A mini update on fluoride adsorption from aqueous medium using clay materials

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ABSTRACT

The occurrence of fluoride ions in water is a common cause of contaminated drinking water. The chronic effects of fluoride on human health cause scientists to worry about its removal from wastewater. Although, many removal strategies have been developed, the adsorption process has proved to be a significant method in defluoridation and water treatment. The use of abundantly present natural materials as adsorbents is beneficial as they not only have the qualities needed to treat the water, but they are also economical and non-toxic. A variety of clay minerals have been tested and proved effective in the defluoridation of water. The present mini review is a brief update of the last seven years of literature on the adsorption properties of clay minerals in the fluoride removal process. This mini review highlights the sources and health effects of fluoride and discusses the effect of various factors on the fluoride removal process. The objective of this review is to take note of fluoride toxicity and its removal techniques. However, more research is still needed to utilize some important clay minerals for fluoride removal in a bid to decrease water pollution.

Keywords: Fluoride; Adsorption; Groundwater; Adsorption; Clays

1. Introduction

Fluorine, a chemical element, ranks 24th in universal abundance and is thirteen among the most common components present in the earth's core (rocks, clay, soils, and coal). Fluoride is the halide anion of fluorine which occurs in the form of sodium fluoride (NaF), hydrogen fluoride (HF), etc., whereas hydrofluosilicic acid (H_2SiF_6) and sodium silicofluoride (Na_2SiF_6) are commonly used to fluoridate water. As, it is present in the environment, living beings can easily be exposed to fluoride through food, water, and air. Fluoride is a normal constituent of the human body; an average human body has around 3 mg. Almost 99% of the body's fluoride is present in calci-fied tissues. Its most common use is in toothpaste where it is useful to prevent tooth decay. Fluoride is present in our diets, dental gels, drugs, beverages, and fluoride supplements. It can be introduced into the human body via water, toothpaste, and dietary supplements. Intake of fluoride in more than a desirable limit is toxic and results in various significant diseases, for instance,bone disorders, thyroid problems, dental fluorosis, infertility, Alzheimer's, arthritis, and even cancer [1]. The maximum acceptable limit for fluoride has been fixed by the European Union Council [2], the World Health Organisation [3], and the Bureau of Indian Standard [4] as 1.5 mg/L in drinking water. The safe limit for fluoride in drinking water is 1.0 mg/L in the U.S. [5]. Therefore, fluoride toxicity and diseases related to it are a global issue. There are many places in the world where the fluoride concentration in ground water—a source of water—is high. Abdominal pain, nau-

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sea, headaches, muscle weakness, hypoglycaemia, and cardiovascular effects are some of the common symptoms of acute fluoride poisoning. It is important to eliminate excessive fluoride ions in order to access good quality water. Many technologies have been used for the defluoridation and water treatment, such as ion exchange [6], precipitation [7], reverse osmosis [8], membrane processes [9,10], nanofiltration [11], electrodialysis [12], advanced oxidation processes [13], microemulsion [14], Nalgonda technique [15], pre-concentration [16], electrocoagulation [17–22], electrolytic defluoridation [23], and physiochemical [24]. Despite the availability of different technologies, adsorption process is the most monitored, famous, effective, reliable, inexpensive, common, uncomplicated, and significant method used extensively by researchers worldwide for the removal of fluoride as well as other pollutants [25–51] from aqueous solution. A great number of adsorbents including biomass [52], carbon-based materials [53], nanomaterials [54], industrial waste products [55], chitosan [56], magnetic adsorbents [57], plant materials [58], and solid waste [59] have been successfully used for defluoridation of aqueous solutions and have produced significant adsorptive results. However, the natural adsorbents have proved to contain effective potential defluoridation properties in both native and modified forms. Clay minerals are very effective because of their high surface area, and thus are extensively utilised to remove metal cations [60], organic compounds [61], dyes [62], insecticide [63] and pharmaceutical products [64] from aqueous solutions. The use of clay in water treatment has many advantages such as low cost, high pore volume, effectiveness, and high uptake capacity [65–68]; hence, they have been used for the defluoridation of water for decades. This mini review highlights the excellent adsorption performance and effects of clay materials and its minerals (alumina, calcium, magnesium, and double-layered hydroxide-based adsorbents) for defluoridation of a water solution.

2. Sources and effects of fluoride

Fluoride is a product of the earth. Fluoride contamination of water is mainly present in areas near mountains and seas. Sellaite (MgF_2), villianmite (NaF), fluorite or fluorspar (CaF_2), cryolite (Na_3AlF_6), bastnaesite $(CO_3)F$, and fluorapatite $Ca_{10}(PO_4)6F_2$, are the main fluoride-bearing minerals. The concentration of fluoride in seawater is approximately 1.2–1.4 mg/L, whereas in groundwater, it is 67 mg/L, and in surface water, it is less than 0.1 mg/L [69]. Sources of fluoride include dusts, gases, contaminated rock-phosphate fertiliser, industrialisation, smelting, water-rock interactions, kiln firing of clay products, urbanisation, the untreated discharge of wastewater, weathering, the combustion of coal, infiltration of rain water, farmland soil, feed supplements, forage crops,etc. Fluorite is one of the primary sources of fluoride in groundwater. A toxic level of fluoride ions, especially in groundwater, is because of crystalline rocks, granites,volcanic rocks, and cyclic evaporation that depends on the characteristic changes of wellsprings, soil, and rocks. Vegetables and fruits also contain low fluoride levels and according to Gupta et al. (2011), fluoride accumulation

in the vegetables of an Indian state was found to be high [70]. It was 26.94 mg/kg in coriander leaves, 24.37 mg/kg in marcellia, 15.26 mg/kg in beans, 14.46 mg/kg in brinjal, and 11.37 mg/kg in spinach leaves, whereas the average of fluoride concentration overall was 7.15 mg/kg. Fluoride deposits in seeds were found to be lower in comparison to other parts of the plant.

As fluoride is present in the environment and is a significant part of the biogeochemical cycle, living beings on earth can easily be exposed to it. A specific proportion of fluoride concentration is desirable, but above that, it becomes extremely toxic and has substantial effects on plants, animals, and human health. Table 1 summarises the maximum, minimum and average concentration value ranges in aqueous solutions from various countries [71–119]. Figs. 1a,b,c, and d show a bar diagram of the maximum acceptable value of fluoride concentrations in Africa, Asia, Europe, and other countries, respectively. Fig. 2 sketches the average fluoride values of various countries in a pie chart diagram.

The accumulation of fluoride inside the plant leaves takes place by root or foliar absorption, whereas in animals it occurs by ingestion [120]. In plants, the gaseous fluorine compound hydrogen fluoride (HF) is the most harmful and has been found to injure the plant species as fluoride-fumigated leaves contained more sugars and less sucrose than normal leaves [121]. Hydrogen fluoride can mix into the air through the combustion process in industry. The type of soil is also a factor for potential toxicity of fluoride on plants. However, fluoride uptake by roots depends on several factors. In one investigation, fluoride was not available to plants at a neutral pH as it bound to the soil surface, whereas in acidic conditions, fluoride showed the highest solubility in soil because of its complexation with aluminium. In alkaline conditions, there was desorption of free forms of fluoride ions because of repulsion by negative charges [122]. Aluminium fluoride complexes may also damage the plant growth by causing paling of leaves and brown tips; aluminium smelters and fertiliser industries are its sources. Fluoride has the capacity to move from the tip to the top of the leaf margins and can cause physiological, biochemical, and structural changes. It may also inhibit respiration processes, photosynthesis, and enzymatic activity, resulting in a decrease in chlorophyll, calcium, proline, and sugar content in plants.

The main source of fluoride toxicity in animals is atmospheric pollution. Animals who eat fluorine-rich plants absorb a large amount of fluorine into their skeletons. The characteristic symptoms of a high intake of fluoride in animals are alterations to the teeth, joints, and bones, along with the development of exostotic lesions, low birth weights, and thyroid hormone effects. The chronic effects of fluoride toxicity on cattle are quite similar to those on men, such as osteoporosis, rickets, weight loss, etc. Fluoride can become more toxic to aquatic animals and may lead to death for fish [123]. Fluoride appears to have a direct effect on the cells involved in enamel formation in rats [124].

The dental effects of fluoride are common in human beings. Choi et al. (2012) reviewed that increased fluoride in drinking water also caused neurodevelopmental delays [125]. Fluoride has both beneficial and harmful effects on teeth. It is beneficial to prevent dental decay, but excess amounts can result in dental fluorosis. Therefore, it is

Table 1
Ranges of fluoride concentration in groundwater of various countries

Country	Minimum concentration range	Maximum concentration range	Average value	References
Asia				
Japan	0.00	12.00	6.00	[71]
Thailand	0.01	14.12	7.07	[72]
Singapore	0.40	0.60	0.50	[73]
Malaysia	0.50	0.90	0.70	[74]
China	1.00	7.20	4.10	[75]
Hong Kong	0.48	0.69	0.59	[76]
South Korea	0.02	2.15	1.09	[77]
India	0.01	18.00	9.01	[78]
Nepal	0.06	1.92	0.99	[79]
Pakistan	0.11	22.8	11.46	[80]
Bangladesh	0.03	1.10	0.57	[81]
Sri Lanka	0.00	5.30	2.65	[82]
Iran	0.25	5.00	2.63	[83]
Iraq	0.00	1.00	0.50	[84]
Jordan	0.00	2.00	1.00	[85]
Kuwait	0.00	1.50	0.75	[86]
Palestine	0.00	1.00	0.50	[87]
Saudi Arabia	0.00	6.20	3.10	[88]
Turkey	0.05	13.70	6.88	[89]
UAE	0.04	0.17	0.11	[90]
Africa				
Algeria	0.40	4.32	2.36	[91]
Cameron	0.19	15.20	7.70	[92]
Egypt	0.00	10.00	5.00	[93]
Ethiopia	0.00	75.00	37.50	[94]
Ghana	1.50	4.00	2.75	[95]
Kenya	0.02	21.50	10.76	[96]
Malawi	0.50	7.02	3.76	[97]
Morocco	0.21	2.97	1.59	[98]
Niger	4.80	6.60	5.70	[99]
Nigeria	0.03	6.70	3.37	[100]
Senegal	0.40	2.85	1.63	[101]
Sudan	0.30	7.00	3.65	[102]
South Africa	0.70	1.00	0.85	[103]
Tanzania	10.50	46.00	28.25	[104]
Tunisia	0.00	3.39	1.70	[105]
Uganda	0.50	2.50	1.50	[106]
Europe				
Finland	0.70	1.80	1.25	[107]
Germany	0.00	8.80	4.40	[108]
Ireland	0.60	0.80	0.70	[109]
Italy	0.23	5.00	2.62	[110]
Norway	0.05	9.04	4.55	[111]
Poland	0.05	2.45	1.25	[112]
Spain	2.88	6.20	4.54	[113]
Sweden	0.10	15.00	7.55	[114]
North America				
Canada	0.00	3.30	1.65	[93]
Mexico	0.05	11.80	5.93	[115]
USA	0.00	4.00	2.00	[116]
South America				
Brazil	0.10	4.79	2.45	[117]
Argentina	0.80	4.20	2.50	[118]
Australia				
	0.60	1.10	0.85	[119]

essential to get rid of fluoride exposure from water. The adsorption process is effective for desalination [126–131] and fluoride removal from the water supply which, in turn, helps to reduce dental problems in the population.

This brief review apprises the findings of fluoride removal from aqueous solutions and features the effects of various factors on adsorption processes. This review presents an expeditious and systematic overview of past defluoridation studies.

3. The effect of various significant adsorption factors on defluoridation

3.1. Concentration

Some studies reported that within the studied range of fluoride concentrations, the amount of fluoride adsorbed (adsorption capacity of an adsorbent) on the clay minerals increases with an increasing concentration up to a certain extent and then reaches a plateau. This plateau is because at high initial concentration, the active adsorption sites become saturated [132]. Calcined meixnerite showed an increase in adsorbed fluoride with an increase in the initial concentration of the fluoride solution [133]. In another study, the adsorption capacity increased with an increase in fluoride concentrations, and finally reached an equilibrium. The adsorption capacity of $CaO_{20}@Al_2O_3$ was higher than Al_2O_3, as the existence of CaO enhanced the F^- removal capacity by forming insoluble CaF_2 [134]. Recently, the defluoridation capacity of commercial zeolite and natural stilbite increased from 2 to 6 mg/g with an increase in the initial fluoride concentration of 5 to15 mg/L because of the presence of increased fluoride ions per unit mass of the adsorbent. The adsorption capacity then remained constant after 20 mg/L [135]. The reason given by Mehta et al. 2016 for the rapid increase in the adsorption capacity at a higher concentration was the high driving force for fluoride adsorption [136]. After that, equilibrium was reached, and no more active sites were left on the surface of the marble waste powder. The maximum adsorption capacity of fluoride on kaolinite was enhanced from 82 mg/L to 122 mg/L when the initial concentration was increased from 0.05 mol/L to 0.1 mol/L. This may also be the result of a raise in the driving force of the concentration gradient.

Some studies however, have observed an opposite trend in which the percentage of fluoride removal decreases at higher concentrations. At high initial fluoride concentration, the binding sites are limited for F^- adsorption which results in a low percentage removal [137], whereas at low concentration, the large number of surface active sites are available for high interaction of F^- ions [138]. The result of one study showed that fluoride removal decreased with increasing initial F^- concentration and equilibrium reached at 10 mg/L. This may be a result of the restriction of total available adsorption sites at elevated concentration [139].

Alemu et al. 2014; however, found that there was no remarkable difference in the percent removal of fluoride on increasing the initial concentration of fluoride [140]. This indicates that the material (aluminium oxide–manganese oxide composite) could be used in a broad range of fluoride concentrations. Table 2 presents the results of various studies on the effect of the initial concentration on fluoride adsorption [141–151].
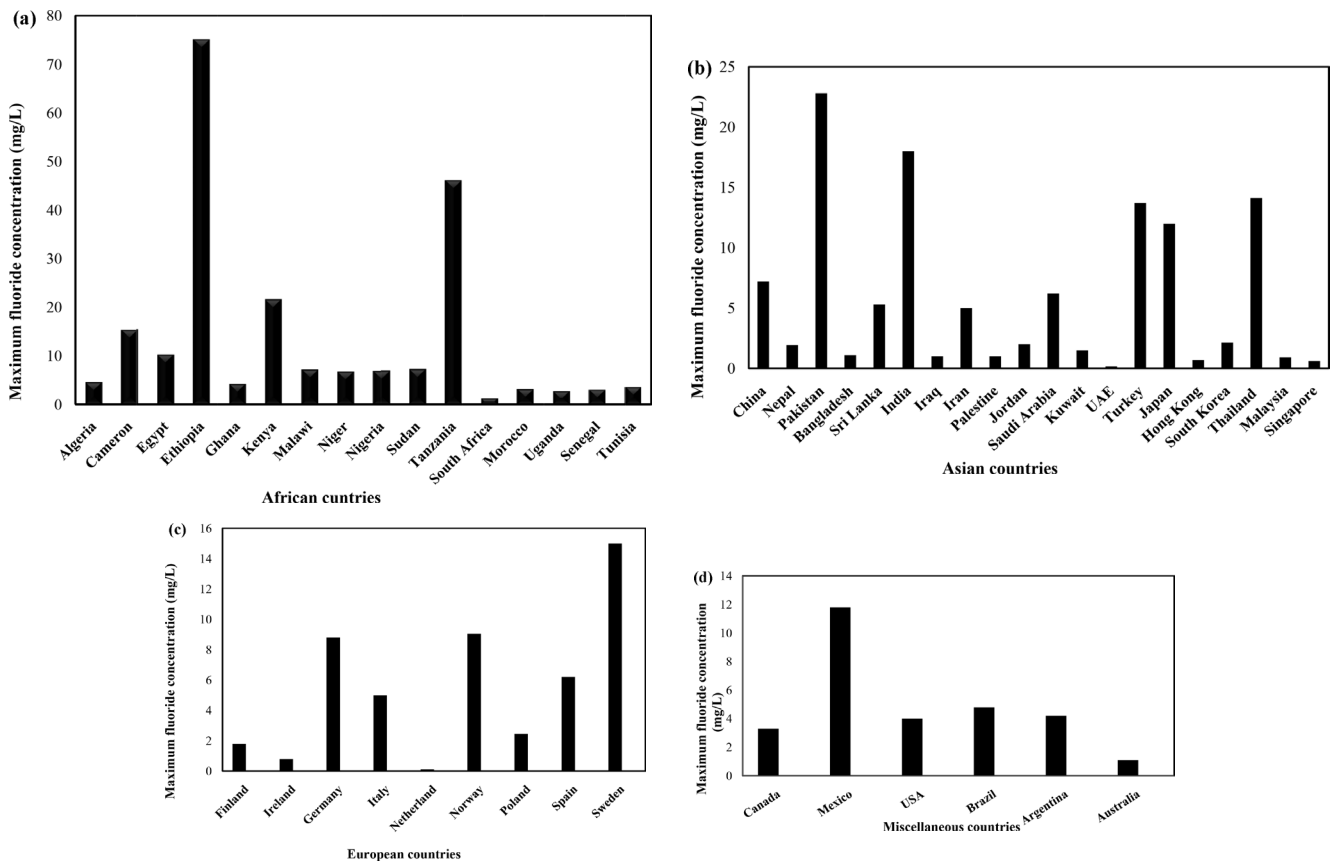
Fig. 1 (a) Maximum fluoride concentration in different (a) African countries, (b) Asian countries, (c) European countries, (d) other countries.

Table 2
The results of various reported studies on the effect of initial concentration on fluoride adsorption

| Adsorbents	Initial F-concentration range (mg/L)	Optimum F-concentration (mg/L)	% Removal	Maximum adsorption capacity (q_e)	References
Thermally Treated Bauxite	1–15	9.0	–	–	[141]
Magnesite-bentonite clay Hybrid	2–50	25.0	99	–	[142]
Anion clay (meixnerite)	12.4–248	75.0	95	–	[133]
Fe³⁺ modified bentonite clay	4–60	10.0–60.0	99.3	–	[143]
Chemically treated laterite	5–15	5.0	90		[144]
CaO loaded mesoporous Al_2O_3	1–1000	74.4	–	135.0	[134]
Smectite-rich clay soil	3–15	3.0	>60		[145]
Modified natural siderite	3–5	3.0	–	5.9	[146]
Calcium and aluminum modified zeolite	2–50	40.0	–	19.0	[52]
Diatomaceous earth	8–100	80.0	–	5.7	[147]
Magnesium-incorporated hydroxyapatite	2–20	20.0	–	2.0	[122]
Modified natural stilbite zeolite	5–40	30.0	–	8.3	[132]
Aluminum hydroxide supported zeolites	5–15	15.0	–	6.0	[135]
Marble waste powder	0–45	45.0	–	4.0	[136]
Ce–Zn binary metal oxide	10–50	50.0	–	55.0	[148]
Calcined Ca-Al-(NO₃) layered double hydroxide	0–50	50.0	–	45.0	[149]
Nepheline prepared from kaolinite	0.05–0.10	0.1	–	122.0	[150]
Synthetic siderite	3–20	20.0	–	0.8	[137]
Light Weight Expanded Clay Aggregate	5–20	20.0	–	3.0	[151]
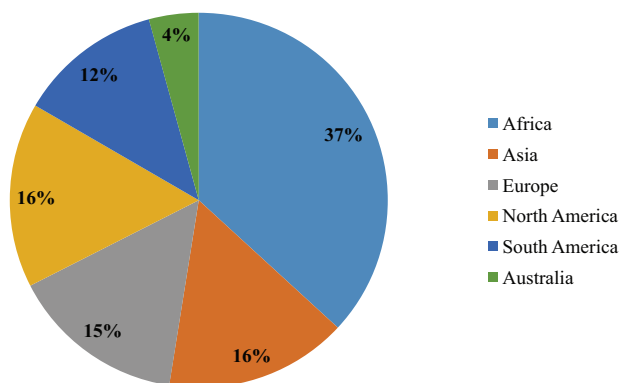
Fig. 2. Pie chart showing the average percentage of fluoride concentration in various countries.

3.2. Time

The effect of contact time is important in learning the binding process of fluoride ions and the time of equilibrium. Generally, the adsorption of fluoride in most studies is rapid and quickly reaches the equilibrium time. The rapid fluoride uptake may be regarded to a greater amount of vacant adsorption sites. It then slows down, however, after reaching the equilibrium. The 99% removal of fluoride from an aqueous solution took a short time (1–30 min.) to reach equilibrium [142,152]. The fluoride adsorption onto MnO_2 coated Na-bentonite was also rapid, and the optimum fluoride uptake was attained within 30 min [153]. It was also observed that with the smectite-rich clay soil, the percentage of F^- increased rapidly from 5 to 30 min, and then after 60 min, the system approached equilibrium [145]. The optimum time for the defluoridation of groundwater using Fe^{3+} modified bentonite clay was also 30 min [143]. The same rate of both adsorption and desorption was observed at 5–10 min. of contact time in one study. At 20 min, fluoride adsorption started to decrease because, at this time, desorption was faster than adsorption [147]. It was noticed that the high affinity of calcium aluminium mixed oxide was within 40 min [154]. The maximum number of fluoride ions was found to attach to Ca-SiO_2-TiO_2 when the contact time reached 70 min, and after that, the saturation point was reached due to the lack of availability of active sites [155].

The maximum efficiency of fluoride removal was 92% at 120 min equilibrium time [132]; this same period of contact time for fluoride removal was found using pyrolusite ore [152]. Contact times of 180 min [136,156] and 240 min [157,149] were also fixed as optimal times in other studies. Some studies, however, also concluded that a longer time (720 min) was needed to reach the equilibrium adsorption capacity [137,138]. Hence, the effect of contact time was not definitive but rapid in most studies.

3.3. Dose

The effect of an adsorbent dose on the adsorption process is a significant factor to find out the appropriate dose and maximum adsorption efficiency of the adsorbent. The common trend is that the percentage of fluoride removal increases with respect to an increase in dose because an increase in the adsorbent dose implies a higher surface area and a greater number of binding sites for fluoride adsorption. One study revealed that the percentage of fluoride removal sharply increased from 63.2% to 97.8% with an increase in adsorbent doses from 0.2 g/L to 1.0 g/L. The results were consistent with the theory of heterogeneous surface sites of oxide systems [158]. In another study, the fluoride removal percentage increased from 35.5% to 78.0% upon increasing the adsorbent dose from 4 g/L to 20 g/L [137]. The same result was obtained, and an optimum dose of 20 g/L was found in other studies also [144]. The removal percentage increased from 2.9% to 95.47% with an increase in the adsorbent dose of 0.2 g/L to 6.0 g/L of magnesium incorporated bentonite clay [138], but increased from 25.0% to 98.5% with increasing pyrophyllite doses from 0.05 g/L to 2.0 g/L [159] because of an enhanced number of active sites.

Some studies have also observed that initially the percentage of fluoride removal increased rapidly with an increase in the adsorbent dose up to a definite level, and then it became stable. The fluoride removal percentage increased from 20% to 90% with an increase in the dose, but when the adsorbent dose was more than 3 g/L, not much increase in fluoride removal was observed [134]. This may be because of a decrease in the effective surface area and the overlapping of active sites at higher doses [160].

A percentage removal of 85% at 1 g/L of calcium-aluminium mixed oxide dose was observed due to an increase in the active sites: fluoride ratio. After that, there was a less proportionate increase in fluoride adsorption [154]. However, in one study, it was also noted that the defluoridation efficiency of calcium impregnated silica decreased after an optimum adsorbent dose because the adsorbent's surface reached the saturation point with fluoride ions, and that there was no further adsorption because of repulsion [155].

In contrast, the adsorption capacity also decreased with an increase in the adsorbent dose; this may be the result of more active sites creating competition among the available adsorption sites [149]. The adsorption capacity of natural and acid-activated diatomite and ignimbrite materials decreased with an increase in the adsorbent dose [161]. The adsorption capacity of the pyrophyllite clay decreased from 1.41 mg/g to 0.31 mg/g with an increase in the doses from 0.05 g/L to 2.0 g/L [159]. However, the linear increase in the adsorption capacity for increasing the adsorbent dose of natural, H_2O_2, and $MgCl_2$ modified lightweight expanded clay aggregate indicated accessibility to a more adsorption sites at a higher dose to adsorb fluoride ions [151]. Fig. 3 highlights the maximum percentage of fluoride removal and optimum doses of clay materials.

3.4. pH

The pH of drinking water depends upon several parameters and sources. The initial pH of a solution affects the adsorptive capacity of the material as it changes the surface properties of the adsorbent. As a result, the pH of a solution is an important factor that influences the fluoride removal process. Many studies have concluded that maximum fluoride removal was around the neutral range of pH 6–7. The adsorption of fluoride turns out to be low in the more acidic (>3) and more alkaline (<7) ranges. The reason for this low adsorption behaviour is that at a low pH, i.e.
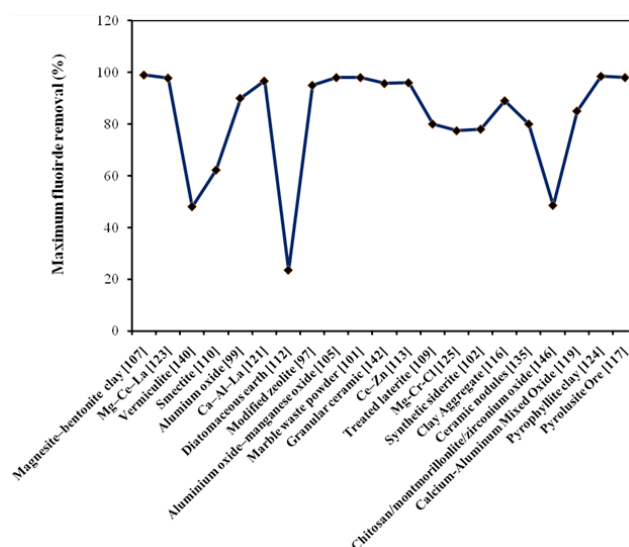
Fig. 3. Maximum percentage removal of F⁻ and optimum doses of clay materials.

acidic conditions, fluoride ions are partially protonated by forming weak hydrofluoric acid (HF), whereas at a higher pH, i.e. alkaline conditions, hydroxyl ions (OH⁻) form and come into the solution to compete with F⁻ in binding with adsorbent surface sites.

The rapid and high percentage removal of fluoride ions (92.7%) was at a pH value of 7 when using activated dolomite [162], but after this pH, the rate of adsorption slowed down because of competition between OH⁻ and F⁻ for surface adsorption. Li et al. (2017) observed the same results recently as they removed fluoride from liquid phase by an adsorbent prepared from red mud [163]. In another study, the optimum pH value was also found to be 7.0, where magnesium-incorporated hydroxyapatite removed 95.5% of fluoride ions from drinking water [139]. The optimum pH value for F⁻ adsorption onto natural diatomite was found to be 7.5, which then decreased and reached zero at a pH value of 9 [164]. A high crystalline natural zeolite with an open pore system was modified to remove fluoride from drinking water. The maximum adsorption capacity was at a pH value of 6.94 and then slightly decreased above a pH value of 8.05 [132]. Sepehr et al. used a lightweight expanded clay aggregate (LECA) for fluoride removal and found that the maximum fluoride removal yield was at pH 6 [151]. Porous granular ceramic adsorbent was synthesised and the fluoride adsorption on it increased with the increasing pH. Adsorption attained a maximum level at a pH value of 6 [165]. The obtained result agrees with another recent fluoride removal study in which the maximum adsorption capacity was obtained at pH 6 [148]. However, Kofa et al. used fire clay pots and found that the maximum F⁻ adsorption was at a pH value of 5 [166].

The clay adsorbents allied with alumina, which is the main constituent of the clay mineral, also removed fluoride ions from an aqueous solution mainly at a neutral pH. This is because, in a weak acidic environment, alumina favours fluoride adsorption. The reason for this behaviour can also be explained by pHzpc values. The pH at which the adsor-

bent surface obtains neutral charge is termed as zero-point charge or point of zero charge. The pHzpc of ionic liquid modified alumina was found to be 7.4, which indicates that the adsorbent surface was positive below pHzpc and negative above pHzpc [167]. The favourable pH range for maximum fluoride removal on the Al(III) floc of 83% was observed at a pH value of 7.2, but it shifted to slightly more acidic (5.4–6.9) on the Al(III)–Fe(III) mixture flocs [168]. The adsorption of fluoride on aluminium oxide–manganese oxide composite material was at its maximum (96.4%) at pH values between 5–7 because of the presence of positive sites on the adsorbent's surface [140]. One study also confirmed that the natural clay removed the maximum level of fluoride ions at 6 pH after modification with lanthanum and aluminium. However, at a higher pH, hydroxyl ions competed with fluoride ions for alumina exchange sites [169]. The maximum fluoride removal by an aluminium salt-based adsorbent was observed at pH 7.4, and after that, precipitation started at pH 7.5 [168]. The fluoride adsorption onto amorphous aluminium hydroxide was also maximal at a pH of 7.0 [169]. It is clear from the above results that the ion exchange took place between the surface hydroxyl groups and fluoride ions in the solution which played the predominant role in the adsorption process [169].

The adsorption capacity of some clay-based adsorbents proved to have better practical application potential as it was found in some reported studies that the fluoride adsorption was excellent in a wide range of pH values ranging from 4 to 10. In a recent study, ceramic nodules from India were prepared and it was demonstrated that the adsorption efficiency sharply decreased below a pH of 4.0 and above a pH of 10.0 [170]. Fluoride removal capacity reached above 90% upto a pH value from 3.0 to 8.0 [158]. The adsorption of fluoride on aluminium oxide (Al_2O_3) almost remained the same within pH 4 to 9 [34]. Modified magnetite adsorbed maximum fluoride ions between pH 4 and 10 [171]. The fluoride adsorption capacity of modified natural siderite remained almost constant at a wide range of pH values ranging from 3.5 to 10.0; the pH of the solution had no major influence on fluoride removal [137]. A composite proved its capability to remove extra fluoride from underground water. The high adsorption of fluoride was noted in this study, as the removal efficiency of the adsorbent was more than 99% from pH 2 to 12 [142].

The opposite behaviour of a pH solution on fluoride adsorption, however, was also noted. Laterite, a hard reddish clay material, was chemically treated for the adsorption of fluoride [172], and it was found that the adsorption increased with a decrease in the pH solution value from 9 to 3. This may be the result of positive surface charge at low pH, so negatively charged fluoride species were adsorbed easily by electrostatic attraction force. It was also reported that because of the change in surface charges of hydroxyapatite powders, the maximum F⁻ adsorption was achieved at a low pH of 3.0 [173]. Table 3 reports the optimum pH of solutions for fluoride adsorption.

3.5. Temperature

Temperature effect is an important physiochemical process that is usually described by thermodynamic parameters at different temperatures. Most studies

Table 3
The effect of solution pH on the adsorption of dyes by different clay materials

Adsorbents	pH range	Optimum pH value	% Removal	References
Thermally Treated Bauxite	2–8	5.0	95.2	[141]
Mukondeni clay soils	2–12	2.0	45.0	[174]
Magnesite-bentonite clay hybrid	2–12	2.0–12.0	99.0	[142]
Mg–Ce–La adsorbent	3–10	3.0–8.0	97.5	[158]
Activated dolomite	6–10	7.0	92.5	[162]
Vermiculite Functionalised with Cationic Surfactant	2–12	4.0	51.1	[175]
Smectite-rich clay soil	2–12	2.0	92.0	[145]
Ca–Al–La composite	3–11	6.8	96.65	[156]
Zeolite	3–11	4.0–8.0	96.0	[52]
Fe^{3+} modified bentonite clay	2–12	2.0–10.0	100.0	[143]
Diatomaceous earth	2–12	2.0	23.4	[147]
Magnesium-incorporated hydroxyapatite	3–11	7.0	94.5	[139]
Aluminium oxide–manganese oxide composite	3–5	5.0	96.4	[140]
Marble waste powder	3–10	7.0	97.6	[136]
Porous granular ceramic	2–11	6.0	89.3	[165]
Hydroxyl aluminum oxalate	2–11	6.5	75.9	[176]
Granular ceramic	1–12	5.0–8.0	88.6	[177]
Chemically treated laterite	3–9	7.0	89.2	[144]
Mg-Cr-Cl layered double hydroxide	6–12	7.0	88.5	[160]
Lanthanum modified magnetite	2–12	4.0–10.0	94.6	[169]
Nanomagnesia/alumina	2–11	6.3–7.3	85.0	[178]
Light Weight Expanded Clay Aggregate	2–10	6.0	79.4	[151]
$Ca\text{-}Zn(OH)_2CO_3$	2–12	7.0	98.0	[179]

reported that the adsorption capacity increased with an increase in temperature up to a certain level, and then it decreased upon a further increase in temperature. One study observed that the adsorption capacity of treated palygorskite adsorbent increased with an increase in temperature from 100°C to the optimal thermal-treated temperature of 300°C due to an increase in BET surface area. After that, the adsorption capacity decreased over 300°C. This may be because at the higher temperature, hydroxyl water is lost and pores become saturated [180]. The same result was obtained when the defluoridation efficiency of calcium-impregnated silica combined with titanium dioxide increased from 300K to 320K. It was then decreased by increasing the accumulation of F⁻ on the adsorbent's surface because of the attractive force between fluoride ions [155]. These results are supported by some from recent research. An optimal temperature for the highest fluoride removal onto river soil was found to be 343K; above that, removal efficiency decreased slowly. This may be because of breakage of the complex at higher temperatures. In another study, 90% of defluoridation was observed from 293 K to 323K; the optimum temperature for defluoridation was 340K, which then decreased at temperatures up to 773K [158].

In some studies, the adsorption was of an endothermic nature. In one study, the adsorption of fluoride increased from 77 mg/g at 298K to 129 mg/g at 323K [150]. The adsorption capacity of chitosan/montmorillonite/ZrO_2 nanocomposite increased from 22.5 mg/g to 25.0 mg/g

with an increase in temperature from 30°C to 50°C [181]. The percentage removal of fluoride on layered double hydroxide showed a sharp increase from 78.2% to 90.2% and from 65.8% to 80.8% with an increase in temperature [160].

The exothermic adsorption process was also noted, however, as fluoride removal was higher at low temperatures. Of the temperatures studied (298–333 K), the maximum fluoride removal was obtained at 298K in one study [161]. Table 4 shows the effect of temperature on the adsorption of fluoride.

3.6. Co-ions

The effect of various coexisting ions on fluoride adsorption is important to study. Many coexisting ions such as chloride, nitrate, sulphate, carbonate, bicarbonate, etc. are commonly exist in water and may affect the adsorption procedure by creating competition with fluoride ions for available surface sites on clay minerals. It has been determined in many studies that co-ions significantly affect the fluoride removal. These coexisting ions create competition with F⁻ on the adsorption surface sites and decrease fluoride removal. The percentage of fluoride removal on stilbite zeolite (STI) was affected and decreased with an increase in the concentration (over 500 mg/L) of coexisting ions (chloride, nitrate, sulphate, carbonate, and bicarbonate) [132]. The adsorption capacity of magnesium-incorporated hydroxyapatite was reduced by increasing anion (chloride, sulphate, nitrate, and phosphate ion) concentrations of 300 mg/L, but the

Table 4
The effect of temperature on the adsorption of fluoride using various clay materials

Adsorbent	Temperature range (K)	Optimum temperature (K)	Type of process	Thermodynamic parameters [$\Delta H°$ (kJ/mol), $\Delta S°$ (J/mol K), $\Delta G°$ (kJ/mol)]	References
Mg–Ce–La	293–323	293–303	Endothermic	3.89, 24.02, –3.84	[158]
Mg-Al-Zr	292.5–322.5		Endothermic	4.75, 59.61, –12.68	[182]
Modified Zeolite	293–313	293	Endothermic	0.007, 13.74, –4.01	[52]
Mg-Al-CO$_3$	288–318	318	Endothermic	25.78, 141.27, –14.45	[183]
Chemical treated laterite	288–315	315	Endothermic	27.80, 0.18, –26.30	[172]
Hydroxyl aluminum oxalate	298–328	328	Endothermic	11.55, 93.36, –19.07	[176]
Ionic liquid-functionalized alumina	293–353	293	Exothermic	–11.96, –, –424.04	[167]
Amorphous aluminum hydroxide	298–318	293	Exothermic	–34.14, –68.51, –13.81	[169]
Nepheline prepared from kaolinite	313–323	323	Endothermic	15.99, 0.09, –12.51	[150]
Ca-SiO$_2$-TiO$_2$	300–343	333	Endothermic	59.43, 249.23, –,	[155]
Synthetic mesoporous Alumina	298–313	298	Endothermic	13.79, 0.048, –0.683	[184]
Nano Calcium-Aluminum Mixed Oxide	323–343	–	Endothermic	6997.86, 18.18, –12507.48	[154]
Polymer/montmorillonite composites	313–323	313	Endothermic	13, 34, 2.84	[185]
Pyrophyllite clay	298–318	298	Endothermic	15.95, 70.25, –4.99	[159]

bicarbonate ions reduced the fluoride adsorption even at lower anion concentrations [139]. The same result was observed in another study which concluded that the presence of some anions enhances Coulomb's repulsion forces between two charged bodies and affects fluoride removal efficiency [178]. These observations were recently corroborated by some studies when the fluoride removal on Mn^{2+}-intercalated bentonite was slightly affected by the presence of coexisting ions. The effect of co-ions was in the order of NO$_3^-$ > Cl$^-$ > SO$_4^{2-}$ > CO$_3^{2-}$ [153], and the percentage of fluoride removal on natural pyrolusite decreased from 93.1% to 25.0% upon an increase in the concentration of coexisting ions (sulphate, chloride, and nitrate) [152]. The presence of all anions decreased the fluoride removal efficiency of ceramic nodules by 46.97% [170].

It was also found that an increase in chlorine, sulphate, and nitrate concentrations slightly influenced fluoride adsorption, but an increase in carbonate and bicarbonate decreased fluoride removal from 97.5% to 47.5% [158,176]. This result can be supported by recent research in which the fluoride removal percentage on MnO$_2$-coated Na-bentonite decreased by 24% in the presence of Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ and decreased by 50% in the presence of CO$_3^{2-}$ [153].

Some studies also noted that the presence of chloride, sulphate, and nitrate had no effect on fluoride removal even at high concentrations, but the presence of phosphate, carbonate, and bicarbonate reduced fluoride adsorption. The presence of HCO$_3^-$ and PO$_4^{3-}$ showed a negative effect and reduced the fluoride adsorption onto modified natural siderite and onto amorphous aluminium hydroxide [169],

but there was no effect for other anions (Cl$^-$, SO$_4^{2-}$, NO$_3^-$) on fluoride removal. Another recent study observed the same result for removing the fluoride from groundwater using modified alumina [167]. Recently, Dessalegne et al. also obtained the same result when studying F$^-$ removal from drinking water on aluminium hydroxide supported zeolites [135].

It was also noted that among the co-ions, PO$_4^{3-}$ caused the greatest decrease in fluoride removal, as demonstrated in many studies. The reduction in fluoride adsorption was from 96.65% to 50.10% when the concentration of PO$_4^{3-}$ was increased from 0 mg/L to 80 mg/L [156]. The adsorption capacity of Mg-Al-CO$_3$ hydrotalcite for fluoride adsorption decreased in the order of PO$_4^{3-}$ > SO$_4^{2-}$ > Cl$^-$ [183]. The same order was observed in some another studies [137,160]. In a recent study the fluoride removal efficiency of fungus hyphae-supported alumina (FHSA) decreased in the order of PO$_4^{3-}$ > SO$_4^{2-}$ > Cl$^-$ > Br$^-$ > NO$_3^-$ [186].

Some different results, however, were also observed. For example, the effect of NO$_3^-$, SO$_4^{2-}$, and HCO$_3^-$ had very little influence, and Cl$^-$ did not affect fluoride removal when using CaO loaded mesoporous Al$_2$O$_3$ [134].

In contrast, some studies noted the positive effects of coexisting ions. Fluoride adsorption increased in the presence of nitrate, chloride, and sulphate ions using chemically treated laterite [172]. In another study, the fluoride adsorption onto granular ceramic increased to a small degree in the presence of chloride and nitrate ions [177]. A slight increase in F$^-$ removal onto porous granular ceramic may be due to an increase in the ionic strength of the solution [165].

4. Adsorption models for fluoride uptake

4.1. Isotherm

The various adsorption isotherm models (Langmuir, Freundlich, D-R, Temkin, Sips, Redlich-Peterson, Toth) are significant to explain the interaction of the adsorbent with the adsorbate in bulk solution. They are not only helpful to calculate the adsorption capacity of the adsorbent but also in understanding the mechanism of adsorption onto the surface phase. The analysis of experimental data by fitting it to the different adsorption isotherm models is an important procedure to find out the suitable adsorption isotherm and the adsorption phenomena. There are many isotherm models which have been used by researchers, but the Langmuir and Freundlich models are the most widely used to describe the adsorption isotherm of fluoride adsorption onto the clay. The Langmuir model [187] suggests that the adsorption occurs on a homogenous surface by forming a monolayer of fluoride. The linear form of the Langmuir model equation is as follows:

$$\frac{1}{q_e} = \frac{1}{q_m \times b} \times \frac{1}{C_e} + \frac{1}{q_m} \tag{1}$$

where equilibrium concentration of fluoride corresponds to C_e, adsorbed fluoride amount per unit weight of adsorbent corresponds to q_e, fluoride amount to form monolayer corresponds to q_m, and the energy constant of the adsorption corresponds to b.

The Freundlich model [188] suggests the adsorption of fluoride onto a heterogeneous surface. The linear form of the Freundlich model equation is as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{2}$$

where equilibrium concentration corresponds to C_e, and the amount of fluoride adsorbed per unit of adsorbent's weight corresponds to q_e. K_f is the Freundlich constant and n is the heterogeneity factor.

Both the linear and nonlinear forms of the Langmuir and Freundlich equations commonly correlated the adsorption of fluoride ions onto the clay materials. The analysis of equilibrium data by isotherm models describes the quantitative results and adsorption mechanism. The different isotherm parameters, R-squared coefficient of determination, R_L values, and error findings were determined in all the studies and then the best-fit model was determined by the higher R^2 and lesser error values. As mentioned above, the Langmuir isotherm generates monolayer formation related to adsorption on homogenous surfaces, whereas the Freundlich equation is valid for adsorption onto a heterogeneous surface. In some studies, both models represented the adsorption of fluoride ions onto the clay equally well [158,165,168,172,189]. However, in most studies, one of these two models could better describe the adsorption process. The Langmuir equation better describes fluoride adsorption onto clay materials by monolayer formation on a homogenous surface [132,135,139,142–145,150,154–156,160,163,169,171,178,180–183,190–193]. In other studies, however, the Freundlich isotherm was better fitted to the experimental data, based on higher R^2 values. These find-

ings indicate multilayer adsorption on the clay surface [136, 137,140,146,147,151,158,160,167,170,173,175,177,184,194,195]. Table 5 presents the list of applicable isotherm models and maximum adsorption capacities (mg/g) of clay materials for fluoride adsorption.

4.2. Kinetics

The kinetics process is important to understand the practical application of clay minerals. The kinetics of fluoride adsorption describes the adsorption rate which is important in designing the adsorption system. Pseudo-first order [200] and pseudo-second order [201] are the most studied adsorption kinetics of fluoride adsorption onto clay minerals.

The pseudo-first-order model equation is as follows:

$$\log(q_e - q_t) = -\left(\frac{K}{2.323}\right) \times t + \log q_e \tag{3}$$

where fluoride adsorbed per unit weight of the clay corresponds q_e, F⁻ adsorption at given time corresponds to t, and rate constant corresponds to K_1.

The equation of pseudo-second-order adsorption kinetics is as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 \times q_e^2} + \frac{1}{q_e} \times t \tag{4}$$

where the adsorption rate constant corresponds to K_2.

The kinetic data were also analysed using the intraparticle diffusion model [202] to clarify the diffusion mechanism which is as follows:

$$q_t = K_{id} \times t^{1/2} + I \tag{5}$$

where an intraparticle diffusion rate constant corresponds to K_{id}, and the amount of F⁻ adsorption at time (min) corresponds to q_t.

Most studies have concluded that adsorption followed the second-order reaction which suggests that adsorption was occurring via chemisorption or valence forces. Some of the studies concluded that adsorption followed the first-order reaction which means that the reaction is more likely due to physisorption or van der Waals forces. In some studies, adsorption followed the intraparticle diffusion process [134,157] and in others, it followed the intraparticle process along with the second-order reaction [102,136,138,142]. Table 6 presents the parameters of kinetic studies and applicable kinetic models for fluoride adsorption by various clay materials.

5. Conclusion, analysis and future research

Clay materials have large pores on their surfaces that can adsorb toxic fluoride ions present in an aqueous solution. Fluoride can easily insert into and be adsorbed on the space between the layers of clay minerals. Both the modified and unmodified forms of clay materials have excellent properties for fluoride extraction. Adsorption is a low-cost and important process which is used for the defluoridation of water. Batch adsorption technique is mostly used

Table 5
Applicable isotherm models and maximum adsorption capacities q_m (mg/g) of clay materials for fluoride adsorption

Adsorbent	Isotherm model	Maximum adsorption capacity (q_m) (mg/g)	Experimental conditions	References
Magnesite-bentonite clay Hybrid	Langmuir	10.00	Contact time: 30 min, Concentration: 25 mg/L, pH: 2–10, Temperature: 30°C, Dose: 0.5 g	[142]
Kaolinite	Freundlich	1.57	Contact time: 30 min, pH: 5, Dose: 2.0 g	[160]
La-doped Pyrolusite ore (LDPO)	–	9.43–12.82	Contact time: 120 min, Concentration: 10 mg/L, pH: 6, Temperature: 25°C, Dose: 0.1 g	[152]
Fe-Al-La trimetal hydroxides	Langmuir	74.07	Contact time: 240 min, Concentration: 4–16 mg/L, pH: 6.8, Temperature: 25°C, Dose: 0.1 g	[163]
Mg–Ce–La	Freundlich	6.44	Concentration: 10 mg/L, pH: 5–6, Temperature: 30°C, Dose: 1.0 g	[158]
Heat activated dolomite	Freundlich	1.74–227.18	Contact time: 5 min, Concentration: 5–500 mg/L, pH: 7, Dose: 2.0 g	[162]
Red mud sintered porous materials	Langmuir	0.50	Contact time: 60 min, Concentration: 1–100 mg/L, pH: 3, Temperature: 15°C, Dose: 2.0 g	[196]
Vermiculite Functionalised with Cationic Surfactant	Freundlich	2.36	Contact time: 70 min, Concentration: 8 mg/L, pH: 6, Temperature: 25°C, Dose: 2.0 g	[175]
Mg-Al-Zr	Langmuir, Freundlich	22.90	Contact time: 360 min, Concentration: 50 mg/L, pH: 7, Temperature: 25°C, Dose: 1.0 g	[182]
Smectite-rich clay soil	Langmuir	0.58	Contact time: 30 min, Concentration: 3 mg/L, pH: 5.5, Temperature: 25°C, Dose: 2.0 g	[145]
Modified natural siderite	Freundlich	3.68	Concentration: 2–25 mg/L, pH: 6.8, Temperature: 15°C, Dose: 0.5 g	[146]
CaO loaded mesoporous Al_2O_3	–	136.99	Contact time: 30 min, Concentration: 30 mg/L, pH: 6.8, Temperature: 30°C, Dose: 3.0 g	[134]
Ca–Al–La	Langmuir	29.30	Contact time: 180 min, Concentration: 10–50 mg/L, pH: 6.8, Temperature: 30°C, Dose: 1.0 g	[156]
Modified Zeolite	Langmuir	8.03	Contact time: 360 min, Concentration: 10 mg/L, pH: 4–8, Temperature: 25°C, Dose: 3.5 g	[52]
Fe^{3+} modified bentonite clay	Langmuir	2.91	Contact time: 30 min, Concentration: 4–60 mg/L, pH: 5.3, Temperature: 26°C, Dose: 2.0 g	[132]
Diatomaceous earth	Freundlich	0.65	Contact time: 30 min, Concentration: 8 mg/L, pH: 2, Temperature: 30°C, Dose: 8.0 g	[147]
Fe(III)-Stilbite zeolite	Langmuir	2.31	Contact time: 120 min, Concentration: 10 mg/L, pH: 6.94, Temperature: 30°C, Dose: 10.0 g	[132]
Chemical treated laterite	Langmuir, Freundlich	36.30	Contact time: 120 min, Concentration: 3–50 mg/L, pH: 6.7, Temperature: 15°C, Dose: 0.5 g	[172]
Zeolite-AO composite	Langmuir	12.12	Contact time: 180 min, Concentration: 10 mg/L, pH: 5–8, Temperature: 23°C, Dose: 2.0 g	[135]
Modified clay	Langmuir	1.30	Contact time: 1200 min, pH: 6, Temperature: 10°C, Dose: 1.0 g	[169]
Marble waste powder	Freundlich	5.25	Contact time: 180 min, pH: 7, Temperature: 30°C, Dose: 2.0 g	[136]
Iron and aluminum leaching from red mud	Langmuir	74.07	Contact time: 240 min, Concentration: 4–16 mg/L, pH: 6.8, Temperature: 25–35°C, Dose: 0.1 g	[163]
Mn–La bimetal composite	Langmuir	292.90	Contact time: 480 min, Concentration: 1–100 mg/L, pH: 5–7, Dose: 0.01 g	[192]
Porous granular ceramic	Langmuir, Freundlich	1.79	pH: 6, Temperature: 25°C, Dose: 2.0 g	[165]
Ionic liquid-functionalized alumina	Freundlich	25.00	Contact time: 60 min, Concentration: 30 mg/L, pH: 5–9, Temperature: 30°C, Dose: 0.2 g	[167]

(*Continued*)

Table 5 (*Continued*)

Granular ceramic	Freundlich	0.98	Concentration: 5–50 mg/L, pH: 6.90, Temperature: 30°C	[177]
Amorphous aluminum hydroxide	Langmuir	63.40	Contact time: 120 min, Concentration: 5–200 mg/L, pH: 7, Temperature: 25°C	[197]
Nepheline prepared from kaolinite	Langmuir	183.00	Contact time: 60 min, Concentration: 5–200 mg/L, pH: 5–5.5, Temperature: 50°C,, Dose: 0.1 g	[150]
Synthetic siderite	Freundlich	1.71	Contact time: 480 min, Concentration: 3–20 mg/L, pH: 6.86, Temperature: 25°C, Dose: 0.2 g	[137]
Modified natural magnetite with Al	Langmuir	1.42	Concentration: 1–30 mg/L, pH: 7.80, , Dose: 0.1 g	[171]
Modified natural magnetite with La	Langmuir	1.51	Concentration: 1–30 mg/L, pH: 7.80, , Dose: 0.1 g	[171]
Modified bentonite	Langmuir	2.26	Contact time: 720 min, Concentration: 15 mg/L, pH: 3–10, Temperature: 25°C,, Dose: 3.0 g	[138]
Al-modified hydroxyapatite	Langmuir	32.57	Concentration: 50 mg/L, pH: 7, Temperature: 25°C, Dose: 0.05 g	[198]
Nanomagnesia/alumina adsorbent	Langmuir	6.50	Contact time: 140 min, Concentration: 5–30 mg/L, pH: 7, Temperature: 25°C, Dose: 0.5 g	[178]
Light Weight Expanded Clay Aggregate	Freundlich	8.52	Contact time: 300 min, Concentration: 5–20 mg/L, pH: 7, Temperature: 25°C, Dose: 6.0 g	[151]
$MgCl_2$ - modified LECA	Freundlich, Langmuir and Temkin	23.86	Contact time: 300 min, Concentration: 5–20 mg/L, pH: 7, Temperature: 25°C, Dose: 6.0 g	[151]
H_2O_2 modified Light Weight Expanded Clay Aggregate	Freundlich, Langmuir and Temkin	17.83	Contact time: 300 min, Concentration: 5–20 mg/L, pH: 7, Temperature: 25°C, Dose: 6.0 g	[151]
Calcium impregnated silica combined with TiO_2	Langmuir	37.23	Contact time: 70 min, Concentration: 50 mg/L, Temperature: 40°C, Dose: 0.1 g	[199]
Chitosan/ montmorillonite/ZrO_2 nanocomposite	Langmuir	23.00	Contact time: 60 min, Concentration: 20 mg/L, pH: 4, Temperature: 30°C, Dose: 0.1 g	[181]
Synthetic mesoporous Alumina	Langmuir	12.00	Concentration: 20 mg/L, pH: 6, Temperature: 25°C, Dose: 1.0 g	[184]
Nano-hydroxyapatite/ stilbite composite	Freundlich	4.02	Contact time: 720 min, Concentration: 2–200 mg/L, Temperature: 23°C, Dose: 10.0 g	[199]
Nano Calcium-Aluminum Mixed Oxide	Langmuir	23.70	Contact time: 40 min, Concentration: 4–34 mg/L, pH: 4, Temperature: 25°C, Dose: 1.0 g	[154]
Alum-bentonite	Langmuir, Freundlich	5.70	Contact time: 30 min, Concentration: 60 mg/L, pH: 2–12, Temperature: 26°C, Dose: 1.0 g	[189]
Aluminum-coated bauxite	Langmuir	5.62	pH: 7, Temperature: 20°C, Dose: 1.0–20.0 g	[191]

to conduct fluoride adsorption experiments, as reported in almost all studies. The effects of important factors such as pH, time, temperature, dose, coexisting ions, and concentration were tested in the adsorption process. The adsorption mechanism and rate have been determined using the adsorption isotherm, kinetic and thermodynamic studies. The tremendous results of the reported studies and the high adsorption capacity proves the applicability of clay materials in removing excess fluoride.

One perspective can be purposed that there is less information in the literature, however, on the utilization of many potential raw forms of clay minerals such as the smectite group, vermiculite, goethite, bentonite, and kaolinite. The use of these important clay minerals has been extensively studied in the removal of toxic metal ions, organic pollutants, dyes, etc., for many years and more research is needed that focuses on using clay for the defluoridation of water. Future research should present the use of advanced characterisation techniques and modification methods. The synthesis of nanoclay hybrid composite is a novel area of research which should be explored further. Statistical analysis of experimental data is quite common nowadays and can be observed in upcoming papers concerning fluoride removal. Regeneration, desorption, and column studies

Table 6
Parameters of kinetic studies and applicable kinetic model for fluoride adsorption by various clay materials

Adsorbent	Pseudo first order kinetic parameters K_1 (1/min), R^2	Pseudo second order kinetic parameters K_2 (g/mg min), R^2	Applicable kinetic model	References
Magnesite-bentonite clay	1.02, 0.85	2.60, 1.00	Pseudo-second order	[142]
Fe-Al-La trimetal hydroxides	0.01, 0.98	6.87×10^{-4}, 0.99	Pseudo-second order	[163]
Ceramic nodules	0.002, 0.818	0.012, 0.998	Pseudo-second order	[170]
Mg-Al-Zr	0.019, 0.863	0.003, 0.937	Pseudo-second order	[181]
Vermiculite functionalised with cationic surfactant	0.027, 0.006	0.675, 0.996	Pseudo-second order	[175]
Modified natural siderite	0.261, 0.988	0.945, 0.995	Pseudo-second order	[146]
Ca–Al–La composite	0.031, 0.883	0.002, 0.994	Pseudo-second order	[156]
Caclined Mg-Al-CO$_3$	1.59×10^{-2}, 0.991	2.80×10^{-4}, 0.996	Pseudo-second order	[183]
Lanthanum and aluminum loaded clay adsorbent	0.011, 0.981	0.113, 0.984	Pseudo-second order	[169]
Marble waste powder	1.579, 0.959	2.748, 0.994	Pseudo-second order	[136]
Porous granular ceramic	0.055, 0.975	0.371, 0.995	Pseudo-second order	[165]
Ionic liquid-functionalized alumina	0.041, 0.785	0.019, 0.996	Pseudo-second order	[167]
Chemically treated laterite	25.77, 0.994	4.4×10^{-5}, 0.999	Pseudo-second order	[144]
Synthetic siderite	0.578, 0.882	34.6, 0.999	Pseudo-second order	[137]
Natural and acid-activated diatomite	2.3×10^{-5}, 0.757	0.360, 1.000	Pseudo-second order	[161]
Ignimbrite materials	4.6×10^{-5}, 0.907	0.187, 0.998	Pseudo-second order	[161]
Nano Calcium-Aluminum Mixed Oxide	0.008, 0.972	0.0267, 0.999	Pseudo-second order	[154]
Aluminum-coated bauxite	0.0284, 0.9908	0.2492, 0.996	Pseudo-second order	[191]

need to be explored in future defluoridation experiments. Water fluoridation studies must continue to protect the affected water and people's wellness. This mini review provides a collection of research results and presents a potential scheme for fluoride removal without any toxic effects on the environment.

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