pH was 5.0 and 3.5 for aluminium oxide and iron oxide type adsorbents. Some clays treated with 1%  $\text{Na}_2\text{CO}_3$  and HCl solutions and warmed to  $< 600^\circ\text{C}$  could enhance the adsorption capacities [22].

Chidambaram *et al.* (2003) removed fluoride from water by natural materials like red soil, charcoal, brick, fly ash and serpentine. The column study revealed that the red soil had good defluoridation capacity followed by brick, fly ash, serpentine and charcoal. The fluoride equilibrium was reached after about 30 min [23].

Puka (2004) studied the defluoridation of water by locally available South Africa clays by exchange of  $\text{OH}^-$  ions with  $\text{F}^-$ . The clay containing aluminium and iron oxide surfaces as well as physical and chemical modified clay resulted into higher fluoride adsorption. Maximum adsorption was achieved at pH 5 for aluminium oxides type adsorbent and pH 4 for iron oxides types such as goethite [24].

Karthikeyan *et al.* (2005) used montmorillonite clay for removal of fluoride from water at neutral pH. Adsorption increased with time and reached an optimum level at 50 min. The particle size of 75 micron gave the maximum fluoride removal of 82%. The optimum pH for maximum fluoride removal was 2.0. The presence of co-anions like chloride, sulphate and nitrate did not significantly affect the adsorption capacity but bicarbonate ions reduced the fluoride removal from 82 to 58%. The adsorption results was best fitted with Langmuir isotherm than Freundlich isotherm model. The Langmuir adsorption capacity was ranging from 1.485 to 1.910 mg/g at temperature range of  $30^\circ\text{C}$  to  $60^\circ\text{C}$ . The thermodynamic study revealed that the adsorption reaction was spontaneous and endothermic. The adsorption process followed intra-particle diffusion model [25].

Ma *et al.* (2005) prepared granular Zr-loaded bentonite (GZLB) with polyvinyl alcohol (PVA) for removing fluoride from aqueous solution. The adsorption capacity of 0.755 mg/g was obtained at pH 6.97 with 6.34 mg/l of initial fluoride concentration. The regeneration by alum increased its adsorption capacity [26].

Ali (2006) used montmorillonite for removal of fluoride from drinking water in batch study. The adsorption equilibrium was reached within 180 min. The maximum fluoride adsorption capacity was 3.37 mg/g at pH 6.0. At

higher pH, above pH pzc (6.5), the fluoride removal gets decreased because of the negative charge of the montmorillonite surface. The adsorption was mainly occurred due to interaction between the metal oxides on the surface of montmorillonite and fluoride ions. The experimental data fitted well with Freundlich and Redlich-Peterson isotherm models [27].

Sarkar *et al.* (2006) used laterite for defluoridation from aqueous solution in batch and column mode. The mechanism of fluoride removal was governed by the zero point charge of laterite ( $\text{pHpzc} = 3.98$ ) and follows a first order rate equation. The Langmuir adsorption capacity of laterite for fluoride was 0.8461mg/g at 303K. Fluoride adsorption decreased from 0.2014 to 0.1586 mg/g as the solution pH increases from 2.1 to 6.7. Breakthrough time followed the order: pH 7.5 > pH 5.0 > pH 10.0. The column efficiency was tested from the bed depth-service time model. The optimum velocity for the column was  $5 \text{ cm}^3/\text{min}$ . The spent adsorbent was eluted at 80.4% with NaOH solution ( $1.0 \times 10^{-1} \text{ mol}/\text{dm}^3$ ). The fluoride removal of 68% was achieved after five cycles [28].

Hamdi and Srasra (2007) used three clay soils (MK, H and ZB) from three regions in Southeast Tunisia for removal of fluoride from acidic industrial wastewater and NaF solution. The optimum pH for maximum fluoride adsorption was 3.0. The experimental results fitted well with Langmuir isotherm than Freundlich isotherm model. The Langmuir adsorption capacity of MK, H and ZB soils were 73, 64.32 and 54.94 mg/g for NAF solution whereas adsorption capacity same materials were 93.45, 84.03 and 69.44 mg/g for wastewater solution. The adsorption capacity of MK soil was more due to the presence of palygorskite clay and calcite but the adsorption of ZB soil was low due to presence of illitokaolinitic fraction and small amount of dolomite [29].

Sarkar *et al.* (2007) studied the defluoridation capacity of laterite at column scale using fixed bed laterite columns. Adsorption capacity of fluoride in batch and column mode was calculated to be 0.1854 and 0.3586 mg/g respectively. The equilibrium data obtained through batch study was fitted to Langmuir and Freundlich isotherm models. The kinetic study revealed that the adsorption was feasible and spontaneous. The breakthrough capacity was found higher compared to the batch capacity. With increased fluoride concentration sharp breakthrough curve was obtained. The breakthrough curve became gentler as the bed height increases. Column capacity did not change up to flow rate of  $6.5 \text{ cm}^3/\text{min}$ . The retained fluoride could be eluted with NaOH solution ( $1.0 \times 10^{-1} \text{ mol}/\text{dm}^3$ ). The column capacity was 68% after five cycles [30].

Meenakshi *et al.* (2008) used raw kaolinite (RK) and micronized kaolinite (MK) clay by mechanochemical activation for defluoridation of water. The optimum pH for maximum removal of fluoride was observed to be 3.0 and defluoridation capacity of RK and MK was 0.120 mg/g and 0.134 mg/g respectively. The equilibrium was reached within 30 minutes for both materials. The presence of co-anions affected the defluoridation capacity in the order of  $\text{F}^- > \text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ . The experimental data of MK fitted well with Langmuir isotherm than Freundlich isotherm

model. The Langmuir adsorption capacity of MK at 303K, 313K and 323K temperature was 0.609, 0.714 and 0.782 mg/g respectively. The adsorption process by MK followed the pseudo-first-order besides intraparticle diffusion models. The adsorption reaction of MK was endothermic and spontaneous process [31].

Gogoi and Baruah (2008) investigated the defluoridation potential of acid activated kaolinite clay and raw kaolinite clay for defluoridation of water. The maximum adsorption of fluoride was obtained at pH of 4.0 with clay of 300 mesh size. The Langmuir maximum adsorption capacity of the acid activated clay for fluoride ranged between 0.0450 to 0.0557 mg/g at temperature range of 25 to 60°C [32].

Kamble *et al.* (2009) used metal oxide (Lanthanum, magnesium and manganese) incorporated bentonite clay for defluoridation of water. 10% La-bentonite showed higher fluoride uptake capacity among Mg-bentonite, Mn-bentonite and bare bentonite. The experimental data fitted well with Langmuir and Freundlich isotherm models. The maximum adsorption capacity of 10% La-bentonite was reported as 4.24 mg/g and maximum fluoride uptake was found to be 1.4 mg/g at an adsorbent dose of 1g/l. The fluoride uptake was more acidic pH than alkaline once and maximum removal was found at pH 5.0. The rate of adsorption was very fast and maximum fluoride uptake was attained within 30 min. The fluoride uptake mechanism was mainly due to ion-exchange of OH<sup>-</sup> ions. The presence of carbonate and bicarbonate ions in the water highly affected the defluoridation capacity [33].

Zhang *et al.* (2009) used modified attapulgite by magnesium and aluminium salts for defluoridation of water. The maximum uptake of fluoride achieved by modified attapulgite with a mass ratio, attapulgite: MgCl<sub>2</sub>.H<sub>2</sub>O:AlCl<sub>3</sub>.2H<sub>2</sub>O = 2:1:2 exhibited a higher fluoride uptake capacity of 41.5 mg/g at temperature of 313K. The experimental data fitted well with both Langmuir and Redlich-Peterson isotherm models. The adsorption of fluoride was increased with temperature showed that the adsorption reaction was endothermic in nature. The adsorption was mainly governed by ion-exchange mechanism [34].

Hamdi *et al.* (2009) used clay soils sample from three regions in Southeast Tunisia like Sebkat El Malah-El Mkhacherma (MK), Jebel Haidoudi (H) and Zemlet El Beidha (ZB) for defluoridation from acidic industrial waste and NaF solution. The optimum pH was 3.0. The equivalent adsorption capacity of MK, H and ZB were 60.18, 57.93 and 51.91 mg/g with fluoride removal of 85, 81.82 and 70.31% respectively. The experimental informations fitted well with Langmuir isotherm than Freundlich isotherm model. The maximum Langmuir adsorption capacity of MK, H and ZB were 71.94, 66.62 and 55.80 mg/g from NaF solution and 93.45, 84.03 and 69.44 mg/g from the acidic wastewater. The adsorption capacity of MH soil was superior since it consists of palygorskite clay and calcite [35].

Thakre *et al.* (2010) used magnesium incorporated bentonite (MB) for removal of fluoride from aqueous solution over a wide pH range of 3-10. The maximum defluoridation capacity of MB was 2.26 mg/g at 5 mg/l of initial fluoride

concentration. Bicarbonate ions highly affected the defluoridation capacity while other co-anions did not altogether influence the evacuation of fluoride. Desorption of 97% was achieved by using 1M NaOH solution but fluoride uptake was decreased from 95.47% to 73% after regeneration [36].

Ramdani *et al.* (2010) used two types of Algerian montmorillonite clay viz. higher percentage of calcium (AC) and without calcium (ANC) for defluoridation of water. The adsorption increased up to pH 4.0 and decreased at higher pH. The Langmuir monolayer capacity for AC and ANC was observed to be 1.013 and 1.324 mg/g respectively. The fluoride uptake mostly occurred due to interaction between the metal oxides on the surface of the montmorillonite and fluoride ions. The chemical activation of clay was found effective in adsorption reaching up to 88% whereas the thermal activation was ineffective as adsorption reached only around 5% [37].

Karthikeyan *et al.* (2010) studied the defluoridation capability of two naturally occurring earth materials (EM) from aqueous solution. The effective fluoride removal was observed with the dose of adsorbent of 6g/50ml and 8g/50ml for EM1 and EM2 respectively. The removal of fluoride was not affected in the pH range of 3 to 9 but gets reduced at higher pH of 11.0. The experimental data fitted well with Freundlich isotherm. The Langmuir adsorption capacity of EM1 and EM2 was observed to be 0.067 and 0.058 mg/g respectively. The adsorption reaction was endothermic in nature. Kinetic studies revealed that the adsorption followed reversible first order kinetics. The adsorption was mainly based on physisorption process as per Dubinin-Radushkevick (D-R) isotherm model [38].

Maiti *et al.* (2011) used acid treated raw laterite for defluoridation of water. The optimum pH for maximum fluoride removal was 5.0. The presence of bicarbonate and phosphate ions highly affected the fluoride removal capacity. The experimental data comfortable well with Langmuir and Freundlich isotherm models. The maximum Langmuir adsorption capacity of adsorbent was found to be 36.3, 37.9 and 39.10 mg/g at 288, 305 and 315K temperature. Desorption of 96% was achieved at pH 12.0 [39].

Ma *et al.* (2011) used granular acid-treated bentonite (GHB) in batch and column mode for defluoridation of water. The optimum pH was 4.95 and the equilibrium of adsorption was reached within 40 min. The kinetic data followed the pseudo-second-order equation. The experimental data fitted well with Freundlich isotherm than Langmuir isotherm model and adsorption capacity of adsorbent was 0.094 mg/g. In column study, the breakthrough capacity and exhaustion capacity increased with the decrease in flow rate and the escalation of initial fluoride concentration. The height of the mass transfer zone increased and the empty bed contact time (EBCT) reduced with the rise of flow rate. The height of the mass transfer zone increased with the rise of initial fluoride concentration. The experimental results were well fitted with Thomas model. Exhausted GHB was renewed by alkali/alum treatment. The total sorption capacity of GHB increased after regeneration and activation [40].

Gomoro *et al.* (2012) used thermally treated lateritic soils for defluoridation of water. The Aluminium oxide contents of Ambo Soil (AS), Yellow Gullale Soil (YGS) and Red Gullale Soil (RGS) were 3.1, 5 and 22.68% and iron oxide were 7.8, 6.23 and 13.09% respectively. The adsorption capacity of AS, YGS and RGS was 2.5, 2.3 and 8.1 mmol/kg respectively. The RGS has a higher adsorption capacity than AS and YGS. The RGS calcinated at 500°C improved the adsorption capacity of natural RGS and adsorption capacity was 16 mmol/kg and the removal was found to be 96% with a dose of 2g and 72 hours of shaking time with 9.09 mmol/L of initial fluoride concentration [41].

Zhang *et al.* (2012) investigated the defluoridation capability of zirconium-modified-Na-attapulgite (Zr-A) adsorbent. The results of adsorption fitted well with the Langmuir model. The maximum defluoridation capacity of Zr-A adsorbent was 24.55 mg/g. The fluoride adsorption kinetic was described well by the pseudo-second-order kinetic model. The Zr-A was used effectively even after six regeneration cycle. The regeneration of adsorbent was carried out successfully [42].

Tikariha *et al.* (2013) studied the defluoridation capacity of clays selected from different areas in Ethiopia. The adsorption was rapid during the first one hour. The adsorption capacity increases with the dose of adsorbent. The defluoridation was favourable in an acidic pH range of 3 to 6 and found maximum at pH 3.0. Clay calcined in the range of 400 to 600 °C gave better adsorption performance. The defluoridation was mainly governed by the presence of metal oxides of Fe and Al in the clays [43].

Kim *et al.* (2013) used pyrophyllite clay for defluoridation of water. This clay mainly consists of Si (74.03%) and Al (21.20%). The maximum adsorbent capacity of pyrophyllite clay was 0.737 mg/g with particle size less than 0.15mm. The equilibrium condition occurred in around 24 hours. The adsorption reaction was endothermic in nature. The fluoride was not sensitive to the pH range of 4 to 6. The effect of sulfate, carbonate and phosphate co-anions were important whereas effect of nitrate and chloride ions were negligible. The clay calcined at 400°C gave 21% higher fluoride removal capacity as compared to un-calcined ones [44].

Chidambaram *et al.* (2013) used locally available red soil with sand in the ratio of 4:1 for maximum removal of fluoride as well as to increase the porosity and permeability of the adsorbent medium packed in fixed column for removal of fluoride. The maximum removal was achieved when the flow rate was less. The sites with Fe-OH and Al-OH bonds present in the red soil were responsible for defluoridation. The pH of solution increased due to the competitiveness of the OH<sup>-</sup> and F<sup>-</sup> ions. The maximum fluoride removal was obtained at neutral pH. The regeneration of the medium was carried out successfully. No electricity was required due to the gravitational flow of water [45].

Mehari *et al.* (2014) used four local materials named burnt clay pot, household ash, keren and Adigerghish soil for defluoridation of water. The optimum pH for crushed clay pot, Keren and Adigerghish soil was 7.0 whereas household ash had an optimum pH of 4.0. The use of fine particle of

household ash, keren and Adigerghish soil showed better performance whereas there was no significant effect of particle size for burnt clay pot. The equilibrium time of adsorption was 120 minutes for all. The adsorption increased with an increase in fluoride concentration. The crushed burnt clay pot has a superior adsorption capacity of 0.26 mg/g while adsorption capacity of Keren soil, Adigerghish soil and household ash were 0.076, 0.083 and 0.097 mg/g for the same mass of 7 g for 5 mg/l of initial fluoride concentration [46].

Mehari *et al.* (2014) has used crushed burnt clay pot as a sorbent in mini column and developed household defluoridation unit for Keren community of Eritrea. The laboratory experiment with the adsorbent filled mini column was carried out with 5 mg/l fluoride solution for three different packed beds, 15, 20, and 25 cm depth and flow rate of 2.5, 5, 10 and 15 ml/min. The author observed that the breakthrough volume and time increased with increasing the bed depth of the column. But, the increase in flow rate reduced the treated volume at breakthrough and decreased the service time. The optimum condition for reducing fluoride from 5 to 1.48 mg/l was achieved at 25 cm bed depth and at 2.5 ml/min flow rate with breakthrough volume 7.3L. The mini column was scaled up to treat 324L of water satisfying the WHO Limit (<1.5mg/l) as well as the constructed household defluoridation unit [47].

Sepehr *et al.* (2014) used natural, H<sub>2</sub>O<sub>2</sub> and MgCl<sub>2</sub> modified Light Weight Expanded Clay Aggregate (LECA) (i.e. NL, HML and MGML) for defluoridation of water. The fluoride removal at pH of 6.0 was 79.4%, 83% and 81.2% for NL, HML and MGML respectively. The equilibrium time was reached within 120 minutes. The experimental data fitted well with Freundlich isotherm model. The Langmuir adsorption capacity was 8.525, 17.83 and 23.86 mg/g for NL, HML and MGML individually. The adsorption process followed the pseudo-second-order kinetic model. The adsorption reaction was spontaneous, exothermic and ends up with a decreasing randomly. The chloride and sulphate ions highly affected the fluoride adsorption capacity. The regeneration of about 82% was obtained with spent NL after 300 min contact time with de-ionized water whereas 98% of regeneration was achieved for spent HML and MGML after 180 min and 200 min. respectively. The regeneration efficiency was found to be about 11, 27 and 92% respectively after fifth cycle [48].

Osei *et al.* (2015) used laterite soil of 150-180 µm from road construction of Agamolga (SiO<sub>2</sub> – 69%), Balungu (Al<sub>2</sub>O<sub>3</sub>-66%) and Dua (Fe<sub>2</sub>O<sub>3</sub> – 45%) for defluoridation from aqueous solution. The aqueous solution of 10 mg/l was decreased to only about 2 mg/l with Dua laterite and about 4 mg/l with Agamolga and Balungu laterites. The performance was further enhanced when laterites were calcined at 400°C for 2h. The performance of Dua laterite was poor. The adsorption data fitted well with both Langmuir and Freundlich isotherm models. The Langmuir adsorption capacity of both untreated Balungu and Agamolga laterite samples was 0.55 mg/g. On the other hand, Freundlich plot gave adsorption capacity of 0.055 for the Balungu and 0.025

for Agamolga samples. The adsorption took place by the ion-exchange process. The adsorption capacities of soil samples were very low for field application [49].

Gitari *et al.* (2015) used Fe (III) modified bentonite clay for defluoridation of water. The optimum Fe (III) loading was done by 100 ppm of  $\text{Fe}^{3+}$  solution with powdered clay for 30 minutes. The modified bentonite could remove 100% of fluoride over the wide range of pH from 2-10 and overcome the drawback related to release of fluoride ions. The adsorption capacity of  $\text{Fe}^{3+}$  modified bentonite clay was observed to be 2.91 mg/g. The experimental data best fitted with Langmuir isotherm model indicating monolayer coverage of the adsorbent [50].

### III. GEOMATERIALS

The geomaterials like coal, gelatin, iron ores, hematites, meixnerite, siderite, quintinite were utilized for fluoride uptakes.

#### A. Coals

Sivasamy *et al.* (2001) have studied the defluoridation capacity of coal based adsorbent as a low cost adsorbent. The adsorption capacity of lignite, fine coke and bituminous coal were 7.09, 6.90 and 7.44 mg/g respectively. For lignite, the higher defluoridation occurred at pH range 6-12 whereas the higher defluoridation for fine coke and bituminous coal occurred at acidic pH below 4. The fluoride removal efficiencies of three coal based adsorbent were between 77.0 and 85.0%. The resulted data fitted well with Langmuir and Freundlich isotherms and followed first-order rate constant and film-pore diffusion coefficients. These coal based adsorbent higher defluoridation capacities as compared to commercial activated carbon [51].

Pekar (2006) used natural lignite from Lignite mined in the South Moravia region of the Czech Republic for defluoridation of aqueous solution. The adsorption capacity of lignite was 4.6 mmol/g. The fluoride removal of 96.6 and 100% was obtained with 2 g/10 ml dose of lignite from  $10^{-3}$  and  $10^{-4}$  mol/l of initial fluoride solution. The experimental data fitted well with Freundlich isotherm than Langmuir isotherm model [52].

Borah and Dey (2009) used low grade Assam coal for defluoridation of water in batch mode. The optimum conditions for the efficient removal of fluoride were achieved by an adsorbent dose of 1.25 g/100 ml water, contact time of 60 min. and particle size of -72BSS or lower. The fluoride removal of 85% was achieved by low grade coal [53].

#### B. Other Geomaterials

Zhou *et al.* (2004) used  $\text{La}^{3+}$  impregnated cross-linked gelatin for defluoridation of drinking water. The maximum adsorption capacity of 98.8% was achieved at pH of 5-7, contact time of 40 minutes and the dose of 0.2g/50ml of fluoride solution. The adsorption obeyed pseudo-first-order equation. The regeneration of exhausted adsorbent was carried out by first alkaline wash with 1.0 mol/l NaOH and after that water wash or acid wash with 1:1  $\text{HNO}_3$  solution to neutral. The regenerated adsorbent decreased defluoridation

capacity from 98.5% to 82.3% after three time regeneration [54].

Sujana *et al.* (2009) studied the defluoridation capacity of low and high iron containing lateritic ores (NL and NH) and overburden from chromite mines of Orissa Mining Corporation (OMC) besides Tata Steel from water. The maximum adsorption of fluoride by OMC, NH and NL at pH of 5.0, 5.16 and 3.6 were observed to be 52.6, 48 and 33.8% respectively. The experimental data fitted well with both Langmuir as well as Freundlich isotherm models. The kinetic study was well described by pseudo-first-order equation. The adsorption reaction was spontaneous and exothermic and it decreased randomly at the solid liquid interface [55].

Teutli-Sequeira *et al.* (2012) used unmodified and modified haematite for defluoridation of water. The unmodified haematite was not efficient to remove fluoride whereas modified haematite with aluminium hydroxide had good defluoridation capacity. The optimum pH range and equilibrium time was found to be 2.34-6.26 and 48 hours respectively. The kinetics of sorption was described by Elovich model. The experimental data fitted well with Langmuir-Freundlich isotherm model. The maximum adsorption capacity of modified haematite was observed to be 116.75 mg/g. The adsorption mechanism was chemisorption on a heterogeneous material [56].

Guo and Reardon (2012) used mechanochemically synthesized anion clay (meixnerite) and its calcined product. The maximum fluoride removal capacity by calcined meixnerite was 16.0 mg/g and about 30% higher than uncalcined meixnerite. The fluoride removal increased from 93.1% to 97.3% with contact time of 25 to 50 h. The kinetics of uncalcined meixnerite and calcined meixnerite followed Lagergren first-order model. The defluoridation capacity at equilibrium ( $q_e$ ) and sorption rate constant was 11.8 mg/g and  $0.075 \text{ h}^{-1}$  for uncalcined meixnerite and 16.1 mg/g and  $0.083 \text{ h}^{-1}$  for calcined meixnerite. The higher fluoride uptake by calcined meixnerite was due to greater availability of fluoride to its interlayer sites, since interlayers were generated during the reaction of the  $\text{F}^-$  containing solution with the calcined material but some  $\text{F}^-$  did not diffuse from the solution into the interlayers to replace existing  $\text{OH}^-$  ions as it did for the uncalcined meixnerite. The authors also emphasized that fluoride diffused from solution to intraparticle active sites and to that of chemical sorption on the active sites of in uncalcined meixnerite was much slower than in calcined meixnerite [57].

Shan and Guo (2013) used modified natural siderite with  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{AlOOH}$  and calcined at different temperature for defluoridation of water. The optimum modified natural siderite (OMNS) was obtained with mass ratio (grams) of 50:0.3:10 for natural siderite:  $\text{Al}_2(\text{SO}_4)_3$ :  $\text{AlOOH}$  and calcined at  $450^\circ\text{C}$  for 3hrs. The adsorption of fluoride was not affected by the pH of solution in the range of 3.5 to 10.0. The kinetic study was well described by the pseudo-second-order kinetic equation. The adsorption reaction was spontaneous and endothermic in nature. The bicarbonates and phosphate ions highly affected the defluoridation capacity. The

breakthrough time of column study was lower at higher fluoride concentration and / or higher flow rate. The fluoride adsorption by OMNS attributed to the co-existence of haematite and  $c\text{-Al}_2(\text{SO}_4)_3$  in the materials [58].

Kim *et al.* (2014) studied the potential of quintinite for defluoridation from aqueous solution. The maximum defluoridation capacity of quintinite was 7.71 mg/g. The adsorption did not change at pH 5-9 but decreased at the highly acidic (pH<3) and alkaline (pH>11) solutions. The equilibrium data fitted well with Freundlich and Redlich-Peterson models as well as it followed the pseudo-second-order kinetic model [59].

Patel *et al.* (2014) used natural haematite iron ore and synthetic magnetite for defluoridation of ground water of Chukru and Karlakot, India having 103.0 mg/l and 4.62 mg/l of fluoride concentration due to interaction of natural rock and water. The 66% of fluoride removal occurred by natural haematite at pH 3.2, adsorbent dose of 7 g/L and 3 mg/l of fluoride solution. The haematite increased the pH of solution and equilibrium did not reach even after a contact time of 45.2 hours. The fluoride removal of 84% was reached after 2 minutes of contact time for a solution with fluoride concentration of 6 mg/l, adsorbent dose of 10 g/l and initial pH of 7 [60].

Kebede *et al.* (2014) used locally available iron ore for defluoridation of water in the Rift Valley region and beyond the area near it. The fluoride removal of 86% from aqueous solution was obtained with 10 mg/l of fluoride solution with 5 g/l dose of adsorbent. The experimental data fitted well with Freundlich isotherm model. The maximum sorption capacity was found to be 1.72 mg/g. The optimum pH and equilibrium time was 6 and 120 minutes respectively. The kinetic study followed the pseudo-first-order kinetic model. The fluoride removal of 89% was achieved with initial fluoride concentration of 14.22 mg/l using 15g/l of iron ore [61].

#### IV. MINERALS

The minerals such as bauxites, pumice, hydroxyapatite, diatomite, lateritic minerals, ferric-polyminerals and silicious minerals were tried for defluoridation of water.

##### A. Bauxites

Mohapatra *et al.* (2004) used four oxides ores such as refractory grade bauxite (RGB), feed bauxite, manganese ore and hydrated oxides of manganese ores (WAD). The RGB showed promising results due to the presence of oxides of aluminium and iron. The adsorption was rapid initially for 5 minutes and reached to equilibrium within 120 minutes. The adsorption increased with an increase in pH up to 5.5 and decreased onward. The adsorption results fitted well with the Langmuir isotherm model and followed pseudo-first-order kinetic equation. The adsorption process was exothermic in nature. The isosteric heat of adsorption showed the adsorption process to be heterogeneous in nature [62].

Ayamsegna *et al.* (2008) used laterite and bauxite tailing for removal of fluoride from water. The defluoridation capacity of bauxite was higher than laterite. The fluoride removal of 92.7% was obtained at 3.5 g of bauxite sorbent at

700°C. The high removal of fluoride was attributed to  $\text{Al}_2\text{O}_3$  (74.8%) in bauxite [63].

Sajidu *et al.*, 2008 used bauxite for defluoridation of water in villages of Southern Malawi. Bauxite is mainly composed of oxides of alumina, iron, silica and titanium. The fluoride removal of 93.8% was achieved with the adsorbent dose of 2.5 g/200mL with 8 mg/l of initial fluoride concentration. The defluoridation of water was mainly done with the presence of gibbsite and kaolinite minerals in bauxite. The gibbsite was responsible for precipitation of  $\text{AlF}_3$  while kaolinite was responsible for exchange of  $\text{OH}^-$  ions with  $\text{F}^-$  ions and thus accomplished fluoride removal mechanism. The kinetic study was well described by the pseudo-first-order kinetic model [64].

Thole (2011) studied the reaction kinetics and breakthrough characteristics of calcined bauxite, gypsum, magnesite and their composite filter. The particle sizes of 1.2-1.4 mm diameter of adsorbents were calcined at 200°C for 2 hours. Breakthrough characteristics were explained by Bed depth service time (BDST), Empty bed residence time (EBRT) and two parameter logistics (2-PL) models. Bauxite, gypsum and magnesite has mean loading capacities of 5.6, 3.4 and 1.7 mg/g. Dose level increased the percentage removal but decreased loading capacity. Second order kinetics observed rate constant of  $4.07 \times 10^{-2}$ ,  $1.87 \times 10^{-2}$  and  $1.59 \times 10^{-2} \text{ gm}^{-1} \text{ min}^{-1}$  for bauxite, gypsum and magnesite respectively. The pH of water were increased by magnesite whereas decreased by composites, bauxite and gypsum. The 50% breakthrough time (t) obtained fitted well with two-parameter logistic model. Highest breakthrough time was obtained with greater doses. Highest loading has been obtained with lowest dose and maximum percentage sorption resulting from the largest dose. The water quality was found within standards for apparent colour, hardness, pH and residual concentration of  $\text{SO}_4^{2-}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Cl}^-$  [65].

Malay and Salim (2011) used activated alumina (AA), activated bauxite (AB) and activated rice husk (ARH) for defluoridation of water in batch study. The slope and equilibrium constant by Freundlich isotherm model for AA (0.152 and 0.601), AB (0.965 and 0.593) and ARH (0.659 and 0.155) revealed that activated alumina was considered as the best adsorbent and activated rice husk was inferior adsorbent. According to Langmuir isotherm the value of  $R_L$  was found in the order of AA (0.448) > AB (0.246) > ARH (0.152) and similarly the value of  $R^2$  was found in the order of AA (0.986) > AB (0.982) > ARH (0.814) [66].

Sujana and Anand (2011) used bauxite for defluoridation of synthetic and ground water samples of Orissa, India. The optimum pH range for the maximum fluoride removal was observed to be 5-7. The presence of sulphate, nitrate and phosphate ions strongly affected the defluoridation capacity whereas carbonate affected moderately. The adsorption process followed the Langmuir isotherm model and fluoride uptake capacity was 5.16 mg/g. The adsorption kinetic was described well by pseudo-first-order kinetic equation. The thermodynamic study revealed that the adsorption process was spontaneous and exothermic in nature [67].

Thole *et al.* (2012) optimized the breakthrough characteristics by using empty bed residence time (EBRT) and bed depth service time (BDST) models for raw bauxite, gypsum, magnesite and their composites. Higher doses obtained lower loading capacities but greater sorption percentages and breakthrough times. Second order kinetic rate constant were 0.73, 1.17, 1.81 and 1.63 gm g<sup>-1</sup>s<sup>-1</sup> for magnesite, gypsum, and bauxite, respectively. A critical depth of 6.56 cm was obtained in fixed bed continuous flow defluoridation with composite materials with BDST model with 12.62 mg/l of initial fluoride concentration, 3.7 ml s<sup>-1</sup> and particle diameter of 1.2-1.4 mm. EBRT model predicted that the deeper beds obtained longer service times due to increase in mass of sorption media with increase in bed depth [68].

Thole *et al.* (2012) studied the effect of particle size on loading capacity for defluoridation of water with 200°C calcined bauxite, gypsum, magnesite and their composite filter. Sorption capacity of these materials increased with decrease in particle size but it enhanced apparent colours, hardness, alkalinity and residual sulphate level. The particle size did not affect the residual concentration of chloride, aluminium and iron. The optimum particle size (diameter) was observed to be 2mm [69].

Sajidu *et al.* (2012) used raw bauxite for defluoridation of ground water and treated it in a model domestic defluoridation unit in batch mode. The optimum bauxite dosage and contact time were observed as 0.150 kg/L and 15.0 minute respectively. Sand and charcoal at a constant dose of 3:1 was used for water clarification and its optimum dose was 0.720 kg/L. The specific water yield by this defluoridation unit was found to be 36.0 L/kg adsorbent [70].

Atasoy *et al.* (2013) used modified bauxite with Na and Mg (B-Na, B-Mg) and calcination of Mg incorporated bauxite at 500°C (B-Mg-500) for defluoridation of water in batch mode. The equilibrium time between bauxite and water was observed to be 3 hours. The adsorption increased with an increase in adsorbent dose. The experimental data fitted well with Freundlich isotherm model. The maximum adsorption took place by B-Mg-500 with Kf value of 0.247. The fluoride removal of groundwater by BR, B-Na, B-Mg and B-Mg-500 was found to be 29, 32, 37 and 55% respectively [71].

Thole *et al.* (2013) developed water filter made of bauxite-gypsum-magnesite (B-G-M) calcined at 350 – 500°C. The highest defluoridation capacity of 11.89 mg/g was obtained with the 3:2:1 to 500°C composite at an adsorbent dose of 1 g/l with fluoride concentration of 12.62 mg/l. The experimental results fitted well with Langmuir isotherm model. The quality of treated water by B-G-M composite filter was failed by WHO standards on sulphates and iron but residual concentration of Cl<sup>-</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup> were within the prescribed limits [72].

Kayira *et al.* (2014) used raw bauxite for defluoridation of groundwater through batch equilibrium study. The fluoride removal of 96.1% was obtained by 8.0 g/L of sorbent and 275 mg/g of fluoride uptake capacity with the same dose and 6.17 mg/l of fluoride concentration. The fluoride removal was mainly attributed to gibbsite present in raw bauxite. The

intraparticle diffusion model discovered that fluoride sorption by the raw bauxite was placed through both surface complexation and penetrative diffusion. The adsorption process was spontaneous and followed pseudo-first order kinetics [73].

Craig *et al.* (2015) studied the fluoride removal capacity of Ghana bauxite, Nammo laterite and activated alumina in small scale defluoridation filter in northern Ghana. The adsorption capacity of activated alumina was higher as compared to bauxite and laterite and could work in wide pH range. The second most adopted adsorbent was bauxite since it was locally available and low in cost. The fluoride removal capacity of bauxite and laterite were 55 to 60 % at pH 4 and reduced to 20% at pH 7.0. The adsorption capacity of activated alumina, Ghana bauxite and Nammo laterite for 4.0 mg/l of ground water solution was 57.10×10<sup>-3</sup>, 1.20×10<sup>-3</sup> and 1.86×10<sup>-3</sup> mmol/g respectively at pH 7.8 and grain size of 0.5 to 1.0 mm [74].

### B. Pumice

Malakootian *et al.*, 2011 used pumice for removal of fluoride from aqueous solution. The fluoride removal efficiency was increased with an increase in adsorbent dose, contact time and pH whereas it gets decreased with an increase in initial fluoride concentration of solution. The maximum fluoride removal of 85.75% was obtained in neutral pH, 180 minutes of contact time, 20 mg/l dose of pumice and 2 mg/l of initial fluoride concentration. The experimental results matched with Freundlich isotherm and pseudo-second-order kinetics. The maximum adsorption capacity and constant rate were found 0.31 mg/g and 0.21 mg/g.min respectively [75].

Asgaria *et al.* (2012) used pumice stone activated by hexadecyltrimethyl ammonium surfactant for defluoridation of water. The fluoride removal of 96% was obtained at the optimum dose of 0.5g/l and pH of 6 after 30 min. by mixing them with the fluoride solution of 10 mg/l. The experimental data fitted well with the Langmuir isotherm model. The maximum sorption capacity of surface modified pumice (SMP) was 41 mg/g. The adsorption process followed the pseudo-second-order kinetic model. The adsorption reaction was spontaneous and endothermic in nature [76].

Mahvi *et al.* (2012) used pumice for defluoridation of water. The optimum pH was 3.0. The experimental data fitted well with Freundlich isotherm model and maximum adsorption capacity of pumice was 13.51 mg/g at 24°C. The adsorption kinetic was well described by the pseudo-second-order model. The co-anions affected the adsorption capacity in the order of PO<sub>4</sub><sup>3-</sup> > HCO<sub>3</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> [77].

Salifu *et al.* (2013) used aluminium oxide coated pumice (AOCP) for defluoridation of water. The AOCP reduced the 5 mg/l of fluoride to 1.5 mg/l with adsorbent dose of 10 mg/l and contact time of 1 hour. The equilibrium isotherm was found in the order of Generalized model > Langmuir type 2 > BET > Temkin > Dubinin-Radushkevich with a maximum capacity of 7.87 mg/g. AOCP was observed to be good for fluoride adsorption in the pH range of 6-9 [78].



Sepehr *et al.* (2013) modified surface of the pumice using aqueous solution of magnesium chloride besides hydrogen peroxide. The defluoridation of water was done by using plain pumice (NP), hydrogen peroxide modified pumice (HMP) and magnesium chloride modified pumice (MGMP). The fluoride removal efficiency of adsorbents at pH of 6.0 was found in order of HMP (70.8%) > MGMP (68.4%) > NP (65.4%). The experimental information fitted well with Freundlich isotherm model and the pseudo-second-order kinetic model. The maximum Langmuir adsorption capacity of HMP was 11.765 mg/g. The thermodynamic study revealed that the adsorption reaction was endothermic associated with increased randomness [79].

### C. Hydroxiapatite

Fan *et al.* (2003) used low cost materials like hydroxyapatite, fluorspar, calcite, quartz and activated quartz by ferric ions for defluoridation of low concentrated water sample. The adsorption capacity of low cost materials with fluoride concentration of  $2.5 \times 10^{-5}$  to  $6.34 \times 10^{-2}$  mg/l at pH of 6.0 founded in order of Hydroxyapatite (90%) > Fluorspar (25%) > Quartz activated using ferric ions (20%) > Calcite (12%) > Quartz (5.6%). The uptake of fluoride on hydroxyapatite was an ion-exchange procedure and follows the pseudo-first and second order equation while the uptake of fluoride on the other was a surface adsorption and follows the pseudo-second-order equation [80].

### D. Other Minerals

Wambu *et al.* (2011) studied fluoride removal from water by using acid treated diatomaceous earth (ATDE). The equilibrium was attained in 10 min. The fluoride removal was increased from 40% to 92% when the solution temperature was raised from 293 to 303K. The adsorption process was slightly affected by pH change and dropped the fluoride removal from 98.8 to 98% when the pH of solution rose from 1.59 to 6.89. The presence of chloride ions slightly affected the adsorption whereas sulphate, nitrate and phosphate ions did not affect the fluoride removal from water. Complete fluoride removal could be achieved at 400 mg/l initial fluoride concentration at 0.5 g/ml dose, 303-313 K temperature and pH =  $3.4 \pm 0.2$ . The Langmuir maximum adsorption capacity of ATDC was 51.1 mg/g. The adsorption process was impulsive and endothermic in nature [81].

Wambu *et al.* (2012) used acid treated lateritic mineral (LM-1) from Kenya for defluoridation of water in batch mode. The percentage of fluoride removal was increased with the presence of nitrate and chlorate ions whereas reduced in the presence of sulphates, chloride and phosphate ions. The optimum condition for maximum fluoride removal was observed at pH 1.59, a dose of 4g/20ml and 313K temperature. The experimental data fitted well with Freundlich isotherm than the Langmuir isotherm model. The Langmuir maximum adsorption capacity of the LM-1 adsorbent was 10.4792 mg/g at 303K. The ion-exchange mechanism of OH<sup>-</sup> with fluoride helped defluoridation [82].

Wambu *et al.* (2012) used ferric poly-mineral (FPM) from Kenya for defluoridation of water in batch mode. The adsorption reaction was fast and about 90% removal was

achieved within 30 min. with 1000mg/l of initial fluoride concentration at pH 3.32 and 293K and using 0.2 g/ml adsorbent dose. The fluoride uptake was decreased with higher concentration of co-anions and found in order of nitrate > phosphate > chloride > sulphate ions. The experimental data fitted well with the Langmuir isotherm model. The Langmuir maximum adsorption capacity of adsorbent was 12.7 mg/g at 323K. The fluoride adsorption onto FPM was a diversified process involving chemisorption surface site followed by gradual intra-particle penetration of F<sup>-</sup> into mesoporous structure of the mineral [83].

Vithanage *et al.* (2012) used laterite rich in iron (40%) and aluminium (30%) for defluoridation of water. The fluoride removal was maximum at pH < 5.0. Fluoride adsorption followed the Freundlich isotherm. The surface complexation modeling showed that both Fe and Al sites of the laterite surface contributes to fluoride adsorption via inner-sphere complexation. The laterite-fluoride interaction was strong chemisorption surface complexation [84].

Wambu *et al.* (2013) used siliceous mineral of a Kenyan origin (M1) for defluoridation of water in batch and column study. The initial batch equilibrium was attained within 20 min. The adsorption capacity was increased with an increase in temperature and decrease in pH of the solution. The fluoride removal close to 100% was obtained using initial fluoride concentration of 200 mg/l at 0.5 g/ml adsorbent dose, 303-333K temperature and pH  $3.4 \pm 0.2$ . The experimental results fitted well with Langmuir isotherm. The maximum Langmuir adsorption capacity was found to be 12.4 mg/g. The co-anions effect on fluoride removal was in order of chloride > nitrate > sulphate > dihydrogen ions. The column study with adsorbent (M1) was studied with different flow rate, bed depth and initial fluoride concentration. The Thomas model was best fitted for adsorption at low flow rate. Thomas adsorption capacity of adsorbent (M1) in column was 11.7 mg/g [85].

Izuagie *et al.* (2015) studied the defluoridation of groundwater by using diatomaceous earth (DE). The maximum adsorption capacity and removal of fluoride for 8 mg/l of spiked water were 0.6525 mg/g and 25.62% at optimum conditions (pH of 2.0., an adsorbent dosage of 8 g/l, contact time of 30 minutes, temperature of 298K and shaking speed of 200 rpm). The presence of phosphate ions greatly reduced the fluoride adsorption capacity at low pH. The adsorption process obeyed Freundlich isotherm and pseudo-second-order kinetic model. The leaching of metal and non-metal species from DE were negligible [86].

## V. LOW COST MATERIALS

Karthikeyan *et al.* (2002) studied the adsorption of fluoride by naturally occurring dolomite. The experimental information fitted well with the Langmuir isotherm model and adsorption followed pseudo-first-order kinetics. The adsorption process was impulsive and endothermic in nature [87].

Gopal *et al.* (2004) studied the defluoridation of drinking water by using chemically modified low cost adsorbents like activated alumina, activated carbon, groundnut husk, saw

dust, chemically treated sand, fly ash, zeolites, clay minerals and other plant products. The adsorption capacity of adsorbents was determined by using Langmuir and Freundlich isotherm models. The equilibrium isotherms were determined at optimum temperature and pH for characterization of adsorbents. The surface bonding was checked by FTIR, XRD and XRF tests [88].

Masamba *et al.* (2005) used Malawi's locally sourced gypsum and gypsum calcined at high temperatures for defluoridation of water. The highest fluoride removal of 67.80% was achieved by gypsum calcined at 400°C due to the presence of less crystalline CaSO<sub>4</sub>. The presence of SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and Ca<sup>2+</sup> further increased the defluoridation process [89].

Cyriac *et al.* (2011) used the carbonate rocks like limestone, dolostone and phosphatic limestone for defluoridation of water. The defluoridation by natural rocks did not required the pH control for adsorption of fluoride [90].

## VI. ZEOLITES

Zeolite has large surface area and having ability to exchange weakly bond cations with those in solution and hence attracted many research to adopt as adsorbent for water and wastewater treatment. Shrivastav and Deshmukh, 1994 used zeolite material of natural origin from Bhopal (MP) for removing fluoride from drinking water. The solution with initial fluoride concentration ranging between 5-15 mg/l was brought down to 0.2 mg/l by using natural zeolite. The spent zeolite was regenerated by using NaCl solution. The experimental data followed Langmuir and Freundlich isotherm models. The rate constant was found by Lagergren and Morris-Weber kinetics. The thermodynamic study revealed that the adsorption reaction was spontaneous and exothermic in nature [91].

Mayadevi (1996) has also studied the fluoride uptake capacities of various zeolites modified using various aluminum salts. These zeolites showed adsorption capacities comparable to that of other defluoridation materials [92].

Gonzalez *et al.* (2001) used synthetic zeolite for arsenate removal from the polluted water [93].

Diaz-Nava *et al.* (2002) studied the defluoridation of water by using sodium, calcium, lanthanum and europium treated natural zeolite from Mexico. The La and Eu treated natural zeolite showed higher fluoride adsorption than Na and Ca treated zeolite. The weight percentages of metals in the zeolite were 1.7, 3.20, 0.32 and 1.49 for Na, Ca, La and Eu respectively [94].

Bowman (2003) studied the application of surface modified zeolite (SMZ) for removal of contaminants from water. SMZ was also used as adsorbent for treatment of oilfield wastewater. The column study with SMZ removed 99-100% of bacteria and viruses present in sewage effluent and regeneration were done by air sparging. The combine action of SMZ with chemical, physical and biological means reduced the environmental pollution [95].

Majdan *et al.* (2003) used zeolite as an adsorbent for removal of heavy metals from contaminated water sources [96].

Shevade *et al.* (2004) also used zeolite for arsenic removal [97].

Onyango *et al.* (2004) have prepared trivalent-cation-exchange zeolite F9 by exchanging Na<sup>+</sup> bond zeolite with Al<sup>3+</sup> or La<sup>3+</sup> ions for defluoridation of water. The isotherm studies were performed by using Langmuir, Freundlich, Langmuir-Freundlich, Redlich-Peterson, Toth and Dubinin-Radushkevitch models. The fluoride uptake by Al<sup>3+</sup>-exchange zeolite was governed by ion-exchange mechanism (E=11.32–12.13 kJ/mol) whereas fluoride uptake by La<sup>3+</sup>-exchange zeolite was governed by physical adsorption (E=7.41–7.72 kJ/mol) as per D-R isotherm study. The defluoridation capacity of adsorbents got affected by the pH of solution and presence of bicarbonate ions in the water. Al<sup>3+</sup>-exchange zeolite has the superior defluoridation capacity than La<sup>3+</sup>-exchange zeolite [98].

Onyango *et al.* (2006) have prepared Al<sup>3+</sup> pre-treated low silica synthetic zeolite for defluoridation of drinking water. The equilibrium defluoridation capacity of prepared zeolite was found to be 37-40 mg/g. as per the equilibrium uptake and adsorption rate the order of adsorption was founded as Al-Na-HUD > Al-F9 > Al-HUD > Al-A4 [99].

Samatya *et al.* (2007) used metal ions (Al<sup>3+</sup>, La<sup>3+</sup> and ZrO<sup>2+</sup>) loaded natural zeolite for removal of fluoride from tap water. The natural zeolite (≤ 45mm) pretreated with HNO<sub>3</sub> solution (ZEO-1), NaNO<sub>3</sub> solution (ZEO-2) and deionized water (ZEO-3) beforehand loading the metal ions. ZEO-1 type zeolite having higher capacity than ZEO-2 and ZEO-3 as Na<sup>+</sup> ions on ZEO-1 could easily exchange with metal ions (Al<sup>3+</sup>, La<sup>3+</sup> and ZrO<sup>2+</sup>). The metal exchange capacities were 0.233, 0.089 and 0.090mmol/g for ZrO<sub>2</sub><sup>+</sup>, La<sup>3+</sup> and Al<sup>3+</sup> exchange zeolite (ZEO-1) respectively. Equilibrium data fitted well with Langmuir and Freundlich models. The Langmuir maximum equilibrium sorption was found to be 2.04-4.13 mg/g for various metals loaded zeolites. The metal loaded zeolite (ZEO-1) had 94% fluoride removal with 2.5 mg/l of initial fluoride concentration at an adsorbent dose of 6.0g/l [100].

Onyango *et al.* (2009) studied the breakthrough analysis of fluoride removal from drinking water by using surface-tailored zeolite in a fixed bed column. The modified zeolite prepared was Al-F9 and Al-HUD but Al-F9 zeolite was selected for detailed column study. The breakthrough capacity (BTC) mainly involved determination of adsorbent exhaust rate (AER) and bed volume (BV) at breakthrough point. The low value of AER and large BV indicate better performance and was obtained at reduced initial fluoride concentration, increased flow velocity besides adsorbent bed mass. The volume of water treated at breakthrough point was 11.87, 5.97 and 3.20 L for 5, 10 and 20 mg/l respectively. The alumina strongly bonds with zeolite resulted into no leaching of aluminium in treated water [101].

Rahmani *et al.* (2010) studied the defluoridation of water by Al<sup>3+</sup> and Fe<sup>3+</sup> pretreated natural Iranian zeolite. The

removal efficiency of 76%, 65% and 20% was observed by  $\text{Al}^{3+}$ -zeolite,  $\text{Fe}^{3+}$ -zeolite and unmodified zeolite respectively with 5 mg/l of fluoride concentration. The equilibrium condition of modified zeolite reached after 20 hours. The fluoride removal efficiency got decreased with an increase in initial fluoride concentration of water. The maximum fluoride removal occurred in acidic pH. The presence of bicarbonate ions in the water increases its pH and hence reduced the defluoridation capacity. The presence of sulphate and chloride in solution generally enhanced the fluoride uptake by  $\text{Al}^{3+}$ -zeolite whereas decreased in case of  $\text{Fe}^{3+}$ -zeolite. Aluminium modified zeolite showed the best higher defluoridation capacity [102].

Wang and Peng (2010) used natural zeolite for the water and wastewater treatment. Various ion-exchange zeolites were used for treatment of ammonium and heavy metal. Some zeolite has the ability to remove anions and organics from aqueous solution. Modification of natural zeolite was done by several methods like acid cure, ion exchange and surfactant functionalization which in-turn gave higher adsorption capacity for organics and anions [103].

Lu *et al.* (2010) used zeolite NaP1 synthesized from coal fly ash as well as modified zeolite NaP1 with NaOH and aluminium potassium sulphate for defluoridation of water. The defluoridation capacity of modified zeolite was more than synthetic zeolite. The equilibrium was reached after 20 minutes and adsorption was around 92.27%. The optimum pH and dose of adsorbent was 6 and 1 g/100 ml. The fluoride removal efficiency was upto 90% when initial fluoride concentration was less than 9 mg/l. The experimental information fitted well with Langmuir isotherm model [104].

Xingbin *et al.* (2010) prepared modified zeolite for defluoridation of water. The pretreatment of zeolite was done by 4% HCl and 1 mol/l NaOH solution and after that soaked in 10%  $\text{AlCl}_3$  solution and condition at 40°C for 20 hours. The adsorption capacity of modified zeolite was observed to be 0.25 mg/g for 20mg/l of fluoride solution. The defluoridation capacity of modified zeolite was affected by pH of solution, concentration of aqueous solution and running speed [105].

Sun *et al.* (2011) used  $\text{FeCl}_3$  modified natural stilbite (Fe(III)-STI) zeolite for defluoridation of water in batch study. The removal efficiency of 92% was achieved with 10 mg/l of initial fluoride concentration at equilibrium time of 2h, pH of 6.94 and dose of 10g/l. The experimental information fitted well with Langmuir isotherm model. The Langmuir maximum adsorption capacity was 2.31 mg/g. The adsorption process tailed the pseudo-first order equation. The regeneration of adsorbent was done with HCl [106].

Sohani *et al.* (2013) used zeolitic adsorbent (scolecite) from Ahmednagar, Pune in India for defluoridation of water. The zeolite adsorbent can be used as a column material and if required synthetic methods can be developed such as membranes (zeolite membranes) [107].

Teutli-Sequeira *et al.* (2014) compared the defluoridation capacity of electrochemically aluminium modified natural adsorbent like hematite, zeolite and calcite from water. The PZC (point of zero charge) were 6.2, 5.8 and 8.4 for

aluminium modified hematite, zeolitic tuff and calcite respectively. The equilibrium data fitted well with Langmuir-Freundlich isotherm and pseudo-second-order and Elovich kinetic models. The aluminium modified zeolite showed highest fluoride removal capacity of 10.25 mg/g and 1.16 mg/g for aqueous solution and drinking water respectively for 10 g/l dose of adsorbent with initial fluoride concentration of 9 and 8.29 mg/l for aqueous solution and drinking water respectively. The final fluoride concentration in treated water was found to be 0.08 and 0.7 mg/l for aqueous solution and drinking water respectively. The main mechanism responsible for fluoride adsorption was chemisorption on heterogeneous materials [108].

Hortiguela *et al.* (2014) used natural zeolite stilbite (CaNa-STI) modified by  $\text{NH}_4^+$  and subsequently  $\text{Ca}^{2+}$  ion-exchange treatment (Ca-NH<sub>4</sub>-STI) for enhancement of defluoridation capacity from water [109].

Adem *et al.* (2015) used zeolites from Ethiopia and Mexico for defluoridation of water. The fluoride uptake by zeolites from Analcime, San Luis Potosi and Zeocat ECO were 84%, 16.2% and 5.6% of initial fluoride concentration of 5 mg/l with an adsorbent dose of 100 g/l. The adsorption phenomenon was mainly governed by the exchange mechanism of Al-OH with  $\text{F}^-$  ions to form Al-F and 5 to 15% of adsorption reaction was took place due to  $\text{Ca}^{2+}$  exchange with  $\text{F}^-$  ions [110].

Cai *et al.* (2015) studied the defluoridation capacity of zeolite in the existence of cadmium, barium and manganese ions. The experimental data fitted well with Hill kinetic model. The presence of Mn and Cd in concentration of 100 mg/l each had increased the adsorption capacity by 2.2 and 1.7 respectively whereas Ba (100 mg/l) initially inhibited adsorption capacity and was not fitted with pseudo-second-order, Hill and intra-particle diffusion models. It was observed that barium (100mg/l and cadmium (10 mg/l) showed best fit with biphasic dose response model [111].

## VII. CONCLUSION

The developing countries such as India depends on ground water for the drinking purpose and in the same way most part of the universe are too depended on it [112-121]. This paper gives an overview of fluoride uptake capacities of clays, Geomaterials, minerals, low cost materials and zeolites from water to resolve the health hazard effects of fluoride on human beings, animals and vegetations. These locally available materials having a great potential to remove fluoride below the prescribed limit as suggested by the World Health Organization (< 1.5 mg/l) as compared to commercially available adsorbents. The fluoride removal efficiencies of adsorbents strongly depends on pH of aqueous media, agitation speed, time of contact, initial fluoride concentration, dose of adsorbent, particle size, surface area, temperature, presence of co-anions etc. The mathematical modelling of kinetics (First-order pseudo, second order pseudo, intra-particle diffusion etc.), isotherms (Langmuir, Freundlich, Temkin etc.) and thermodynamic in batch as well as modeling of fixed bed column studies of adsorption

process by various adsorbents were summarized to know the nature of adsorption reaction and their ability to produce safe water yield. The reuse and regeneration of adsorbents were explained, keeping in view the techno-economic viability of adsorbents for actual field performance to meet the target effectively without scaring the health. Future studies will focus on development of effective and economic defluoridation adsorbents with proper domestic or community units for developing countries to meet their demand for safe drinking water.

## REFERENCES

- [1] D. K. Malay, and A. J. Salim, "Comparative Study of Batch Adsorption of Fluoride Using Commercial and Natural Adsorbent," *Research Journal of Chemical Sciences*, vol. 1, no. 7, pp. 68-75, Oct. 2011.
- [2] M. Amini, K.C. Abbaspour, M. Berg, L. Winkel, S. J. Hug, E. Hoehn, H. Yang, and C.A. Johnson, "Statistical modeling of global geogenic fluoride contamination in groundwaters," *Environmental Science and Technology*, vol. 42, no. 10, pp.3662-3668, 2008.
- [3] A.K. Susheela, "A Treatise on Fluorosis," *Fluoride*, vol. 34, no. 3, pp. 181-183, 2001.
- [4] B. Das, J. Talukdar, S. Sarma, B. Gohain, R. K. Dutta, H. B. Das, and S. C. Das, "Fluoride and other inorganic constituents in groundwater of Guwahati, Assam, India," *Current Science*, vol. 85, no. 8, pp. 657-661, Sept. 2003.
- [5] R. K. Dutta, G. Saikia, B. Das, C. Bezbaruah, H. B. Das, and S. N. Dube, "Fluoride contamination in groundwater of central Assam, India," *Asian Journal of Water, Environment and Pollution*, vol. 3, no. 2, pp. 93-100, 2006.
- [6] D.Chakraborti, C. R. Chanda, G. Samanta, U. K. Chowdhury, S. C. Mukherjee, A. B. Pal, B. Sharma, K. J. Mahanta, H. A. Ahmed, and B. Sing, "Fluorosis in Assam, India," *Current Science*, vol. 78, no. 12, pp. 1421-1423, June 2000.
- [7] M. Sarkar, A. Banerjee, and P. P. Pramanick, "Kinetics and mechanism of fluoride removal using laterite," *Industrial and Engineering Chemical Research*, vol. 45, no. 17, pp. 5920-5927, 2006.
- [8] C. A. Bower, and J. T. Hatcher, "Adsorption of fluoride by soils and minerals," *Journal of Soil Science*, vol. 103, no. 3, pp. 151-154, 1967.
- [9] J. A. I. Omueti, and R. L. Jones, "Fluoride adsorption by Illinois soils," *Journal of Soil Science*, vol. 28, pp. 546-572, 1977.
- [10] A. K. Chaturvedi, K. C. Pathak, and V. N. Singh, "Fluoride removal from water by adsorption on China clay," *Applied Clay Science*, vol. 3, Issue 4, pp. 337-346, Sept. 1988.
- [11] S. Hauge, R. Osterberg, K. Bjorvatn, and K. A. Selvig, "Defluoridation of drinking water with pottery: effect of firing temperature," *Scandinavian Journal of Dental Research*, vol. 102, no. 6, pp. 329-333, Dec. 1994.
- [12] K. Bjorvatn, and A. Bardsen, "Use of activated clay for defluoridation of water," 1st International Workshop on Fluorosis Prevention and Defluoridation of Water, Ngurdoto, Tanzania, October 18-22, 1995, The International Society for Fluoride Research, pp. 49-55.
- [13] C. Zevenbergen, L. P. Van Reeuwijk, G. Frapporti, R. J. Louws, and R. D. Schuiling, "A simple method for defluoridation of drinking water at village level by adsorption on ando soil in Kenya," *Science of the Total Environment*, vol. 188, Issue 2-3, pp. 225-232, Oct. 1996.
- [14] G. Mugs, F. Zewge, M. Socher, "Preliminary investigations on the defluoridation of water using fired clay chips," *Journal of African Earth Science*, vol. 21, Issue 4, pp. 479-482, May 1996.
- [15] K. Bjorvatn, A. Bardsen, and R. TekleHaimanot, "Defluoridation of drinking water by use of clay/soil," 2nd Int. Workshop on Fluorosis Prevention and Defluoridation of Water, Nazreth, Ethiopia, November 19-25, 1997, The International Society for Fluoride Research, pp. 100-105.
- [16] M. Srimurali, A. Pragati, and J. Karthikeyan, "A study on removal of fluorides from drinking water by adsorption onto low cost materials," *Environmental Pollution*, vol. 99, Issue 2, pp. 285-289, 1998.
- [17] P. M. H. Kau, D. W. Smith, and P. Binning, "Fluoride retention by kaolin clay," *Journal of Contaminant Hydrology*, vol. 28, Issue 3, pp. 267-288, Oct. 1997.
- [18] Y. Wang, and E. J. Reardon, "Activation and regeneration of a soil sorbent for defluoridation of drinking water," *Applied Geochemistry*, vol. 16, Issue 5, pp. 531-539, April 2001.
- [19] W. Wang, R. Li, J. Tan, K. Luo, L. Yang, H. Li, Y. Li, "Adsorption and leaching of fluoride in soils of China". *Fluoride*, vol. 35, no.2, pp. 122-129, 2002.
- [20] M. Agarwal, K. Rai, R. Shrivastav, and S. Dass, "A study on fluoride sorption by montmorillonite and kaolinite," *Water Air & Soil Pollution*, vol. 141, Issue 1, pp. 247-261, Nov. 2002.
- [21] M. Agarwal, K. Rai, R. Shrivastav, and S. Dass, "Defluoridation of water using amended clay," *Journal of Cleaner Production*, vol. 11, no. 4, pp. 439-444, June 2003.
- [22] P. P. Coetzee, L. L. Coetzee, R. Puka, and S. Mubenga, "Characterisation of selected South African clays for defluoridation of natural waters," *Water SA*, vol. 29, no. 3, pp. 331-338, July 2003.
- [23] C. Chidambaram, A. L. Ramanathan, S. Vasudevan, "Fluoride removal studies in water using natural materials," *Water SA*, vol. 29, no. 3, pp. 339-343, July 2003.
- [24] L. R. Puka, "Fluoride adsorption modeling and the characterization of Clays for defluoridation of natural waters," MSc Thesis (RAU), 2004. <https://ujdigispace.uj.ac.za/handle/10210/413>.
- [25] G. Karthikeyan, A. Pius, and G. Alagumuthu, "Fluoride adsorption studies of montmorillonite clay," *Indian Journal of Chemical Technology*, vol.12, pp. 263-272, May 2005.
- [26] Y. X. Ma, F. M. Shi, X. L. Zheng, J. Ma, and J.M.Yuan, "Preparation of granular Zr-loaded bentonite and its defluoridation properties from aqueous solutions," *Journal of Harbin Institute of Technology (New Series)*, vol. 12, pp. 236-240, 2005.
- [27] A. Tor, "Removal of fluoride from an aqueous solution by using montmorillonite," *Desalination*, vol. 201, Issue 1-3, pp. 267-276, Nov. 2006.
- [28] M. Sarkar, A. Banerjee, P. P. Pramanick, A. R. Sarkar, "Use of laterite for the removal of fluoride from contaminated drinking water," *Journal of Colloidal and Interface Science*, vol. 302, Issue 2, pp. 432-441, Oct. 2006.
- [29] N. Hamdi, and E. Srasra, "Removal of fluoride from acidic wastewater by clay mineral: Effect of solid-liquid ratios," *Desalination*, vol. 206, Issue 1-3, pp. 238-244, Feb. 2007.
- [30] M. Sarkar, A. Banerjee, P. P. Pramanick, and A. R. Sarkar, "Design and operation of fixed bed laterite column for the removal of fluoride from water," *Chemical Engineering Journal*, vol.131, Issue 1-3, pp. 329-335, July 2007.
- [31] S. Meenakshi, C. Sairam Sundaram, and R. Sukumar, "Enhanced fluoride sorption by mechanochemically activated kaolinites," *Journal of Hazardous Materials*, vol.153, Issue 1-2, pp. 164-172, May 2008.
- [32] P. K. Gogoi, and R. Baruah, "Fluoride removal from water by adsorption on acid activated kaolinite clay," *Indian Journal of Chemical Technology*, vol. 15, pp. 500-503, Sept. 2008.
- [33] S. P. Kamble, P. Dixit, S. S. Rayalu, N. K. Labhsetwar, "Defluoridation of drinking water using chemically modified bentonite clay". *Desalination*, vol. 249, Issue 2, pp. 687-693, Dec. 2009.
- [34] J. Zhang, S. Xie, and Y. S. Ho, "Removal of fluoride ions from aqueous solution using modified attapulgite as adsorbent," *Journal of Hazardous Materials*, vol. 165, Issue 1-3, pp. 218-222, June 2009.
- [35] N. Hamdi, and E. Srasra, "Retention of fluoride from industrial acidic wastewater and NaF solution by three Tunisian clayey soils," *Research Report Fluoride*, vol. 42, no. 1, pp. 39-45, Jan.-Mar. 2009.
- [36] D. Thakre, S. Rayalu, R. Kawade, S. Meshram, J. Subrt, and N. Labhsetwar, "Magnesium incorporated bentonite clay for defluoridation of drinking water," *Journal of Hazardous Materials*, vol. 180, Issues 1-3, pp. 122-130, Aug. 2010.
- [37] A. Ramdani, S. Taleb, A. Benghalem, and N. Ghaffour, "Removal of excess fluoride ions from Saharan brackish water by adsorption on natural materials," *Desalination*, vol. 250, Issue 1, pp. 408-413, Jan. 2010.
- [38] M. Karthikeyan, V. Gopal, K. P. Elango, "Adsorption of fluoride ions onto naturally occurring earth materials," *Journal of Applied Science and Environmental Management*, vol. 14, no. 4, pp. 90 - 95, Dec. 2010.
- [39] A. Maiti, J. K. Basu, and S. De, "Chemical treated laterite as promising fluoride adsorbent for aqueous system and kinetic modeling". *Desalination*, vol. 265, Issues 1-3, pp. 28-36, Jan. 2011.
- [40] Y. Ma, F. Shi, X. Zheng, J. Ma, and C. Gao, "Removal of fluoride from aqueous solution using granular acid-treated bentonite (GHB): Batch and column studies". *Journal of Hazardous Materials*, vol. 185, Issues 2-3, pp. 1073-1080, Jan. 2011.
- [41] K. Gomoro, F. Zewge, B. Hundhammer, and N. Megersa, "Fluoride removal by adsorption on thermally treated lateritic soils," *Bulletin of the Chemical Society of Ethiopia*, vol. 26, no.3, pp. 361-372, 2012.
- [42] G. Zhang, Z. He, and W. Xu, "A low-cost and high efficient zirconium-modified-Na-attapulgite adsorbent for fluoride removal from aqueous solutions," *Chemical Engineering Journal*, vol. 183, pp. 315-324, Feb. 2012.
- [43] A. Tikariha, and O. Sahu, "Low cost adsorbent for defluoridation of water," *International Journal of Environmental Monitoring and Analysis*, vol. 1, no. 2, pp. 65-70, 2013.

- [44] J. H. Kim, C.G.Lee, J. A. Park, J. K. Kang, N. C. Choi, S. B. Kim, "Use of pyrophyllite clay for fluoride removal from aqueous solution". *Desalination and Water Treatment*, vol. 51, pp. 3408–3416, 2013.
- [45] S. Chidambaram, S. Manikandan, A. L. Ramanathan, M. V. Prasanna, C. Thivya, U. Karmegam, R. Thilagavathi, K. Rajkumar, "A study on the defluoridation in water by using natural soil," *Applied Water Science*, vol. 3, Issue 4, pp. 741–751, Dec. 2013.
- [46] B. B. Mehari, A. O. Mayabi, L. T. Hadgu, "Preliminary Assessment of Low Cost Local Sorbent Materials for Water Defluoridation in Keren, Eritrea," *International Journal of Sciences: Basic and Applied Research*, vol. 18, no 1, pp. 45-58, 2014.
- [47] B. B. Mehari, A. O. Mayabi, B. K. Kakoi, "Development of Household Defluoridation Unit Based on Crushed Burnt Clay Pot as Sorbent Medium:A Case of Keren Community, Eritrea," *Environment and Natural Resources Research*, vol. 4, no. 3, pp. 67-82, 2014.
- [48] M. N. Sepehr, "Defluoridation of water via Light Weight Expanded Clay Aggregate (LECA): Adsorbent characterization, competing ions, chemical regeneration, equilibrium and kinetic modeling," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 45, Issue 4, pp.1821–1834, July 2014.
- [49] J. Osei, S. K. Y. Gawu, A. I. Schafer, F. A. Atipoka, and F. W. Y. Momade, "Impact of laterite characteristics on fluoride removal from water," *Journal of Chemical Technology and Biotechnology*, p. 1-10, 2015.
- [50] W. M. Gitari, T. Ngulube, V. Masindi, J. R. Gumbo, "Defluoridation of groundwater using Fe<sup>3+</sup>-modified bentonite clay: optimization of adsorption conditions," *Desalination and Water Treatment*, vol. 53, pp. 1578–1590, 2015.
- [51] A. Sivasamy, K. P. Singh, D. Mohan, and M. Maruthamuthu, "Studies on defluoridation of water by coal-based sorbents," *Journal of Chemical Technology and Biotechnology*, vol. 76, Issue 7, pp. 717–722, 2001.
- [52] M. Pekar, "Affinity of the south Moravian lignite for fluoride anion," *Petroleum & Coal*, vol. 48, no.3, pp. 1-5, 2006.
- [53] L. Borah, N. C. Dey, "Removal of fluoride from low TDS water using low grade coal," *Indian Journal of Chemical Technology*, vol. 16, no. 4, pp.361–363, 2009.
- [54] Y. Zhou, C. Yu, and Y. Shan, "Adsorption of fluoride from aqueous solution on La<sup>3+</sup>-impregnated cross-linked gelatin," *Separation and Purification Technology*, vol. 36, Issue 2, pp. 89–94, Apr. 2004.
- [55] M. G. Sujana, H. K. Pradhan, and S. Anand, "Studies on fluoride sorption on some geomaterials," *Journal of Hazardous Materials*, vol. 161, Issue 1, pp.120–125, Jan. 2009.
- [56] A. Teutli-Sequeira; M. Solache-Rios; and P. Balderas-Hernandez, , "Modification Effects of Hematite with Aluminum Hydroxide on the Removal of Fluoride Ions from Water," *Water Air & Soil Pollution*, vol. 223, Issue 1, pp. 319–327, Jan. 2012.
- [57] Q. Guo, E. J. Reardon, "Fluoride removal from water by meixnerite and its calcination product," *Applied Clay Science*, vol. 56, pp. 7–15, Feb. 2012.
- [58] Y. Shan, and H. Guo, "Fluoride adsorption on modified natural siderite: Optimization and performance," *Chemical Engineering Journal*, vol. 223, pp.183–191, May 2013.
- [59] J. H. Kim, J. A. Park, J. K. Kang, J. W. Son, I. G. Yi, S. B. Kim, "Characterization of quintinite particles in fluoride removal from aqueous solutions," *Environmental Engineering Research*, vol. 19, no. 3, pp. 247-253, 2014.
- [60] S. C. Patel, R. Khalkho, S. K. Patel, J. M. Sheikh, D. Behera, S. Chaudhari, and N. Prabhakar, "Fluoride contamination of groundwater in parts of eastern India and a preliminary experimental study of fluoride adsorption by natural haematite iron ore and synthetic magnetite," *Environ Earth Science*, vol. 72, Issue 6, pp. 2033–2049, Sept. 2014.
- [61] B. Kebede, A. Beyene, F. Fufa, M. Megersa, and M. Behm, "Experimental evaluation of sorptive removal of fluoride from drinking water using iron ore," *Applied Water Science*, pp. 1-9, 2004.
- [62] D. Mohapatra, D. Mishra, S. P. Mishra, G. Roy Chaudhury; R. P. Das, "Use of oxide minerals to abate fluoride from water". *Journal of Colloid and Interface Science*, vol. 275, Issue 2, pp. 355–359, July 2004.
- [63] J. A. Ayamsegna, W. B. Apambire, N. Bakobie, S. A. Minyila, and Ghana, "Removal of fluoride from rural drinking water sources using geomaterials from Ghana". 33rd WEDC International Conference, Accra, Ghana, 2008, pp. 441-446.
- [64] S. M. I. Sajidu, W. R. L. Masamba, B. Thole, J. F. Mwatseteza, "Groundwater fluoride levels in villages of Southern Malawi and removal studies using bauxite," *International Journal of Physical Science*, vol. 3, pp. 1–11, Jan. 2008.
- [65] B. Thole, "Defluoridation kinetics of 200°C calcined bauxite, gypsum, and magnesite and breakthrough characteristics of their composite filter." *Journal of Fluorine Chemistry*, vol. 132, Issue 8, pp. 529–535, Aug. 2011.
- [66] D. K. Malay, and A. J. Salim, "Comparative Study of Batch Adsorption of Fluoride Using Commercial and Natural Adsorbent," *Research Journal of Chemical Sciences*, vol. 1, no. 7, pp. 68-75, 2011.
- [67] M. G. Sujana, S. Anand, "Fluoride removal studies from contaminated ground water by using bauxite," *Desalination*, vol. 267, Issues 2-3, pp. 222–227, Feb. 2011.
- [68] B. Thole, F. Mtalo, and W. Masamba, "Groundwater Defluoridation with Raw Bauxite, Gypsum, Magnesite, and Their Composites," *Clean – Soil, Air, Water*, vol. 40, no. 11, pp. 1222–1228, Nov. 2012.
- [69] B. Thole, F. Mtalo, W. Masamba, "Effect of particle size on loading capacity and water quality in water defluoridation with 200°C calcined bauxite, gypsum, magnesite and their composite filter," *African Journal of Pure and Applied Chemistry*, vol. 6, no. 2, pp. 26-34, Jan. 2012.
- [70] S. Sajidu, C. Kayira, W. Masamba, J. Mwatseteza, "Defluoridation of Groundwater Using Raw Bauxite: Rural Domestic Defluoridation Technology," *Environment and Natural Resources Research*, vol. 2, no. 3, pp. 1-6, 2012.
- [71] A. D. Atasoy, and M. O. Sahin, "Adsorption of Fluoride on the Raw and Modified Cement Clay," *Clean–Soil, Air, Water*, vol. 42, no. 4, pp. 415–420, April 2014.
- [72] B. Thole, W. R. L. Masamba, and F. W. Mtalo, "Water defluoridation by bauxite-gypsum-magnesite (B-G-Mc) based filters calcined at 350 – 500°C," *International Journal of Physical Science*, vol. 8, no. 19, pp. 956-962, May 2013.
- [73] C. Kayira, S. Sajidu, W. Masamba, and J. Mwatseteza, "Defluoridation of Groundwater Using Raw Bauxite: Kinetics and Thermodynamics". *Clean – Soil, Air, Water*, vol. 42, no. 5, pp. 546-551, May 2014.
- [74] L. Craig, L. L. Stillings, D. L. Decker, and J. M. Thomas, "Comparing activated alumina with indigenous laterite and bauxite as potential sorbents for removing fluoride from drinking water in Ghana," *Applied Geochemistry*, vol. 56, pp. 50-66, May 2015.
- [75] M. Malakootian, M. Moosazadeh, N. Yousefi, and A. Fatehizadeh, "Fluoride removal from aqueous solution by pumice: Case study on Kuhbonan water," *African Journal of Environmental Science and Technology*, vol. 5, no. 4, pp. 299–306, April 2011.
- [76] G. Asgaria, B. Roshanib, and G. Ghanizadeh, "The investigation of kinetic and isotherm of fluoride adsorption onto functionalize pumice stone," *Journal of Hazardous Materials*, vol. 217–218, pp.123–132, May 2012.
- [77] A. H. Mahvi, B. Heibati, A. Mesdaghinia, A. R. Yari, "Fluoride Adsorption by Pumice from Aqueous Solutions," *E-Journal of Chemistry*, vol. 9, Issue 4, pp. 1843-1853, 2012.
- [78] A. Salifu, B. Petrusevski, K. Ghebremichael, L. Modestus, R. Buamah, C. Aubry, and G. L. Amy, "Aluminum (hydr)oxide coated pumice for fluoride removal from drinking water: Synthesis, equilibrium, kinetics and mechanism," *Chemical Engineering Journal*, vol. 228, pp. 63–74, 2013.
- [79] M. N. Sepehr, V. Sivasankar, M. Zarrabi, and M. Senthil Kumar, "Surface modification of pumice enhancing its fluoride adsorption capacity: An insight into kinetic and thermodynamic studies," *Chemical Engineering Journal*, vol. 228, pp. 192–204, July 2013.
- [80] X. Fan, D. J. Parker, and M. D. Smith, "Adsorption kinetics of fluoride on low cost materials," *Water Research*, vol. 37, Issue 20, pp. 4929–4937, Dec. 2003.
- [81] E. W. Wambu, C. O. Onindo, W. J. Ambusso, and G. K. Muthakia, , "Fluoride Adsorption onto Acid-Treated Diatomaceous Mineral from Kenya," *Materials Sciences and Applications*, vol. 2, pp. 1654-1660, 2011.
- [82] E. W. Wambu, C. O. Onindo, W. J. Ambusso, G. K. Muthakia, "Fluoride adsorption onto an acid treated lateritic mineral from Kenya: Equilibrium studies," *African Journal of Environmental Science and Technology*, vol. 6, no.3, pp. 160-169, March 2012.
- [83] E. W. Wambu, C. O. Onindo, W. Ambusso, G. K. Muthakia, "Equilibrium Studies of Fluoride Adsorption onto a Ferric Poly–mineral from Kenya," *Journal of Applied Science and Environmental Management*, vol. 16, no.1, pp. 69-74, March 2012.
- [84] M. Vithanage, L. Jayarathna, A. U. Rajapaksha, C. B. Dissanayake, M. S. Bootharaju, T. Pradeep, "Modeling sorption of fluoride on to iron rich laterite," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 398, pp. 69– 75, March 2012.
- [85] E. W. Wambu, C. O. Onindo, W. Ambusso, G. K. Muthakia, "Removal of Fluoride from Aqueous Solutions by Adsorption Using a Siliceous Mineral of a Kenyan Origin," *Clean – Soil, Air, Water*, vol. 41, Issue 4, pp. 340–348, April 2013.
- [86] A. A. Izuagie, W. M. Gitari, and J. R. Gumbo, "Defluoridation of groundwater using diatomaceous earth: optimization of adsorption conditions, kinetics and leached metals risk assessment," *Desalination and Water Treatment*, pp. 1-13, 2015.



- [87] G. Karthikeyan, A. Pius, and G. Alagumuthu, "Kinetic thermodynamic studies on adsorption of fluoride by dolomite," *Indian Journal of Chemical Technology*, vol. 9, no. 5, pp. 397-401, Sept. 2002.
- [88] K. Gopal, S. B. Srivastava, S. Shukla, and J. L. Bersillon, "Contaminants in drinking water and its mitigation using suitable adsorbents: An overview," *Journal of Environmental Biology*, vol. 25, Issue 4, pp. 469-475, 2004.
- [89] W. R. L. Masamba, S. M. Sajidu, B. Thole, J. F. Mwatseteza, "Water defluoridation using Malawi's locally sourced gypsum," *Physics and Chemistry of the Earth*, vol. 30, Issues 11-16, pp. 846-849, 2005.
- [90] B. Cyriac, B. K. Balaji, K. Satyanarayana, and A. K. Rai, "Studies on the use of powdered rocks and minerals for defluoridation of natural water," *Journal of Applied Geochemistry*, vol. 13, no. 1, pp. 62-69, 2011.
- [91] P. K. Shrivastava, and A. Deshmukh, "Defluoridation of water with natural zeolite," *Journal of Institution of Public Health Engineers (India)*, vol. 4, pp. 11-14, 1994.
- [92] S. Mayadevi, "Adsorbents for the removal of fluoride from water," *Indian Chemical Engineer Section A*, vol. 38, pp. 155-157, 1996.
- [93] M. P. Elizalde-Gonzalez, J. Mattusch, W. D. Einicke, and R. Wennrich, "Sorption on natural solids for arsenic removal," *Chemical Engineering Journal*, vol. 81, Issues 1-3, pp. 187-195, Jan. 2001.
- [94] C. Diaz-Nava, M. T. Olguin, and M. Solache-Rios, "Water defluoridation by Mexican heulandite-clinoptilolite," *Separation Science and Technology*, vol. 37, no. 13, p. 3109-3128, 2002.
- [95] R. S. Bowman, "Applications of surfactant-modified zeolites to environmental remediation," *Microporous Mesoporous Materials*, Vol. 61, Issues 1-3, pp. 43-56, July 2003.
- [96] M. Majdan, S. Pikus, and M. Kowalska-Ternes, "Equilibrium study of selected divalent d-electron metals adsorption on A-type zeolite," *Journal of Colloid and Interface Science*, vol. 262, Issue 2, pp. 321-330, June 2003.
- [97] S. Shevade, and R. G. Ford, "Use of synthetic zeolites for arsenate removal from pollutant water," *Water Research*, vol. 38, Issues 14-15, pp. 3197-3204, Aug. - Sept. 2004.
- [98] M. S. Onyango, Y. Kojima, O. Aoyi, E. C. Bernardo, and H. Matsuda, "Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9," *Journal of Colloid and Interface Science*, vol. 279, Issue 2, pp. 341-350, Nov. 2004.
- [99] M. S. Onyango, Y. Kojima, A. Kumar, D. Kuchar, M. Kubota, and H. Matsuda, "Uptake of fluoride by Al<sup>3+</sup> - pretreated low-silica synthetic zeolites: adsorption equilibrium and rate studies," *Separation Science and Technology*, vol. 41, Issue 4, pp. 683-704, 2006.
- [100] S. Samatya, U. Yuksel, M. Yuksel, and N. Kabay, "Removal of fluoride from water by metal ions (Al<sup>3+</sup>, La<sup>3+</sup> and ZrO<sup>2+</sup>) loaded natural zeolite," *Separation Science and Technology*, vol. 42, Issue 9, pp. 2033-2047, 2007.
- [101] M. S. Onyango, T. Y. Leswif, A. Ochieng, D. Kuchar, F.O. Otieno, and H. Matsuda, "Breakthrough analysis for water defluoridation using surface-tailored zeolite in a fixed bed column," *Industrial & Engineering Chemical Research*, Vol. 48, Issue 2, pp. 931-937, 2009.
- [102] A. Rahmani, J. Nouri, S. Kamal Ghadiri, A. H. Mahvi, and M. R. Zarem, "Adsorption of fluoride from water by Al<sup>3+</sup> and Fe<sup>3+</sup> pretreated natural Iranian zeolites," *International Journal of Environmental Research*, vol. 4, Issue 4, pp. 607-614, 2010.
- [103] S. Wang, and P. Peng, "Natural zeolites as effective adsorbents in water and wastewater treatment," *Chemical Engineer Journal*, vol. 156, Issue 1, pp. 11-24, Jan. 2010.
- [104] H. Lu, B. Wang, and Q. Ban, "Defluoridation of Drinking Water by Zeolite NaP1 Synthesized From Coal Fly Ash," *Energy Sources- Part A*, vol. 32, Issue 6, pp. 1509-1516, 2010.
- [105] S. Xingbin, X. Chengju, and H. Zhaochao, "The fluoride-adsorption capacity and influencing factors study of Zeolite," 2010 International Conference on Challenges in Environmental Science and Computer Engineering (CESCE) (Volume:1), 6-7 March 2010, pp. 358 - 361.
- [106] Y. Sun, Q. Fang, J. Dong, X. Cheng, and J. Xu, "Removal of fluoride from drinking water by natural stilbite zeolite modified with Fe(III)," *Desalination*, vol. 277, Issue 1-3, pp. 121-127, Aug. 2011.
- [107] N. Sohani, and R. Trivedi, "Utilization of Zeolite Adsorbent for Defluoridation of Drinking Water," *International Journal of Engineering Sciences & Research Technology*, vol. 2, no. 12, pp. 3391-3395, Dec. 2013.
- [108] A. Teutli-Sequeira, M. Solache-Rios, V. Martinez-Miranda, I. Linares-Hernandez, "Comparison of aluminum modified natural materials in the removal of fluoride ions," *Journal of Colloid and Interface Science*, vol. 418, pp. 254-260, March 2014.
- [109] L. Gomez-Hortiguera, A. B. Pinar, J. Perez-Pariente, T. Sani, Y. Chebude, I. Diaz, "Ion-exchange in natural zeolite stilbite and significance in defluoridation ability," *Microporous and Mesoporous Materials*, vol. 193, pp. 93-102, July 2014.
- [110] M. Adem, T. Sani, Y. Chebude, G. Fetter, P. Bosch, I. Diaz, "Comparison of the defluoridation capacity of zeolites from Ethiopia and Mexico," *Bulletin of the Chemical Society of Ethiopia*, vol. 29, no. 1, p. 53-62, 2015.
- [111] Q. Cai, B. D. Turner, D. Sheng, S. Sloan, "The kinetics of fluoride sorption by zeolite: Effects of cadmium, barium and manganese," *Journal of Contaminant Hydrology*, Vol. 177-178, pp. 136-147, June - July 2015.
- [112] S. S. Waghmare, T. Arfin, N. Manwar, D. H. Lataye, N. Labhsetwar and S. Rayalu, "Preparation and Characterization of Polyalthia longifolia Based Alumina as a Novel Adsorbent for Removing Fluoride from Drinking Water," *Asian Journal of Advanced Basic Sciences*, vol. 4(1), pp. 12-24, Sept. 2015.
- [113] D. Thakre, P. Dixit, S. Waghmare, N. Manwar, N. Labhsetwar and S. S. Rayalu, "Synthesis Optimization and Fluoride Uptake Properties of High Capacity Composite Adsorbent for Defluoridation of Drinking Water," *Environmental Progress & Sustainable Energy*, pp. 1-10, June 2015.
- [114] S. S. Waghmare and T. Arfin, "Fluoride Removal from Water By Calcium Materials: A State-Of-The-Art Review," *International Journal of Innovative Research in Science, Engineering and Technology*, vol. 4(9), pp. 8090-8102, Sept. 2015.
- [115] S. S. Waghmare and T. Arfin, "Fluoride Removal From Water By Mixed Metal Oxide Adsorbent Materials: A State-Of-The-Art Review," *International Journal of Engineering Sciences & Research Technology*, Vol. 4(9), pp. 519-536, Sept. 2015.
- [116] S. S. Waghmare and T. Arfin, "Fluoride induced water pollution issue and its health efficacy in India- A review," *International Journal of Engineering Research & General Science*, Vol. 3(5), pp. 345-358, Sept. - Oct. 2015.
- [117] S. S. Waghmare and T. Arfin, "Fluoride Removal from Water by various techniques: Review," *International Journal of Innovative Science, Engineering & Technology*, vol. 2(9), pp. 560-571, Sept. 2015.
- [118] S. S. Waghmare and T. Arfin, "Fluoride removal from water by carbonaceous materials: Review," *International Journal of Modern Trends in Engineering and Research*, Vol. 2(9), pp. 355-361, Sept. 2015.
- [119] S. S. Waghmare, T. Arfin, "Fluoride Removal from Water by Aluminium Based Adsorption: A Review," *Journal of Biological and Chemical Chronicles*, Vol. 1(1), pp. 1-11, 2015.
- [120] S. S. Waghmare, T. Arfin, "Fluoride Removal from Industrial, Agricultural and Biomass Wastes as Adsorbents: Review," *International Journal of Advance Research And Innovative Ideas in Education*, Vol. 1 (4), pp. 628 - 653, Oct. 2015.
- [121] S. S. Waghmare, T. Arfin, "Defluoridation By Adsorption With Chitin - Chitosan-Alginate - Polymers - Cellulose - Resins - Algae And Fungi - A Review," *International Research Journal of Engineering and Technology*, Vol. 2 (6), pp. 1179 - 1197, Sept. 2015.



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