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Fluoride removal from water using alumina and aluminum-based composites: A comprehensive review of progress

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ABSTRACT

Fluoride concentration in drinking water has become a global challenge due to its effects on the human body. While small level ($1–1.5\,mg\cdot L^{-1}$) strengthens enamel and bone formation, higher concentration ($>1.5\,mg\cdot L^{-1}$) leads to dental and skeletal fluorosis. Globally, over 200 million people drink fluorinated water and more than 70 million people suffer from fluoride related diseases. As such, treating fluorinated water through the adsorption method has been the most ideal method due to its low cost, availability of adsorbents, pollution-free treated water and environmental friendliness. This review article summarizes the use of alumina and aluminum-based composites for fluoride removal. These adsorbents have been classified into three categorize based on their modifications thus: raw alumina-based adsorbents/geomaterials, activated alumina and modified activated alumina and aluminum-based adsorbents. Minimal activation ($300–400\,^{\circ}C$) and modification improve their overall adsorption capacity by increasing their specific surface area ($250–1000\,m^2\cdot g^{-1}$) which ultimately improves the pore size and volume. Also, some can remediate as high as $450\,mg\cdot g^{-1}$ of fluoride at a wider pH range ($3–12$) with stable thermodynamic properties. This grants them the ability to easily form aluminumfluoro complexes (AlF_x) for enhanced adsorption at near-neutral pH ($5.5–6.5$) making them the most ideal adsorbents.

1. Introduction

With an increasing human population coupled with urbanization and industrialization, the quest for safe drinking water continues to surge.

However, most water sources are contaminated with several pollutants (Agarwal et al., 2003). This has led to a decline in water availability such that by 2022, the average water available per person is predicted to decline by one-third (Institute of Peace and Conflict Studies (IPCS), 2002). Among all water pollutants, the emission of fluoride into drinking water has raised many public health concerns because of its carcinogenic and accumulative behavior (Mjengera & Mkongo, 2002; Oren et al., 2004; Vinati et al., 2015; Wang & Reardon, 2001). According to the World Health Organization (WHO) (2004, 2006) reports and the Australian National Health and Medical Report Council (NHMRC) report in 2004, the maximum contaminant level (MCL) of fluoride in drinking water should not exceed $1.5\,mg\cdot L^{-1}$. However, evidence indicates that high fluoride concentration in groundwater exceeding $30\,mg\cdot L^{-1}$ occurs widely across the globe in over 30 countries notably in Asia, the United States of America and Africa (Azbar & Turkman, 2000; Moturi et al., 2002). While higher concentrations are often associated with groundwater, the emission of fluoride in freshwater differs across regions due to differences in underlying rock mineral and climatic conditions. However, some substantial differences in fluoride concentration in freshwater between developed and developing countries exist. For instance, fluoride concentration in freshwater in some villages in China and India exceeds $8.26\,mg\cdot L^{-1}$ (Su et al., 2015). As high as $8\,mg\cdot L^{-1}$ has been reported in eastern and northern Africa (WHO, 2004). More so, $3.3\,mg\cdot L^{-1}$ has been reported in drinking water prepared from well in Canada. Fluoride levels exceeding $2.0\,mg\cdot L^{-1}$ in freshwater has been reported in some parts of the United States of America while in Australia, it ranges from $3-9\,mg\cdot L^{-1}$ (Fitzgerald, 2000; WHO, 2006).

Due to this wide occurrence of fluoride, different countries have different maximum contaminant levels. For instance, in India, the maximum contaminant level is $1.0\,mg\cdot L^{-1}$ which is the same as in Bangladesh and China. The United States of America however, sets its standards from $0.6\,mg\cdot L^{-1}$ to $0.9\,mg\cdot L^{-1}$ (WHO, 2006). While ingestion of fluoride within the recommended limit promotes teeth and bone formation, taking in excess fluoride is detrimental to human health. Drinking fluorinated water over a long period causes a slow crippling scourge on the skin called crippling fluorosis. In a more severe case, excess fluoride can also inhibit and disrupt normal physiological functions of the human body (Edmunds & Smedley, 2005; Goswami et al., 2015). Globally, about 200 million people drink fluorinated water out of which about 70 million people are living with mild to severe health complications (Cherukumilli et al., 2017). Global estimate further suggests that about 2.4 billion people are suffering from caries of permanent teeth while 486 million children are suffering from caries of the primary teeth as a result of drinking water with excess fluoride ions (WHO, 2006).

Consequently, several water-treatment technologies have been developed over the past few decades. Some studies (Bhatnagar et al., 2011; Sehn, 2008; Singh et al., 2013) have classified the various technologies for fluoride removal from water into five major categories namely: adsorption, ion-exchange, electrodialysis, reverse osmosis, nano-filtration and coagulation/precipitation. Among all these techniques, the adsorption method of fluoride removal has proven to be relatively better due to its low installation and maintenance cost, ability to retain fluoride ions even at low concentrations and easily accessible wide-range of adsorbents (Koteswara Rao & Metre, 2014; Mohapatra et al., 2009; Renge et al., 2012). Furthermore, among other advantages already mentioned, the adsorption method has a good fluoride removal capacity, the design and operation of the plant are simple and easy, the adsorbents have good potential for re-use with unique environmental friendliness and finally, the treated water has no signs of taste, color and odor (Kalavathy & Giridhar, 2017; Kari et al., 2011; Rao and Metre, 2014).

In line with this, several studies (Goswami et al., 2015; Jamode et al., 2004; Kalavathy & Giridhar 2017; Koteswara Rao & Metre, 2014) have been conducted on the development of low cost and effective adsorbents. For instance, the nature of fluoride adsorption on some novel adsorbents such as clay which contains oxides of aluminum, iron, and silicon, has been investigated by most researchers (Liu et al., 2009; Puka, 2004; Sujana & Anand, 2011; Vinati et al., 2015). Some studies (Fan et al., 2003; Mohaptara et al., 2009) have described the possible fluoride adsorption mechanism of amorphous alumina supported carbon nanotube (CNT) (Li et al., 2001), amorphous acidic alumina (Goswami & Purkait, 2012), calcite (Yang et al., 1999), magnesia-amended activated alumina (MAAA) (Maliyekkal et al., 2008), alumina cement granules (ALC) (Ayoob & Gupta, 2009) brick and fly ash (Piekos & Paslawaska, 1999), lanthanum-impregnated silica gel (Wasay et al., 1996), Alumina impregnated with rare earth metals such as Lanthanum (Shi et al., 2013), Bauxite (Sujana & Anand, 2011), Lanthanum impregnated Bauxite (Vardhan & Srimurali, 2016), red mud (Cengeloglu et al., 2002; Puka, 2004), soils and other geomaterials (Dang et al. 2011; Ramdani et al., 2010; Tor, 2006).

This literature review examines recent studies on fluoride adsorption using alumina and aluminum-based composites. These are a broad category of adsorbents even recognized by the WHO as one of the best demonstrated available adsorbents for fluoride removal. Alumina and aluminum-based composites offer a unique ability for selective fluoride adsorption due to the thermodynamic stability between fluoride ion and the aluminum. However, some limitations such as narrow pH range and slow adsorption rate need to be looked at to improve its performance in the foreseeable

future as the quest for clean drinking water continues to increase globally. In this review, the alumina and aluminum-based composites have been summarized and further discussed to pinpoint some of the breakthroughs and drawbacks. These adsorbents have been further categorized under three types based on their levels of modifications for treating fluorinated water thus activated alumina, modified activated alumina and aluminum-based adsorbents and raw alumina and aluminum-based adsorbents/geomaterials.

2. Activated alumina and aluminum-based composites

This section of the paper focused on the use of activated alumina (AA) and aluminum-based composites for adsorption of fluoride. The advantages of activation as well as some defects have also been highlighted and the mechanisms of adsorption and adsorption efficiency of various materials have been reviewed and compared. Activated alumina is a kind of aluminum oxide, semi-crystalline (Rabia et al., 2018) with surface area significantly over $200 \, m^2 \cdot g^{-1}$ and mostly used as desiccant and sorbent for elements such as fluoride, arsenic and selenium in water. It has a high surface area to weight ratio due to its high porosity with amphoteric properties (Salvador et al., 2015). Its amphoteric nature allows it to behave as an acid in basic medium and as a base in acidic medium. Because of its high affinity, it is mostly a preferable desiccant for moisture removal from air as well as a catalyst in natural gas and refining operations. There are two common methods of activating Al_2O_3 thus, thermal treatment otherwise called physical activation and chemical treatment with acid in the laboratory.

The capacity of alumina to effectively adsorb an adsorbate is influenced by two major factors thus available adsorptive sites for chemisorption and available surface area for physisorption. The adsorptive sites and surface area can be improved by activation (Barakat, 2011; Wang et al., 2009). Three forces (van der Waals forces, dipole-dipole interaction and hydrogen bonding) are responsible for the physisorption where no electron exchange occurs (Rabia et al., 2018) between the adsorbent and the adsorbate since it does not involve activation energy. The chemisorption on the other hand mostly involves two types of electron exchange. This could either be a covalent bond called weak chemisorption or by ionic bond called strong chemical adsorption. The high surface area of an adsorbent enhances its adsorption efficiency. Chua et al. (2009) and Cui et al. (2015) found out that activated alumina had a surface area ranging from 500 to $2000 \, m^2 \cdot L^{-1}$ which significantly enhanced adsorption rate. Also, activation influences the transport of adsorbate from the bulk-fluid to the fluid-solid interface due to improvement in the mesopores and macropores (Cui et al., 2015).

2.1. Activated alumina

Goswami and Purkait (2012) investigated the effectiveness of amorphous acidic alumina as an adsorbent for defluorination at a pH range of 3.8–9.0 with an initial fluoride concentration of 1.9–19 mg·L^{-1}. Amorphous aluminum hydroxide Al(OH)$_3$, alumina or gibbsite (Al$_2$O$_3$) were used. Results from their study showed that maximum fluoride uptake (9 mol·kg^{-1}) occurred at pH 5.5–5.6. The uptake of fluoride ions decreased at lower pH due to the preferential formation of AlF$_x$ soluble species. However, fluoride uptake increased at higher pH attributable to the fact that OH$^-$ displaced the F$^-$ form of the solid Al(OH)$_3$. Ghorai and Pant (2004) studied the fluoride removal capacity of AA (grad OA-25). Adsorption capacity of 1450 mg·kg^{-1} was recorded at neutral pH (7). The rate of adsorption of fluoride ions was also observed to have increased within pH 4–7 and decreased afterward. The hydroxyl and silicate ions competed with fluoride ions for alumina exchange sites at a pH > 7. At pH<7, alumina fluoro complexes were formed in the presence of alumina ions in the treated water.

Moreover, to ensure an improved adsorption capacity of alumina, it must undergo pretreatment methods thus heating and washing in an acid. Heating alumina specifically refers to preparing it through pyrolysis mostly using gibbsite Al(OH)$_3$ or gibbsite containing materials. Heating is usually done in two ways, either rapidly otherwise called flash calcination (usually done at high temperature) or slowly which results in the production of a substantial crystalline product (Rozic et al., 2001). Rapid decomposition usually takes place in flue gas at 400–800 °C within an exposure time of one second (1 s) or less whereas slow decomposition is mostly achieved by steam. Shimelis et al. (2006) conducted an experiment using untreated hydrated alumina (UHA) and thermally treated hydrated Alumina (THA) produced from the hydrolysis of locally manufactured aluminum sulfate. The fluoride adsorption capacities of these two adsorbents were studied for comparative purposes. The adsorption capacities of both THA and UHA were 23.7 mg·g^{-1} and 7.0 mg·g^{-1}, respectively. High fluoride ion removal was observed for both adsorbents within a pH range of 4–9. The mechanism behind the increased adsorption of fluoride ions could be attributed to an increase in the availability of binding or active sites of the adsorbents as a result of increased surface area and increased adsorbent dosage. The adsorption capacities of both sorbents were directly proportional to temperature up to a certain threshold thus adsorption capacity of the adsorbent increased from 0 to 200 °C but further increased in thermal temperature resulted in a decrease in adsorption. This could probably be because, at about 200 °C thermal temperature, aluminum hydroxide gets hardened due to loss of water (Karthikeyan et al., 2014) which resulted in a decrease in

F^- removal efficiency upon the further increase in temperature. Kinetics studies showed that the absorption data at ambient temperature was well fitted with the Freundlich isotherm model. The adsorption isotherm curves of different doses of UHA and THA and the breakthrough curves are both shown in Figures 1 and 2 below.

The surface of alumina was impregnated with alum for the removal of excess fluoride ions in wastewater. High adsorption (92.6%) was recorded at a pH of 6.5 and decreased with a further increase in pH (Tripathy et al., 2006). Also, Sivasankari et al. (2010) reported that 98% of fluoride ions were removed using 1.0 g of powdered activated alumina and 1.4 g granular polymer-agglomerated alumina from centration of 100 mL of $10 \, mg \cdot L^{-1}$
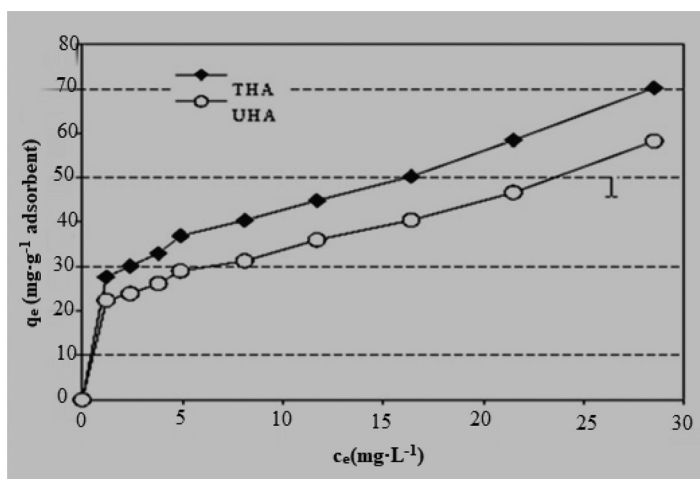
Figure 1. Adsorption isotherm of different doses of UHA and THA (initial F^- concentration $= 50 \, mg \cdot L^{-1}$, contact time $= 24 \, h$, initial pH $= 7.0$ [Reproduced from **Ref.** Rozic et al. 2001].
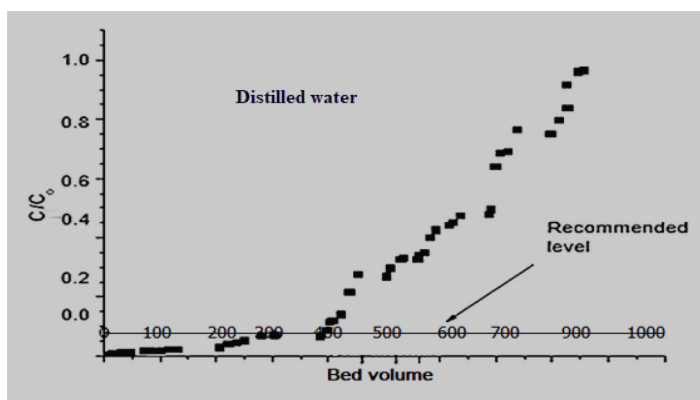
Figure 2. Adsorption of F^- onto THA depicting the Breakthrough curve (Co $= 20 \, mg \cdot L^{-1}$, mass of adsorbent $= 4.5 \, g$, flow rate $= 4 \, mL \cdot min$, bed height $= 25 \, cm$, internal diameter $= 0.9 \, cm$). [Reproduced from **Ref.** Rozic et al. 2001].

fluoride solution at pH 6. Similarly, Kamble et al. (2010) undertook a study on fluoride ion removal using alumina derived from alkoxide nature.

The adsorption isotherm as shown in Figure 1 above, is the relationship between the concentration (bulk aqueous phase activity) of adsorbate and the amount adsorbed at a constant temperature. As shown above (Figure 1) both curves depict a continuous increase at a constant temperature. The curves never reached a point of saturation. The equilibrium adsorption capacity of the treated adsorbent was higher than the untreated adsorbent.

The highest adsorption of fluoride occurred at a pH 5 and 7 with a well-fitted pseudo-second-order model as per the kinetic study. Contrary to the findings of Kamble et al. (2010), when nano-alumina was used as an adsorbent for fluoride removal, the maximum adsorption capacity of $14\,mg{\cdot}g^{-1}$ was achieved at pH 6.5 at temperature 25 °C and the data followed the pseudo-first-order model (Kumar et al., 2011).

Furthermore, a highly ordered mesoporous alumina (Meso-Al-400) and calcium doped alumina (Meso-Al-roca) were both used as adsorbents for fluoride removal from water. The highest de-fluorination efficiency was $300\,mg{\cdot}g^{-1}$ and $450\,mg{\cdot}g^{-1}$ at pH 5 within a temperature of 298 K for 12 h of contact time (Li et al., 2011). Also, Lee et al. (2010) used mesoporous alumina obtained from aluminum tri-sect-butoxide in the presence of both cetyltrimethylammonium bromides (MA-1) or stearic acid (MA-2) and commercially activated alumina and conducted a comparative study on their fluoride removal capacities. Both (MA-1) and (MA-2) were used as structure-directing agents to enhance adsorption capacity. The highest adsorption capacities for both (MA-1) and (MA-2) adsorbents were $7.5\,mg{\cdot}g^{-1}$ and $14.26\,mg{\cdot}g^{-1}$, respectively, whereas the corresponding maximum adsorption capacities of boehmite and gamma-alumina were $6.13\,mg{\cdot}g^{-1}$ and $6.36\,mg{\cdot}g^{-1}$. Gupta et al. (2013) carried a study on fluoride adsorption using activated alumina infused with chloride. The study reported that approximately 60–70% of fluoride was adsorbed onto the absorbent's surface. However, a slight decrease in fluoride removal capacity was observed attributable to the presence of competing ions especially the chloride ions. Even though activated alumina is currently regarded as the state-of-the-art sorbent for fluoride sorption (WHO, 2006), however, one limiting factor is that optimum fluoride sorption mostly occurs at slightly acidic medium (Davison et al., 1982) mostly below pH 6.0 with a narrow pH range which limits its practical application. Therefore, there is a need for modified methods that would remove fluoride ions from water at almost neutral pH. Table 1 gives a summary of a comparative evaluation of some modified alumina and aluminum-based composites for defluorination. It provides a partial quantitative summary or reflection of this article. In it includes the following information: initial concentration of

Table 1. Comparative evaluation of some alumina and aluminum-based adsorbents for de-fluorination.

Adsorbent	Conc. $mg \cdot L^{-1}$	pH range	Temp. (°C)	Contact time (min)	Maximum adsorption $(mg \cdot g^{-1})$	Surface area $mg^2 \cdot L^{-1}$	Ref.
Fe–Al–Ce nano-adsorbent	42	6.5–7.5	Ambient	2160	2.77	–	Chen et al. (2011)
Mg-doped nano-ferrihydrite	10–150	1–10	20–45	30–480	64	248.6	Wang and Reardon (2001)
Fe– Al– Ce hydroxide	10–250	7	25	1440	51.3	56.4	Zhang et al. (2011)
Nano-alumina		2–8	25	10–120	14	–	Koteswara Rao and Metre (2014)
CaCl$_2$ Modified natural zeolite	25–100	4–9	25–45	5–1200	1.766	–	Yang et al. (1999)
Mg/Fe layered double hydroxide	5–50	2.5–11	250–50	0–600	50.91	145.3	Kang et al. (2013)
Graphene	5--40	3.6–10.2	0–50	1–110	48.31	3.08	Li et al. (2011)
Activated carbon (rice straw)	5–20	2–10	25–55	60–1440	18.9	122.9	Ahn et al. (2009)
Activated carbon (*Arachis hypogia*)	2–10	3–12	30–60	60–120	14.79	2.12	Alagumuthu and Rajan (2010)
Al$_2$O$_3$ modified zeolitic tuff	0.5–10	5.5–8	Ambient	50–4320	10.25	139.22	Shimelis et al. (2006)
Al(OH)$_3$ coated pumice	5	3–11	20	0–4800	7.87	5.5	Salifu et al. (2013)
Lantha@Bauxite (LIB)	–	6.5–8.5	20–250	–	18.18	–	Vardhan and Srimurali (2016)
Raw Bauxite	–	5.0–6.0	10–150	15–120	10.9	14–17	Cherukumilli et al. (2017)

experiment, pH range of the study, heating temperature, maximum adsorption and surface area of adsorbents.

2.2. Modified activated alumina-based composites

This section of the paper focused on the use of modified activated alumina-based composites for fluoride adsorption. Mechanisms of adsorption and fluoride removal capacities of different materials have been reviewed. The surface of an adsorbent can be modified with various metal oxides and hydroxides (Ahn et al., 2009; Sun et al., 2014), acids and bases (Fashi et al., 2018), surfactants, oxidizing agents (Owlad et al., 2010) and other rare earth metals. The essence of modification is to improve the adsorption efficiency of activated alumina by changing its surface chemistry and morphological properties. Modification improves the affinity of the solute toward the adsorbent for enhanced adsorption. There are several ways of modifying an adsorbent. Common modification methods include physical treatment, chemical treatment, functionalization and impregnation (Girish, 2018; Lira et al., 2016). After modification, the performance of the resulting modified adsorbent to a larger extent depends on the modifying agent. Fashi et al. (2018) explored the chemical modification of Al_2O_3 surfaces with piperazine which resulted in a change in the concentration of active or binding sites. While modifying Al_2O_3 may decrease the specific surface area, the average pore sizes increases which significantly influences adsorption efficiency (Sergey et al., 2019). It also makes the adsorbent stable with promising regeneration capacity (Jain et al., 2015) and leads to strong affinity due to an increase in hydroxyl groups (Peng et al., 2017). It is equally important to note that, not all modifications may result in an improved sorption rate. This could be due to underlying factors such as the physical and chemical composition of the modifying agent and other underlying experimental conditions

2.2.1. Alumina/manganese composites

Teng et al. (2009) used a redox process and prepared hydrous manganese oxide impregnated with aluminum. To evaluate the adsorption behavior, the authors carried out both batch and column experiments. The maximum fluoride removal was recorded at a pH between 4 and 6 and the Langmuir adsorption capacity was $7.09 \, mg \cdot g^{-1}$ at pH 5.2. Fluoride ion uptake onto the hydrous manganese oxide-coated alumina (HMOCA) obeyed the pseudo-second-order equation. The study further indicated that the presence of competing anions such as HCO_3^-, SO_4^{2-} and PO_4^{3-} had negative effects on the adsorption of fluoride which greatly reduced fluoride ion uptake onto the adsorbent surface. At equilibrium, the pH of the solution

increased and later decreased under alkaline medium. The mechanism responsible for fluoride adsorption by HMOCA could be ion exchange between OH^- and F^- in the initial acidic medium (Daifullah et al., 2007). The liberation of OH^- ions after adsorption was thought to be responsible for the increase in initial pH. On the other hand, after the pH increased beyond 6 (pH > 6.0) ion-exchange could no longer be responsible for the adsorption of F^- unto the adsorbent's surface. Van der Waals forces were responsible for F^- adsorption because, at that stage, protons were released to pave way for the adsorption of Na^+ ions which led to the decrease in final pH. Another reason could be the competition between OH^- and F^- on the active adsorption sites (Teng et al., 2009). Both external and intra-particle diffusion contributed significantly to the rate of transfer and removal. The adsorption mechanism is shown below in equation 1 and 2.

$$HMCOA.XH_2O_{(Solid)} + F^-_{(aq)} \rightarrow HMCOA(X-1)(X-1)$$
$$H_2OH + F^-_{(Solid)+} \ OH^- \tag{1}$$
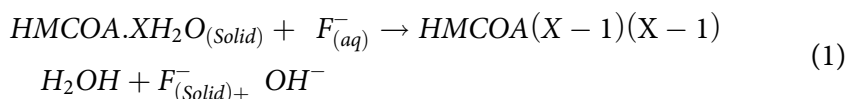
This mechanism was seen to be favorable when pH < 6.0. At pH > 6.0, F^- was adsorbed through the following mechanism:

$$HMCOA.XH_2O_{(Solid)} + Na^+_{(aq)} + F^-_{(aq)}$$
$$\rightarrow HMCOA(X-1)H_2O.OH^-Na^+F^-_{(Solid)} + H^+ \tag{2}$$
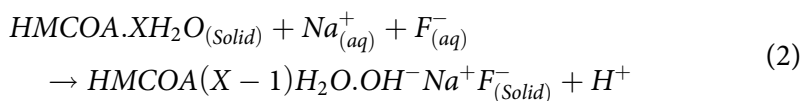
Moreover, Manganese oxide-coated activated alumina was studied for its fluoride removal capacity by Tripathy and Raichur (2007). They observed that the manganese coated activated alumina had fluoride removal up to $0.2 \, mg \cdot L^{-1}$ at pH 5.5 within a contact time of 3 h. The adsorbent achieved a maximum removal capacity of 98% at pH 5.5 (from $10 \, mg \cdot L^{-1}$ initial concentration down to $0.2 \, mg \cdot L^{-1}$). When co-existing ions were added, the adsorption capacity of the adsorbent started decreasing. In similar studies, Maliyekkal et al. (2006) experimented on a novel sorbent (magnesia-amended activated alumina) investigating its capacity to effectively remove fluoride ions from drinking water. MAAA was prepared by calcining magnesium hydroxide impregnated alumina at 450 °C. They reported that MAAA showed higher fluoride adsorption than activated alumina. Batch sorption studies were carried out as a function of contact time, pH, initial fluoride concentration, and adsorbent dose. The effects of other competing ions were carried out in real groundwater samples. The physicochemical properties of MAAA were characterized using X-ray powder diffraction (XRD) in Figure 3c, scanning electron microscope (SEM) in Figure 3a, energy dispersive X-ray (EDA) in Figure 3b and a gas adsorption porosimetry analyses. Their results indicated that within a contact time of 3 h, more than 95% removal of fluoride ($10 \, mg \cdot L^{-1}$) was achieved at neutral
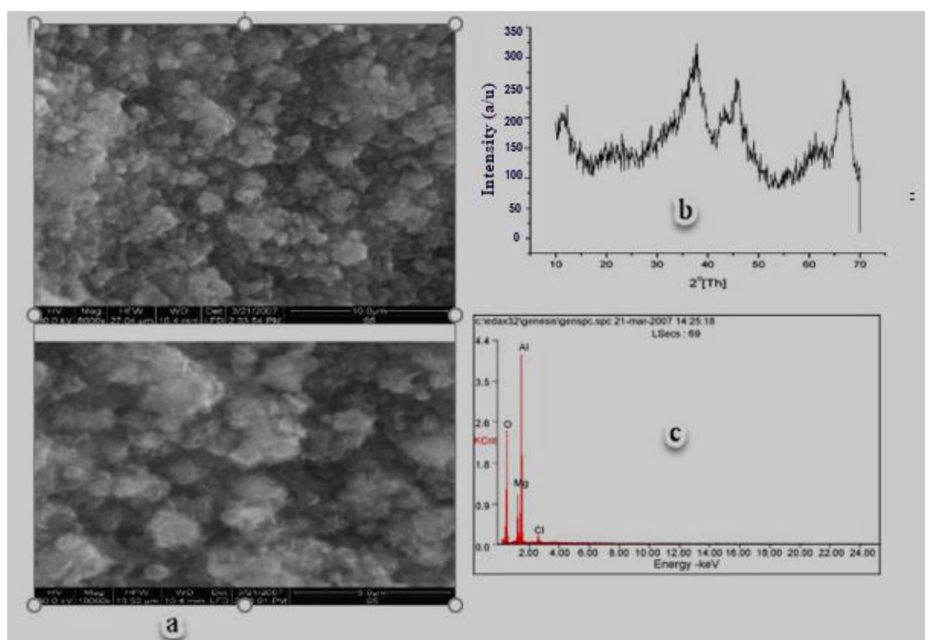
Figure 3. SEM micrograph depicting the magnesia-amended activated alumina (a), EDA spectrum showing magnesia-amended activated alumina (b), X-Ray diffraction pattern of magnesia-amended activated alumina (c) [Reproduced from **Ref.** Maliyekkal et al. 2006].

pH. Sorption of fluoride onto MAAA was found to be pH-dependent and a decrease in sorption was observed at higher pHs.

The EDX technique was used for the spot elemental analysis of MAAA. The EDX spectrum as shown in Figure 3c above shows indirect evidence that magnesia was coated on the surface of AA. Analyzing the X-ray pattern (Al21.333O32, JCPDS-80-0955) as indicated in Figure 3b above, the study noticed that virtually all the peaks that appeared in the X-ray diffraction pattern best suited the alumina. The authors concluded that the amorphous nature of the magnesia or small volume of magnesia was responsible for such an observation. Maliyekkal et al. (2006) studied manganese oxide coated alumina (MOCA) and reported that it was effective in removing fluoride ions below the statutory $1.5 \, mg \cdot L^{-1}$ for drinking as prescribed by WHO. They further indicated that MOCA had a higher load capacity ($2.85 \, mg \cdot g^{-1}$) compared with $1.08 \, mg \cdot g^{-1}$ for activated alumina.

2.2.2. Alumina/calcium mineral composites

Calcium based adsorbents generally have a strong affinity for fluoride, low-cost to procure and are also biocompatible with the human body making them good adsorbent for defluorination (Waghmare & Arfin, 2015). A novel alumina cement granules (ALC) was studied for its defluorination

capacity from natural groundwater systems and synthetic water prepared using conditions similar to natural freshwater by Ayoob and Gupta (2009). The study observed that $2 \, g \cdot L^{-1}$ doses of ALC effectively reduced the F^- concentration in water from $8.65 \, mg \cdot L^{-1}$ to below $1.0 \, mg \cdot L^{-1}$ with $2.27 \, mg \cdot L^{-1}$ being the maximum adsorption capacity at a flow rate of $4 \, mL \cdot min^{-1}$. The adsorption was not significantly affected within the pH range of 3.0–11.5 which was in agreement with the findings of Shimelis et al. (2006) who found a broad range of pH (4–9) for fluoride adsorption on aluminum hydroxide. The mechanism behind why the percentage of fluoride removal remained nearly constant on such a wide range of pH (3.0–11.5) could be due to the electropositivity (Nigussie et al., 2007) and neutral sites at the surface of the adsorbent. Also, electrostatic repulsion of F^- to the negatively charged surface of the adsorbent due to Van der Waals force accounted for the progressive decrease of F^- uptake after pH > 11.5. Some existing co-anions such as sulfate, nitrate, chloride and bicarbonate did not show any significant effect on the adsorption of fluoride onto the adsorbent. However, a higher concentration of phosphate and silicate ions significantly reduced the fluoride uptake by ALC. Since ALC was novel, it was important to determine its properties. BET method was used to determine the surface area of the adsorbent at liquid nitrogen temperature using FlowSorb II 2300 (Micrometrics Instruments Corporation, USA). The properties of ALC media are presented in Table 2 below.

Column studies were performed at the same initial F^- concentrations of $8.65 \, mg \cdot L^{-1}$ to evaluate and compare the field application potential of ALC in both natural and synthetic water systems. The breakthrough profiles are shown in Figure 4 as well as in Table 3 below for a more elaborate view. They observed that the time for breakthrough and exhaust in synthetic water (17 and 139 h) was more than that of natural water (3 and 14 h). The study then concluded that there is a reduction in scavenging potential in treating natural water compared to synthetic systems

Mondal and George (2013) carried out a comparative study between AA and calcium-magnesium-aluminum (CAM) powder on fluoride adsorption capacity from fluorinated water. The report indicated that the adsorption

Table 2. Properties of ALC media. Ayoob and Gupta (2009).

Properties	Quantitative Value
Geometric mean size (mm)	0.212
Bulk density (gcm^{-3})	2.33
Specific Gravity	2.587
Al_2O_3 (%)	78.49
CaO (%)	15.82
SiO_2 (%)	5.39
Fe_2O_3 (%)	0.30
pH of the PZC	11.32
BET surface area (mg$^2 \cdot g^{-1}$)	4.385
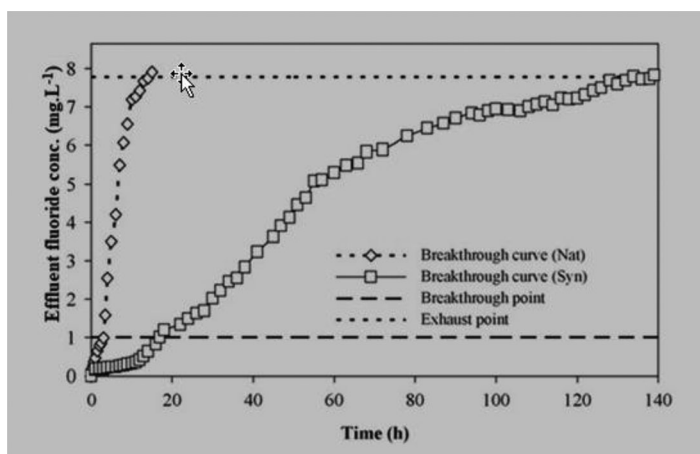
Figure 4. Curves of fluoride sorption breakthrough onto ALC in both natural and synthetic water (Co $=$ 8.65 mg·L^{-1}, pH 6.9 $\pm$ 0.4, $T=$ 300 K, flow rate $=$ 8 mL·min^{-1}). [Reproduced from **Ref.** Ayoob & Gupta 2009].

Table 3. A comparative evaluation of adsorbent performance in both synthetic and natural water [Reproduced from Ref. Ayoob & Gupta 2009].

		Nature of the medium	
S.no	Systems of study	Synthetic	Natural groundwater
1	Dose of the requirement of ALC in a batch study (for an initial fluoride concentration of 8.65 mg·L^{-1}, pH of 6.9 $\pm$ 0.4	2 g·L^{-1}	10 g·L^{-1}
2	Langmuir saturated monolayer adsorption capacity ($q$max)	10.214 mg·g^{-1}	0.935 mg·g^{-1}
3	The minimum adsorption capacity of ALC by column study ($q$min,col)	1.847 mg·g^{-1}	0.317 mg·g^{-1}
4	Maximum adsorption capacity of ALC by column study ($q$col)	6.965 mg·g^{-1}	0.75 mg·g^{-1}

of fluoride ions in both adsorbents increased within the pH range of 6.0-8.0 and a further increase in pH indicated a negative trend. Both adsorbents had the same trend of adsorption for pH nevertheless, CAM had a higher fluoride removal capacity than AA. The adsorption process was multilayered, non-uniform and heterogeneous, a clear indication of well fitted Freundlich equation ($R^2=$0.998) and the adsorption kinetics followed the pseudo-second-order model.

Dayananda et al. (2014) prepared a mesoporous Al_2O_3 loaded on calcium oxide (CaO) as an adsorbent for fluoride removal from water. Exactly 20% by weight of CaO loaded mesoporous Al_2O_3 removed 90% of fluoride ions from water within a contact time of 15 min using 3 g·L^{-1} of dose. However, the pure Al_2O_3 removed a paltry of 22% of fluoride ions from water within one hour. Both Al_2O_3 and CaO@Al_2O_3 had maximum fluoride removal capacity of 24.45 mg·g^{-1} and 136.99 mg·g^{-1}, respectively. The higher fluoride removal capacity of CaO@Al_2O_3 attributable to the impregnation of Calcium led to the formation of CaF_2 as opposed to the

pure Al_2O_3. Dahi described the Nalgonda technique which was carried out in a village in Tanzania called Ngurdoto. A pipe borne water was subjected to treatment variations. It underwent both seasonal and non-seasonal variations between 12.5 and $8.8\,mg{\cdot}L^{-1}$. In the demonstration, 12.8 g alum and 6.4 g lime were added to 20 L bucket and the fluoride level in the water was reduced to $2.1\pm0.7\,mg{\cdot}L^{-1}$ which is still above the WHO recommended limit of $1.5\,mg{\cdot}L^{-1}$. Although the Nalgonda technique has been claimed to be very effective in reducing fluoride ions in water however, critics still exist. For instance, Meenakshi and Maheshwari (2006) have listed the following critics, however, it can still serve as auxiliary methods of detoxifying water where community resources are scarce or where one cannot afford bottled water or when getting an alternative source of fluoride-free drinking water becomes impossible. The critics are outlined below

1. Only a smaller portion of fluoride ions are removed by the process (18–33%) in a precipitate form and convert the rest (67–82%) into soluble Al^{3+}–F^{-} complexions. These ionic forms are toxic substances (Apparao & Karthikeyan, 1986) cited by Mohapatra et al. (2009).
2. $SO_4{}^{2-}$ ion concentration from the aluminum sulfate coagulant sometimes reaches high levels. In some few instances, it crosses the maximum permissible limit of $400\,mg{\cdot}L^{-1}$.
3. When the residual aluminum produced exceed 200 ppb in treated water, it can cause dementia thereby affecting the musculoskeletal respiratory and cardiovascular systems (Nayak, 2002).
4. The process causes secondary water pollution thus changes the taste of the treated water.
5. The process is tiresome and demanding as it requires consistent analysis of feed and treated water to calculate the correct dose of chemicals to be added due to fluctuations in the water matrix
6. It involves a high maintenance cost. For instance, a plant of 10,000 L capacity on the average requires Rs. 3000 every year (Mohapatra et al., 2009).
7. The process is not automatic, it requires regular checks during the treatment process.
8. It produces a large quantity of sludge which requires a large area of space for drying.
9. Silicates have adverse effects on defluorination in the Nalgonda technique and temperature also affects defluorination capacity.
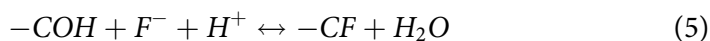
2.2.3. Aluminum/magnesium composites

Nazari and Halladj (2014) conducted a study on the fluoride adsorption capacity of magnesia/alumina doped Υ-Al_2O_3 with MgO nanoparticles

(NPs) through the sonochemical approach. The presence of other ions such as phosphate significantly affected the rate of adsorption whereas Cl^-, SO_4^{2-} and HCO_3^- ions had slight effects on the fluoride removal capacity of the adsorbent. The study further observed that optimum removal up to 85% and adsorption capacity of $5.6\,mg{\cdot}g^{-1}$ was attained at pH 6.3–7.3 within a contact time of 140 min at an adsorbent dose of $0.5\,g{\cdot}L^{-1}$. A kinetic study indicated that the data well fitted with the Langmuir equation with a pseudo-second-order kinetic model. Earlier studies by Maliyekkal et al. (2008) developed magnesia amended activated alumina. Alumina was impregnated with magnesium hydroxide and further calcined the resulting product at a temperature of $450\,°C$. Within 180 min of contact time, more than 95% of the fluoride removal ($10\,mg{\cdot}L^{-1}$) was achieved at a neutral pH hence bringing the concentration down to $0.5\,mg{\cdot}L^{-1}$ which is within both the WHO and the American recommended permissible levels. Sips equation was used to deduce the maximum sorption capacity and was found to be $10.12\,mg{\cdot}g^{-1}$. The maximum fluoride removal occurred at a pH 5.0–7.5 and the adsorption kinetics fitted the Pseudo-second order which also indicates that the F^- removal was due to the chemisorption process. The study again established that most of the competing ions that were present in the natural drinking water had negligible effects on the fluoride ion removal and the rate of sorption of magnesia amended activated alumina was higher than activated alumina. Following Raichur and Basu (2001), when the pH of the solution increases after sorption had occurred as in the case of Maliyekkal et al. (2008), and F^- increases with decreasing initial pH, then such a reaction mechanism could be a ligand exchange mechanism. The two-step reaction mechanism is shown below.

$$-COH + H^+ \leftrightarrow -COH_2^+ \tag{3}$$
$$-COH_2^+ + \ F^- \leftrightarrow -CF + H_2O \tag{4}$$
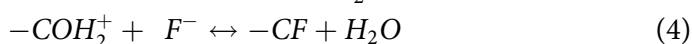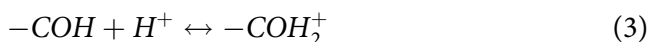
The net reaction equation is shown below

$$-COH + F^- + H^+ \leftrightarrow -CF + H_2O \tag{5}$$

$-COH$ represents the OH^- on the adsorbent's surface. In this case, F^- could be seen as being fully located on the surface of the adsorbent.

2.2.4. Aluminum plus iron composites

Dang et al. (2011) investigated the fluoride removal potential of $Fe_2(SO_4)_3$ modified granular activated alumina (1–2 mm). The sorption experiment was carried out with a sorbent dose of $1.0\,g{\cdot}L^{-1}$ at a wide range of initial fluoride concentration of (0.5–$180\,mg{\cdot}L^{-1}$) at pH 7. The result from their study indicates that the adsorption isotherm studies fitted well with the Langmuir model at low equilibrium concentrations (0.5–$5.0\,mg{\cdot}L^{-1}$). They

concluded that the Freundlich isotherm model fitted only at high equilibrium concentrations (5.0–150 mg·L^{-1}). An earlier experiment conducted by Biswas et al. (2007) investigated the adsorption potential of iron-III aluminum-III mixed oxides. Effect of pH, contact time, co-existing ions and sorbent dose were studied. The hydrous iron III-aluminum III mixed oxides adsorbent was characterized by both SEM (Figure 5a and b) and XRD (Figure 5c) as shown below. The aluminum and iron hydroxide were both co-precipitated from the chloride mixture in equimolar quantities using ammonia. The solution (mixed oxides) was allowed to age over time to form dried binary metal oxides. The dried binary metal oxide had higher fluoride adsorption capacity than either Ferric hydroxide or aluminum hydroxide. The maximum pH for fluoride uptake occurred from 4 to 10 at an equilibrium time of 90 min. The adsorption isotherm followed the Langmuir model with pseudo-second-order best fit as per a kinetic study.

Similarly, Chubar et al. (2005) carried out a novel experiment using an iron exchanger based on double hydrous oxide ($Fe_2O_3Al_2O_3XH_2O$) precipitated from equimolar aluminum and Ferric chloride by the addition of ammonia. Four competing anions were investigated thus, fluoride, chloride, bromide and bromate ions. The maximum adsorption of fluoride ions (90 mg·g^{-1}) occurred at pH 4 and the adsorption process followed the Langmuir model. The adsorbent effectively removed all the four anions
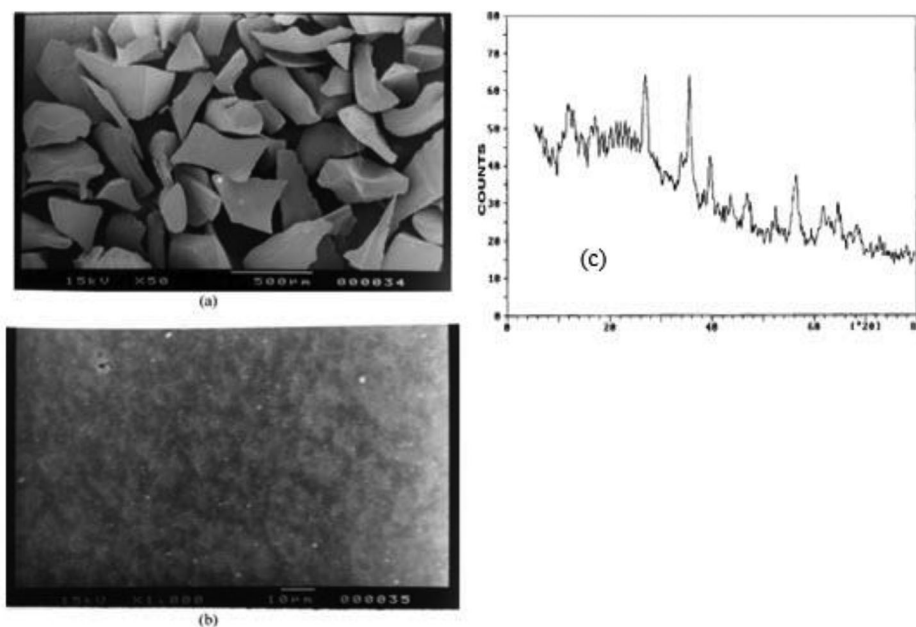
Figure 5. SEM photomicrographs of iron- (III)-aluminum (III) mixed oxide: (a) 50× magnification and (b) 1000× magnification; (c) XRD pattern of the hydrous iron (III)-aluminum (III) mixed oxide. [Reproduced from **Ref.** Biswas et al. 2007].

(F^-, Cl^-, Br^- and BrO_3^-) at a pH range of 3.0–8.5. Kinetics study on the F^- and Br^- sorption fitted well with the pseudo-second-order model and fluoride ions were the most adsorbed ions onto the adsorbent. Four years later, Sujana et al. (2009) undertook an experiment investigating the adsorption of As (III) and As (V) anionic species on an amorphous Fe–Al oxide with different molar ratios.

2.2.5. Aluminum plus lanthanum composites

Extensive research has been conducted on the defluorination capacity of some rare earth metals such as Lanthanum. Shi et al. (2013) investigated an equimolar mixture of Lanthanum oxide impregnated granular activated alumina (LAA) for the removal of fluoride ions in water. Lanthanum impregnation on alumina was repeated 5 times and further calcined at a temperature of 573 K. The study pointed out that, the calcination resulted in about a 19.1% increase in the content of Lanthanum and was also responsible for the optimum fluoride adsorption of 16.9 mg·g^{-1}. The study again observed that Lanthanum oxide impregnated granular activated alumina adsorbed 70.5–77.2% fluoride in the pH range of 3.9–9.6 higher than Puri and Balani (2000) compared the fluoride removal capacity of two adsorbents thus, alumina impregnated with Lanthanum hydroxide and original alumina. The adsorption capacity of the original alumina was 0.170–0.190 mM·g^{-1}. Whereas the adsorption capacity of the alumina impregnated with lanthanum hydroxide was found to be 0.340–0.365 mM·g^{-1}. Fluoride adsorption was significantly affected by the presence of phosphate and sulfate ions whereas ions such as chloride, bromide, iodide and nitrate did not significantly influence the adsorption of fluoride onto the adsorbent (Teutli-Sequeira et al., 2014). Maximum adsorption of fluoride occurred at a pH range of 5.7–8.0 and was more effective when fluoride concentration decreased from 7 to 0.003 nM and the adsorption process followed the Langmuir model.

2.2.6. Aluminum/carbon composites

Carbon is one of the materials that have been widely researched for its defluorination potential because it is easily accessible and relatively cheaper. Carbon has three allotropes (Allotropy or allotropism is simply the ability of some chemical elements to exist in two or more different forms, in the same physical state). Diamond, graphite and Fullerene are the three allotropes of carbon. Diamond is not good for fluoride adsorption but graphite and fullerene have been reported as good adsorbents for fluoride adsorption (Mohapatra et al., 2009). Jin et al (2015) studied alumina modified expanded graphite (Al_2O_3/E-G) composite using facile solution method at 45 °C as a medium for 2 h for the removal of fluoride ions from drinking water.

Maximum fluoride removal of 94.4% at an adsorption capacity of 1.18 mg·g^{-1} was observed by (Al$_2$O$_3$/E-G) at a pH range of 3–7. The study further noted that such a high adsorption rate was possible because fluoride adsorption was not affected by the pH of the aqueous solution. As such, the adsorbent was more effective for removing lower concentrations of fluoride ions beyond permissible levels. Abe et al. (2004) compared the fluoride adsorption capacities of different carbon adsorbents. The authors concluded on the adsorption capacities of the various carbon adsorbents on the following order; bone char > Coal charcoal > wood charcoal > Carbon black > Petroleum cake. Moreover, Gupta et al. (2007) investigated the fluoride removal potential of waste carbon slurries generated from fuel-oil generators. The solid from the slurry was calcined at a temperature of 45 °C, washed in Sodium hydroxide solution and finally purified by washing in fluoride-free water. The product was heated at 100 °C and further separated into the various components. The composition was as follows (Carbon 92.0%, Al 0.45%, Fe 0.6%). The optimum adsorption occurred at pH 7.6 and it removed fluoride down beyond WHO recommended level of <1.5 mg·L^{-1}.

2.3. Raw alumina-based adsorbents/geomaterials

This category of the study focused on alumina-based materials that have been used as adsorbents in their raw form without any modification as well as other geomaterials available in literature such as red mud, clays, soils and raw form of bauxite. However, in some instances, modified versions of some sorbents have been provided for better appreciation of the differences between the two forms of adsorbents. Mechanisms of adsorption of some of them have been discussed and fluoride adsorption capacity of different materials compared.

2.3.1. Red mud/soil

According to Soni and Shikha (2013), red soil has relatively high porosity and iron oxides, as such, reaction with fluoride leads to the formation of other useful products. In their research using red mud as an adsorbent for fluoride removal from water, the maximum fluoride adsorption occurred at pH range 5.0–7.0 which is very suitable for practical purposes. The fluoride adsorption took place in two stages with the first stage accounting for about 70–80% adsorption of fluoride within 20 min. This could be due to the relatively larger surface area of the red mud that caused initial fluoride to accumulate at the surface of the mud (Wang & Reardon, 2001). Table 4 shows the typical composition of red mud from Australia. The second stage, however, was slower taking about 120 min due to the penetration of fluoride ions to the inner active sites of the adsorbent. A batch and column

Table 4. Composition of an Australian red mud (White et al. 2003).

Chemical	Formula	%w/w
Aluminum Oxide	Al_2O_3	17–22
Calcium Oxide	CaO	4–5
Iron Oxide	Fe_2O_3	25–35
Silicon dioxide	SiO_2	25–30
Sodium carbonate	Na_2CO_3	2.8
Sodium Oxide	Na_2O	2–3
Titanium Oxide	TiO_2	2–4

adsorption study were carried out on granular red mud (GRM) to investigate its fluoride removal potential. Pretreatment was carried out to obtain the desired pH (Wang & Reardon, 2001) for the sorption experiment and the regeneration of the adsorbent was carried out by pumping 0.2 M of NaOH into the loaded GRM column. The experimental conditions were augmented and data were well fitted to the isothermic and kinetic models. The column data fitted to the Thomas model and good agreement was achieved for both the predicted and experimental values (Tor, 2006; Tor et al., 2009). Similarly, heavily weathered tertiary soil was studied for its potential for treating fluorinated water (Wang & Reardon, 2001). Both sorption and column studies were carried out to obtain an optimal regeneration and activation procedure and to characterized F^- sorption. The soil was mainly composed of quartz, feldspars, illite, goethite and about 6.75% of iron (III) oxide which was the principal sorbent of F^- in the soil. Other competing ions such as Cl^-, SO_4^{2-}, and HCO_3^- had negligible effects on F^- removal. Due to the high zero point of charge (pH_{Zpc}) of goethite, it easily transforms into ion-exchanger mostly at pHs lower than its PH_{Zpc}. As such, the mechanism of sorption of F^- unto the sorbent can be well represented with a two-step ligand exchanger model.

$$\equiv FeOH + H^+ \leftrightarrow\ \equiv FeOH_2^+ \tag{6}$$

$$\equiv FeOH_2^+ + F^- \leftrightarrow\ \equiv FeF + H_2O \tag{7}$$
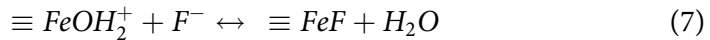
This translate into a net equation as shown below

$$\equiv FeOH + H^+ + F^- \leftrightarrow\ \equiv FeF +\ H_2O \tag{8}$$
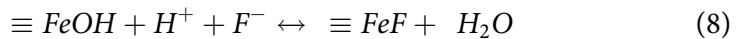
Chidambaram et al. (2003) investigated three different natural materials on their capacity for fluoride removal from water. Untreated charcoal (UC), brick and fly-ash (BFA) and red mud (RM) were studied. Untreated charcoal adsorbed only a paltry of 0.5–1.0 mg·L^{-1} of fluoride, brick and fly-ash adsorbed 6.6–5.6 mg·L^{-1} of fluoride within 30 min and the red mud adsorbed up to 9 mg·L^{-1} of fluoride within 15 min. However, just like in the brick and fly-ash, adsorption of fluoride in the red soil after 30 min reduced to 0.09 mg·L^{-1}, to 0.035 mg·L^{-1} in 90 min and finally to 0.039 mg·L^{-1} in 120 min.

2.3.2. Bauxite

Bauxite is a naturally existing ore obtained from the production of aluminum. Generally, it has several aluminum minerals with oxides of silica, iron, titanium and other trace impure metals. Several studies on using bauxite for wastewater remediation have characterized bauxite into its components. However, slight variation in its composition exists depending on its origin. The composition of typical bauxite is shown below in Table 5.

Sujana and Anand (2011) explored the effectiveness of using untreated bauxite as an adsorbent for fluoride removal from groundwater in Orissa, India. Characterization studies on bauxite before and after adsorption experiment was carried out using XRD, FTIR and SEM-EDX. The analysis showed that the major constituents of raw bauxite were, Al_2O_3 (52.5%), Fe_2O_3 (22.50%), SiO_2 (2.40%), TiO_2 (1.4%) and moisture constituted about 19.50%. The BET surface area of Bauxite was $38\,m^2 \cdot g^{-1}$ whereas the pH_{pzc} was 6.2. The maximum pH range for fluoride adsorption was found to be in the range 5–7 which is suitable for practical applications and commercial purposes. The study also pointed out that the presence of other competing ions such as sulfate, nitrate and phosphate showed significant adverse effects whereas carbonate ions did not affect adsorption to any significant level (Habuda-Stanic et al., 2014). Kinetic study showed that the Langmuir adsorption capacity was $5.16\,mg \cdot g^{-1}$ and followed the pseudo-first-order equation. The adsorption potential of heat-activated bauxite for the removal of anionic pollutants such as Cr (VI) and As (III) was investigated by Wang and Reardon (2001).

Furthermore, Vardhan and Srimurali (2016) carried out a comparative investigation between novel Lanthanum impregnated bauxite (LIB) and raw bauxite for the removal of fluoride ions from water. Both XRD and SEM techniques were used to characterized LIB. Both the SEM image and EDA spectra are presented in Figure 6 and Table 6, respectively. White-colored precipitate was formed on the SEM image. The authors therefore, attributed the formation of white-colored dense precipitates in the SEM image to the impregnated lanthanum on the background granules of bauxite similar to the findings of Mandal and Mayadevi (2008). The elements Al, La, Ti and Fe can be observed in the EDX spectrum suggesting subsidiary evidence of the presence of lanthanum on bauxite. Analysis from the particle

Table 5. Chemical composition of Bauxite (Samal et al., 2013).

Composition	Percentage (%)
Alumina (Al_2O_3)	33.2–76.9
Iron oxide (Fe_2O_3)	0.1–48.8
Silica (SiO_2)	0.3–37.8
Titania (TiO_2)	Up to 4
Water (H_2O)	8.6–31.4
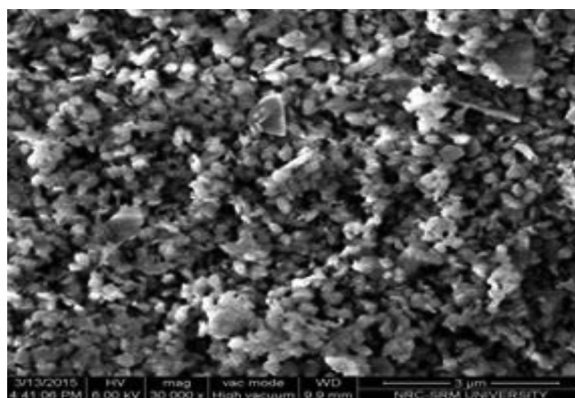
Figure 6. SEM image of LIB [Reproduced from **Ref.** Vardhan & Srimurali 2016].

Table 6. EDX of LIB.

Element	Atomic number	Series	Unn.C (Wt%)	Norm.c (Wt%)	Atom.c (at.%)	Error (1 sigma) (Wt%)
Ti	22	L-series	68.8	64.47	58.48	16.60
Al	13	K-series	21.13	19.8	31.88	1.28
Fe	26	L-series	10.85	10.17	7.91	3.87
La	57	M-series	5.93	5.56	1.74	4.38

Unn C (Wt%): The unnormalized concentration in weight percent of the element;.
Norm C (Wt%): The normalized concentration in weight percent of the element;.
Atom. C(at%): The atomic weight percent;.
Error (1 sigma) [Wt%]: The error in the weight percent concentration at 1 sigma level.

size distribution indicated that over 90% of LIB and bauxite particles/aggregates fell in the range of 40–55 μm

To ascertain its adsorption potential, the following parameters were studied; the dose of sorbent, kinetic equilibrium sorption capacity, pH and the influence of other competing ions. At the end of their experiment, they found out that $2\,g{\cdot}L^{-1}$ dose of LIB removed 99% of fluoride from an initial concentration of $20\,mg{\cdot}L^{-1}$, whereas bauxite at $6\,g{\cdot}L^{-1}$ could remove 94% of fluoride from an initial fluoride concentration of $20\,mg{\cdot}L^{-1}$ as shown in Figure 7 below. The influence of other competing ions such as NO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-} and HCO_3^- were studied. NO_3^- caused a further reduction in fluoride concentration whereas Cl^-, SO_4^{2-}, PO_4^{3-} and HCO_3^- increased fluoride concentration. A pH range of 6.5–8.5 was optimum for the maximum $(18.18\,mg{\cdot}g^{-1})$ adsorption to occur when LIB was used as an adsorbent whereas an optimum pH of 5.0–6.5 only adsorbed a maximum of $7.722\,mg{\cdot}g^{-1}$ fluoride when raw bauxite was used as adsorbent. Kinetics and isothermic studies showed that LIB conformed to the Langmuir model and fitted well with the pseudo-second-order equation as reproduced in Figure 8 below. The authors concluded that the removal of fluoride by bauxite was lower compared with LIB due to the higher affinity of lanthanum for fluoride.
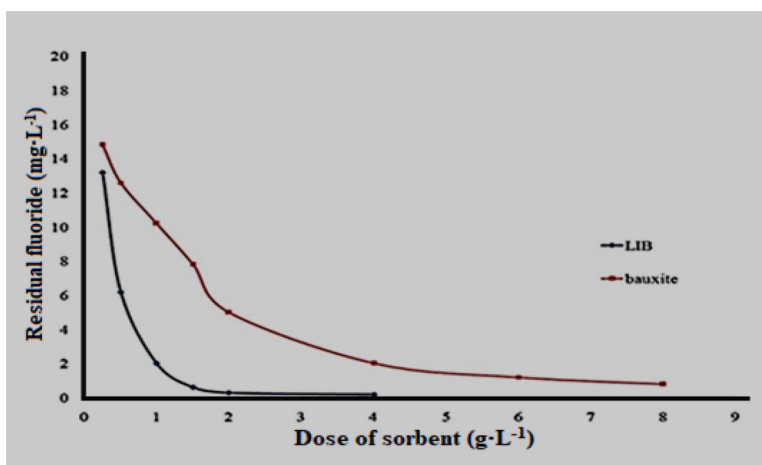
Figure 7. Comparison of the influence of doses of LIB and bauxite on fluoride removal. Initial fluoride $= 20\,mg\cdot L^{-1}$ [Reproduced from **Ref.** Vardhan & Srimurali 2016].
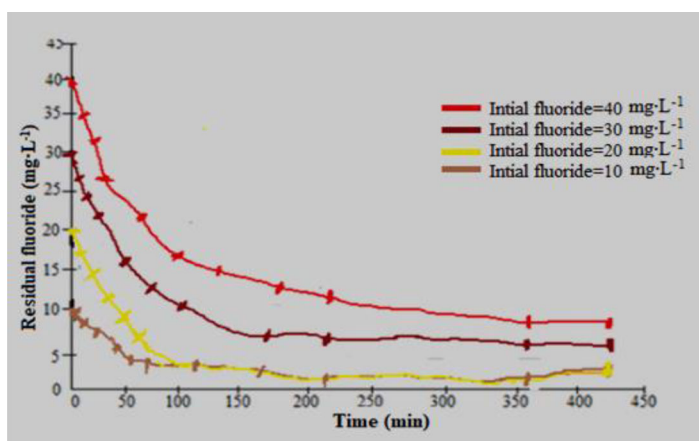
Figure 8. Kinetics of fluoride removal by LIB at various initial concentrations of fluoride (adsorbent dose $= 2\,g\cdot L^{-1}$) [Reproduced from **Ref.** Vardhan & Srimurali 2016].

Additionally, Cherukumilli et al. (2017) investigated factors governing the performance of four different raw bauxites for fluoride remediation of groundwater. Bauxite from four countries (Guinea, Ghana, US and India) were used for comparative study purposes. The bauxite was characterized by X-ray fluorescence (Figure 9b), XRD (Figure 10c), gas sorption analysis and adsorption isotherm/envelopes. All ores had comparative surface areas ranging from 14 to $17\,m^2\cdot g^{-1}$ with similar intrinsic affinities capacity for fluoride removal. Fluoride removal was strongly pH-dependent through the ion-exchange method and maximum removal occurred at pH 5.0–6.0. They also observed that doses of 10–$23\,g\cdot L^{-1}$ effectively remediated $10\,mg\cdot L^{-1}$. However, traces of $CaCO_3$ that were seen in the bauxite from India significantly hindered fluoride adsorption and increased the pH. The study,
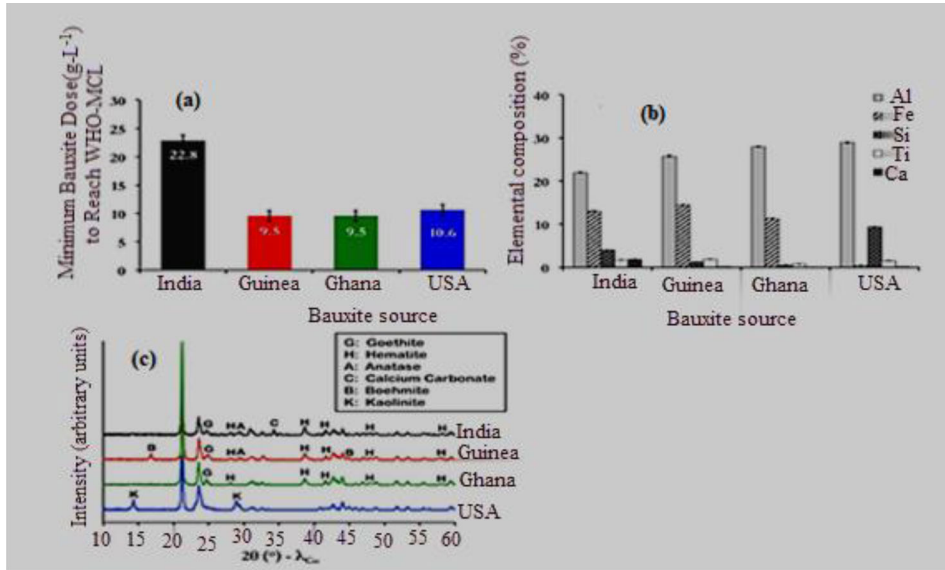
**Figure 9.** Characterization of 4 different bauxite ores according to (A) Smallest doses required to remove $10\,mg\cdot L^{-1}$ below the WHO-MCL ($1.5\,mg\cdot L^{-1}$) in synthetic Sri Lankan groundwater; initial pH of 6.0, (B) X-Ray fluorescence analysis showing the composition of elements, (C) XRD depicting the mineralogy of the four different bauxite. Unlabeled peaks indicate gibbsite. In panel A, averages from duplicate experiments and error bars are the largest of the range from duplicate tests and measurement errors are associated with the fluoride probe. Measurement errors during the ED-XRF analysis are shown in panel B. [Copyright © 2020 American Chemical Society.].
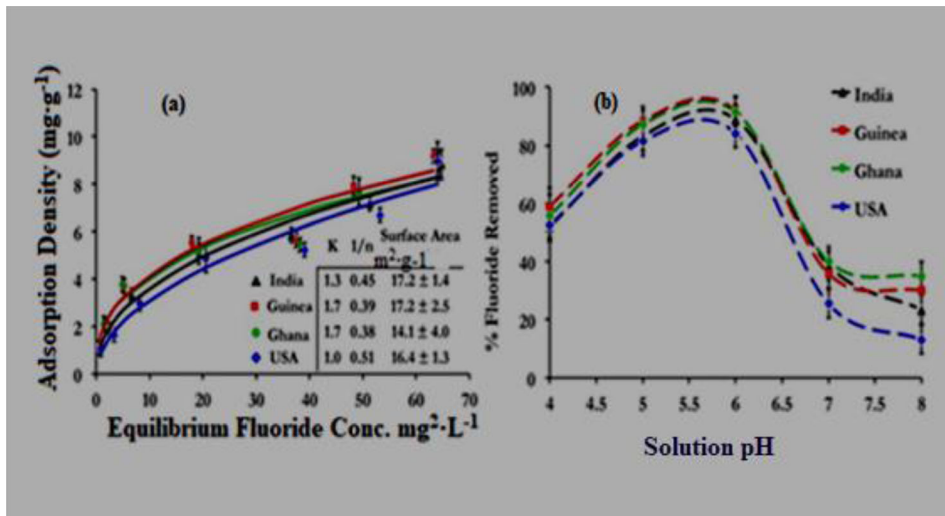
Figure 10. Adsorption Isotherms (A) and (B) Envelopes of the four bauxite ores. Both depicting, respective, effects of fluoride concentration at equilibrium and pH on fluoride removal. The Adsorption isotherms were characterized in $50\,mM$ MES + $5\,mM$ HCO_3^-, at a constant pH of 6.0. The solid lines are the Freundlich model fit generated by ISOFIT (fitted model constants and BET surface area is also indicated). Adsorption envelopes were characterized in $5\,mM$ HCO_3^- + buffers, at constant ionic strength, with dashed lines drawn to guide the eye and not to represent a model fit. Averages from duplicate experiments and error bars are the largest of the range from duplicate tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe, Tristar II 3020) [Copyright © 2020 American Chemical Society].

therefore, concluded that fluoride remediation with the best performing bauxite obtained from Guinea was 23–33 times less expensive than activated alumina as shown in Figure 11 below.
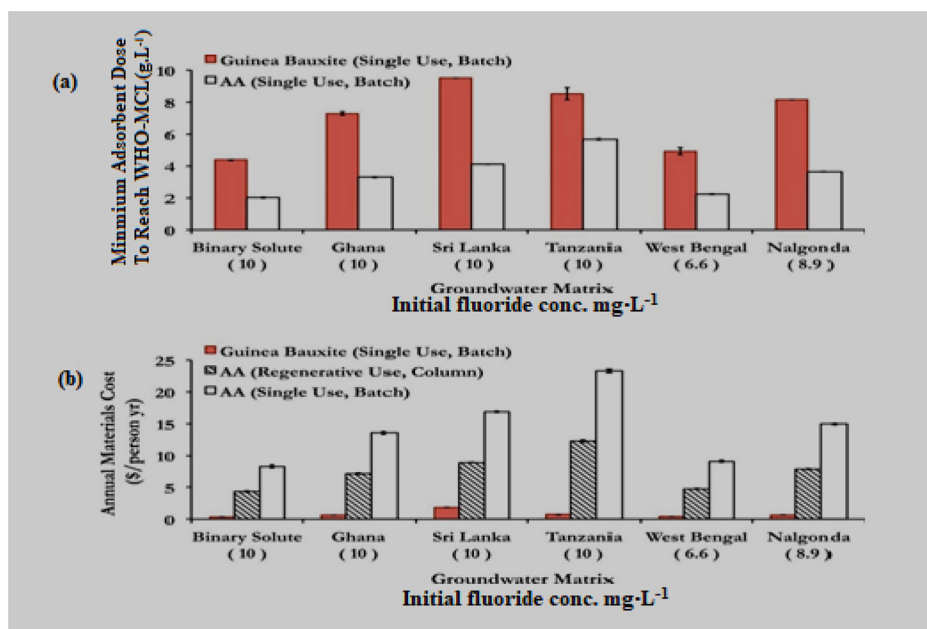
Figure 11. Comparison of (A) smallest required doses and (B) Annual per capita material costs for remediating several synthetic groundwater matrices containing $10\,mg \cdot L^{-1}$ and two real groundwater matrices (West Bengal and Nalgonda) to the WHO-MCL ($1.5\,mg \cdot L^{-1}$) using milled Guinea bauxite through a single-use batch process and unmodified AA (both in single-use batch process and in column process with media regeneration). We present averages and error bars represent the larger of the range from duplicate tests and measurement errors associated with the fluoride probe. [Copyright © 2020 American Chemical Society.].

2.3.3. Clays and soils

Clay as a natural product dug from the earth consists of decomposed organic and inorganic materials that have accumulated for over millions of years. The first all-inclusive study on adsorption of fluoride using minerals and soils as adsorbents was originally published by Bower and Hatcher (1967). Since then, there has been a widespread of studies investigating the potentials of various origin of clay and soils for their defluorination capacity such as; illite-goethite soils in China (Wang & Reardon, 2001), montmorillonite from Algeria (Ramdani et al., 2010) and fired clays. The various uses of red mud include but not limited to the following; construction and building materials, plastics, pigments and coating, ceramics and wastewater treatment. Different clay types from Algeria were investigated for their fluoride removal capacity by Ramdani et al. (2010), a higher percentage of calcium was found in one of the clays (AC) whereas the other was without

calcium (ANC). The Langmuir monolayer capacity between ANC and AC was 1.324 mg·g^{-1} and 1.013 mg·g^{-1} at an optimum pH 4 but both decreased at higher pH. The effectiveness of both thermal and chemical activation was studied. Thermal activation was less effective as adsorption reached only 5% whereas chemical activation was significantly effective as adsorption reached 88%. The study based on their findings concluded that interaction between the metal oxides at the surface of the montmorillonite and the fluoride ions was responsible for the chemical activation.

Puka (2004) stated that, when using clay as an adsorbent for fluoride removal, the structure of the clay is a major determining factor of the charge on the surface of the clay as well as the type of exchange that can occur with ions in solution. Positive surfaces favor the adsorption of negatively charged ions like fluoride ion and pH significantly affects the adsorption capacity because pH modifies the charge on the edges of the phyllosilicates and those with variable charged minerals such as gibbsites, hematite and goethite (Mandal & Mayadevi, 2008; Srimurali et al., 1998). Additionally, Onyango et al. (2004) researched the potential of zeolites for removing fluoride ions from aqueous solutions. They formed Zeolite F$^-$ 9 surface active sites through an exchange of Na$^+$-bound zeolite with Al^{3+} or La^{3+} because they have a good affinity for fluoride. Fluoride adsorption was affected by the solution of the PH and bicarbonate content because the bicarbonate buffered the PH of the solution to higher values and thus diminished the affinity of the active sites for fluoride sorption. Comparatively, Al^{3+} exchanged zeolites had better fluoride adsorption capacity than La^{3+}. By measuring pH at point of zero charges (pH$_{pzc}$), at pH< pH$_{pzc}$ and pH > pH$_{pzc}$ they observed that, the Na$^+$loaded zeolite carried a negative surface charge over all other pH values whereas the zeolite loaded with the trivalent ions completely showed different behavior.

Moreover, the pH$_{pzc}$ of the Al^{3+}-modified zeolite was 8.15 with positively charged Z-AlOH$_2^+$ at the surface. The positive surface charges were balanced by negative centers due to O-atoms and the hydroxylated aluminum ions (George et al., 2010). Comparatively when Al-exchanged zeolites were immersed in water, the amount of solid increased by 10% while the pH decreased from 5.7 to 5.2–5.32 further confirming that the surface charge was positive. However, when the unmodified zeolite was treated in the same way, the pH rather increased from 5.7 to 8.1–8.2 while the La^{3+} loaded pH increased to 7.6 also suggesting that the surface charge was negatively charged and perhaps received H$^+$ from the solution (Wajima et al., 2009; Zhao et al., 2012). The authors concluded that the Al-exchanged zeolite was by electrostatic attraction whereas the La^{3+}-exchanged zeolite was by chemical attraction. Three Tunisian clays (H, MK and ZB) were investigated for their capacity to remove fluoride ions from acidic solution (Hamdi & Srasra,

2007). Solid-liquid percentages (10, 20 and 30%) were used and equilibrium was reached within 48 h and MK clay had the highest adsorption of 10% for clay-lixiviate suspension. The adsorption isotherm of MK clay fitted well with the Langmuir model with a sorption capacity of 93.45 mg·g^{-1}. The report concluded that the MK and H clays showed superiority in fluoride adsorption than the ZB clay and adsorption was higher at lower pH.

Furthermore, clay minerals have been modified with several metal oxides for enhanced fluoride adsorption. For example, when laterite was subjected to sequential acid-based treatment; it improved its adsorption capacity due to increased surface area from 17.5 mg·g^{-1} to 178 mg·g^{-1} (Maiti et al., 2011). Again, a comparison was drawn between acid-activated kaolinite and raw kaolinite (Gogoi & Baruah, 2008). The acid-activated kaolinite had a higher adsorption capacity than the raw kaolinite with maximum adsorption of acid-activated kaolinite ranging between 0.0450 mg·g^{-1} and 0.0557 mg·g^{-1}. Tor (2006) also investigated the removal of fluoride ions from aqueous solution using montmorillonite treated with hydrochloric acid. Several factors such as the influence of pH, initial fluoride concentration, contact time and adsorbent dosage on adsorption were investigated and kinetic isothermic models were used for results interpretation. Vinati et al. (2015) undertook a state-of-the-art review on clay and clay minerals for fluoride removal from water. The authors based on previous works gave a comprehensive schematic diagram depicting the fluoride adsorption mechanisms by various minerals. Figure 12 below depicts the mechanism of fluoride adsorption by various clay minerals.
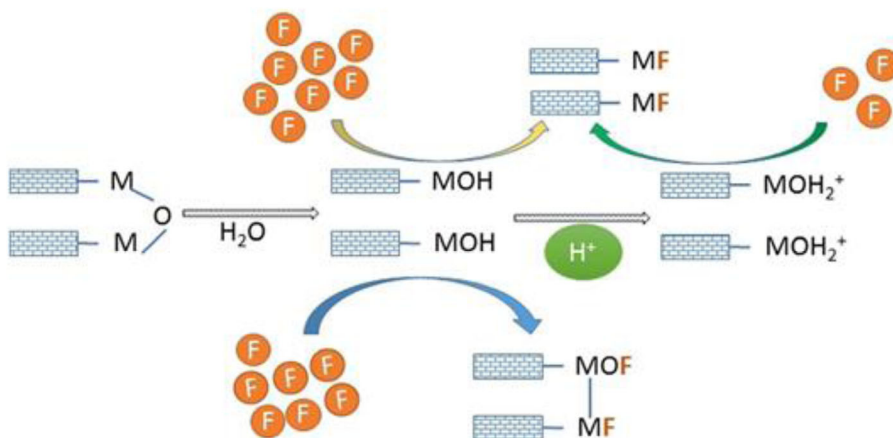
Figure 12. A comprehensive scheme showing the mechanism of fluoride adsorption by various clay minerals. Si, Fe or Al (mental oxides) are represented by M on clay mineral surface. They change form to metal hydroxides through hydrolysis and get further protonated to –OH$_2$. Only –OH$_2$ takes part in ligand exchange at low fluorine concentration. However, at high F concentration metal hydroxide can serve as an exchange site. [Reproduced from **Ref.** Vinati et al. 2015].

3. Conclusion and prospects

This paper has provided a comprehensive review of the adsorption method of treating fluorinated water using alumina and aluminum-based composites. Despite the numerous methods for fluoride removal, the adsorption method of water treatment continues to increase due to its numerous advantages such as relatively low-cost, accessibility of wide-ranges of adsorbents, limited secondary pollution to treated water, ease of operation of the plant and environmental friendliness. Also, evidence suggests that removal of fluoride by activated alumina and aluminum-based adsorbents is already an established technology which has been recognized by the WHO as one of the best demonstrated available technology for fluoride removal. In this paper, the activated alumina and aluminum-based composites have been classified under three major categories mainly based on their level of modifications for treating fluorinated water thus activated alumina, modified activated alumina and aluminum-based composites and finally raw alumina and aluminum-based composites/geomaterials. So far from the review, the following concluding remarks could be made

1. The adsorption technique of fluoride removal is a good-easy-to-operate method thus, one does not need high technical skills to operate the plant. Some modified adsorbents have shown high defluorination capacity ($450\,mg \cdot g^{-1}$) which can be guaranteed to meet the WHO MCL ($< 1.5\,mg \cdot L^{-1}$).

2. Alumina and aluminum-based adsorbents are generally preferable adsorbents for fluoride remediation because they are relatively inexpensive, easily accessible with limited/no secondary water pollution (color, odor and taste) potential for regeneration and environmental friendliness.

3. Activating the alumina and aluminum-based composites minimally (300–400 °C) saves cost and has the potential to increase their specific surface area ranging from 250 to $1000\,mg^{2} \cdot g^{-1}$. At this point, they become mesoporous with more adsorptive sites granting them the ability for higher adsorption efficiency.

4. Aside activation, modifying alumina and aluminum-based composites with materials such as cations, acids, bases, oxidizing agents and other rare-earth metals significantly improve their ability to remediate fluoride ions from water at a wider pH range (3–12), grant them larger surface area with good pore size and volume distribution.

5. Among the raw alumina-based sorbents, Raw bauxite has proven to be effective for remediating fluoride in its own right. Raw bauxite can remediate fluoride effectively at almost neutral pH (5.5–7.0) and 23 to 33 times less expensive than activated alumina which makes it practically applicable for rural communities and the resource-poor.

Therefore, using activated alumina alone for fluorinated water treatment is not enough because it has limitations such as narrow pH range and less adsorptive sites for chemisorption which does not grant higher removal efficiency unlike modified activated alumina and its composites.

Future studies should consider the use of locally available adsorbents that are effective and economically efficient so that local people can bear the cost on a large scale. Again, as part of safeguarding against cost, it would be worthwhile to study the suitability of different chemicals and modifying agents for regenerating the spent adsorbents. In furtherance, using activated alumina-based adsorbents alone is not enough, activated alumina should be modified with elements with a higher affinity for fluoride to ensure a higher adsorption rate since highly electropositive elements easily form preferential complexes with fluoride ion (F^-). In a nutshell, modeling studies should also be considered to correctly understand differential adsorption mechanisms for different adsorbents.

Authors contribution

Sikpaam Issaka Alhassan did conceptualization, formal writing of the manuscript, data curation and final revision and proof-reading on grammar, Lei Huang; revision, Yingjie He; revision, Lvji Yan; revision, Bichao Wu; revision and Haiying Wang; conceptualization, funding acquisition and proof-reading.

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