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Water defluoridation with special emphasis on adsorbents-containing metal oxides and/or hydroxides: a review

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Abstract

Fluoride contamination in drinking water has been recognized as one of the major worldwide problems since this represents a serious threat to human health. The World Health Organization (WHO) recommends the guideline value (maximum permissible limit) of 1.5 mg L\textsuperscript{-1} for fluoride in drinking water. Unfortunately, many countries have high fluoride concentrations (up to 30 mg L\textsuperscript{-1}) in water supplies that may cause widespread fluorosis and skeletal illnesses among the population. Many methods have been developed for fluoride removal from water including adsorption, ion exchange, electrodialysis and precipitation. Nevertheless, more efficient and cost-effective processes and materials are needed to comply with the fluoride maximum permissible limit. Adsorption has been widely used because it is the most cost-effective methodology for the removal of ionic contaminants from aqueous solutions. Various adsorbent materials have been used to remove fluoride from water, for instance activated alumina, activated carbon, bone char, minerals, among others, but unfortunately their chemical stability and/or selectivity and adsorption capacity is something that still has to improve substantially. During the last decade, metal oxyhydroxides in powder form and supported on different matrixes have been of great interest for fluoride removal. This review condenses the advances on this last topic that is still under study.

Key words: fluoride, adsorption, metal oxyhydroxides, water treatment.

1. Introduction

Fluoride source occurs in a geological environment. Minerals like sellaite (MgF\textsubscript{2}), fluorspar (CaF\textsubscript{2}), cryolite (Na\textsubscript{3}AlF\textsubscript{6}) and fluorapatite [3Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}Ca(F,Cl\textsubscript{2})] can release fluoride ions (F\textsuperscript{-}) when the conditions of temperature, pH, anion-exchange, among others, favor their dissolution [1]. The occurrence of F\textsuperscript{-} in groundwater is also due to the anthropogenic discharges from commercial and/or domestic activities, and from industry (i.e. semiconductor manufacturing, glass and ceramic production, uranium and aluminum refinement, toothpaste, fertilizer, electroplating, etc.).
At present, groundwater is the primary source of drinking water for roughly 30 percent of the world’s population and is often the main source of fluoride intake by humans in areas where fluorosis is endemic [2]. The relationship of fluoride-human health is quite extensive, and is focused on the adverse effects on teeth and bones (dental and skeletal fluorosis), DNA structure (genetic mutations, birth defects), and illnesses spread (cancer, Alzheimer disease, renal and neurological damage), among others [3].

Fluoride is considered beneficial at levels around of 0.7 mg L\(^{-1}\) but it is hazardous if it exceeds 1.5 mg L\(^{-1}\), which is the World Health Organization (WHO) limit in drinking water and this is followed in most nations. High fluoride concentrations in groundwater, up to 30 mg L\(^{-1}\), can be found in many parts of the world, and is endemic in at least 25 countries across the globe [4-6]. The most affected areas are parts of China, India, Sri Lanka, South Africa, and in less proportion in rural and semi-urban areas of United States of America, central Europe, northern Mexico and central Argentina. This problem is exacerbated by the need to drink more water because of the heat and dry climates, and the limited water resources in Third World countries. Even in developed nations, fluoride removal (or defluoridation) from public drinking water supplies has been a contentious issue that ends in more stringent fluoride limits [7]. Efforts to reduce fluoride from drinking water to acceptable limits are essential, which require a great deal of investment in research. There are several methods and techniques that can be employed for water defluoridation (precipitation/coagulation, ion-exchange, membrane technique, etc.), and its choice depends on the fluoride ions concentration, existing treatment processes, treatment costs, handling of residuals and versatility of the given technique [8]. However, these methods have some limitations like performance, production of waste, and high costs of installation. Adsorption has shown to be a better choice to remove pollutants from water, such as fluoride ions, because of its lower cost, flexibility and simplicity of design, high efficiency, and high selectivity [9]. A variety of adsorbent materials have been used to remove fluoride from water, such as carbon based adsorbents, agricultural and industrial wastes, metallic oxides and hydroxides or oxihydroxides [8-13]. Nevertheless, recent developments have discovered that metals, in their form of oxides or oxyhydroxides, by their selves or loaded in several materials are good candidates to remove fluoride from water. Unfortunately, this knowledge is dispersed in the literature, hence, the aim of this review is to condense the most relevant studies on fluoride removal from water by adsorption, emphasizing the novel metal oxide/oxyhydroxides adsorbent materials.

2. Technologies for fluoride removal from water

Several techniques have been developed in order to decrease the fluoride concentration to safe limits in water supplies. Defluoridation methods, based on the nature of the type of process involved, can be generally grouped into precipitation/coagulation, adsorption and/or ion exchange, and filtration by membranes. The principle involved in precipitation-coagulation technology is that the fluoride ions adsorb
on the flocs and are then subsequently removed either simultaneous or in succeeding treatment units such as sedimentation, fixed beds or microfiltration units. On the other hand, adsorption is characterized by the use of adsorbents where fluoride is concentrated and removed from water. Parameters such as pH, temperature, and interfering anions have been considered in this research topic since they can greatly affect the adsorption process [10]. The adsorbent materials include activated carbon, activated alumina, ion-exchange resins, fly ash, clay, minerals, soils, among others [11]. On the other hand, membrane techniques involve the use of semi-permeable membranes that are briefly discussed in section 2.2.

2.1 Precipitation/coagulation

Coagulation with aluminum salts has been employed for a long time to remove fluoride ions [12, 13]. Coprecipitation or adsorption may occur when Al(III) ions are added to fluoride-containing water. The efficiency of the removal of fluoride by a fixed amount of aluminum salt depends on pH, alkalinity, the coexisting anions, and other solution characteristics [14]. The most appropriate pH for defluoridation using the coagulation technique is 5.5–6.5 [15]. Nalgonda technique, is one of the most popular defluoridation methods in countries like India, Kenya, Tanzania and Senegal, it involves the addition of calculated quantities of alum, lime and bleaching powder to the water. After the mixing, the water is processed with flocculation, sedimentation, filtration and disinfection [11]. Nevertheless, this technique presents several disadvantages like a high concentration of SO$_4^{2-}$ ions and residual aluminum levels in the treated water.

On the other hand, the electrocoagulation (EC) process utilizes “sacrificed” anodes to form an active coagulant which is used to remove the pollutant by precipitation and flotation in situ. Compared with traditional chemical coagulation (CC), the electrocoagulation process requires less space and does not require chemical storage, dilution, and pH adjustment [16]. It is proven to be effective in water treatment system for small or medium size communities [17].

Although many studies have investigated the removal of fluoride by aluminum (Al) coagulation, few studies have been focused on the effects of colloids, such as kaolin suspensions. Lui et al., [18] studied the effects of fluoride at different molar ratios of fluoride to Al ($R_{F:Al}$) on turbidity removal, zeta potential, flocs growth, and residual Al levels in a series of batch experiments. The authors found that at insufficient Al doses, the fluoride showed adverse effects at $R_{F:Al}$ above 10:10, whereas the opposite effect was observed at $R_{F:Al}$ below 2:10 at pH<8. At pH greater than 8, little effect was observed over a wide $R_{F:Al}$ range of 1:10 to 30:30. The adverse effects of fluoride were related to the decrease of zeta potential, smaller flocs and elevated levels of Al residual. Moreover, this study indicated that after adsorbing fluoride, the freshly-prepared aluminum hydroxides (in-situ Al$_2$O$_3$·H$_2$O) that were spent may be reclaimed as coagulant for colloid removal after being dissolved by an acid solution. Some other researchers such as Hu et al., [19] studied the effect of the molar ratio of hydroxide and fluoride ions ($\gamma$-OH and $\gamma$F) with
respect to Al(III) ions in coagulation and electrocoagulation (EC). This study showed that the efficiency of
defluoridation was approximately 100% when the sum of γ-OH and γF (γ-OH+F) was close to 3. This
finding reveals that fluoride and –OH ions can co-precipitate with Al(III) ions and develop AlₙFₘ(OH)ₙ₋ₘ.

Also, Sujana et al., [20] studied the removal of fluoride from aqueous solution by using aluminum
sludge. This study considered the contact time, the adsorbent and adsorbate concentration, temperature,
pH, and the effect of the concentrations of other anions. The treated alum showed a heterogeneous surface
in nature which was reflected in the heterogeneous binding sites. The optimum pH for complete removal
of fluoride ions was 6, the adsorption rate was faster during the initial 5 minutes and the equilibrium was
reached within 240 minutes. The adsorption process followed a first-order kinetics and could be affected
with an increase in temperature from 307 to 337 K, besides, defluoridation in the presence of phosphate
and silicate at 10-50 mg L⁻¹ has an adverse effect on the fluoride removal. Furthermore, Zhu et al., [21]
used a new approach to investigate fluoride distribution in the defluoridation process by
electrocoagulation, which was divided into three parts: remained in water, removal by electrodes, and
adsorption on hydroxide aluminum flocs. The fluoride distribution was investigated in terms of various
critical parameters such as pH, charge loading, current density and the initial concentration of fluoride.
The results demonstrated that defluoridation can be performed with high efficiency between pH 6.0-7.0,
and would become dominant even under basic conditions (pH≥7.5). The optimal charge loading and
current density were established at 4.15 Faradays m⁻³ and 9.26 Amperes m⁻², respectively. The general
relation between the overall defluoridation efficiency and initial F⁻ concentration decreased from 92 to
80% while the range increased from 3 to 15 mg L⁻¹. A chemical complex of Alₙ(OH)ₘFₖ³n₋ₘ₋ₖ was
formulated to explain the mechanism inside the EC defluoridation process. Following with the
electrocoagulation process, Hu et al., [22] developed a variable order kinetic (VOK) model derived from
the Langmuir equation to simulate the fluoride removal kinetics by electrocoagulation with bipolar
aluminum electrodes. The results showed that parameters Γ_max and k for the VOK model were constant
when the initial fluoride concentration varied. On the other hand, they observed that the current efficiency
is independent upon initial fluoride concentration but this varies with current density. Therefore, their
results revealed good agreement between the predictive equation and the experimental data. However,
they found limitations in the VOK model since this could not simulate systems with an initial acidity of
0.5 or 1.0 mM and with a high initial fluoride concentration.

Moreover, Gong et al., [23] studied the effects of aluminum fluoride complexes by a series of batch
experiments. The transformation of the fluoride species in coagulation was studied by a simultaneous
determination of free fluoride and total fluoride at different pH and fluoride concentrations. For total
fluoride removal, the optimal pH was 7.0, and up to this value complexes were completely dissociated to
free fluoride. Comparison between coagulation with complexation and adsorption by Al(OH)₃ flocs
demonstrated that coagulation shows higher fluoride removal efficiency between pH 6.0 and 9.0, and the process of coagulation involved an Al-F complexation, an Al hydrolysis and a precipitation. During the adsorption process, the fluoride was removed by an ion exchange with –OH. Besides, it was implied that l-F complexation promotes fluoride removal in coagulation. Furthermore, the characterization by FTIR and XPS also showed that Al-F-OH co-precipitates in coagulation.

2.2 Membrane Processes

Membrane processes imply the use of a semi-permeable membrane as an interphase between adjacent phases, and acts as a barrier controlling material transport between them. The driving force to transport in membrane separation is generally a difference in chemical potential created due to a concentration or pressure gradient across the membrane, or by an electric field. Two important phenomena that significantly reduce membrane permeability and selectivity are concentration polarization and membrane fouling. Membrane techniques like reverse osmosis, nanofiltration, dialysis and electrodialysis have been applied industrially in fields ranging from medicine to the chemical industries in the removal of inorganic ions, being one of them fluoride [24]. The use of these techniques can be very attractive for water treatment processes to avoid some difficulties that precipitation, coagulation and adsorption may present during their use.

2.2.1 Reverse osmosis

Reverse osmosis produces extremely pure water. This is a physical process in which contaminants are removed by applying higher pressure on the feedwater to direct it through a semipermeable membrane (see Figure 1). The process is the reverse of natural osmosis as a result of the applied pressure to the concentrated side. The current applications are in desalination of drinking water and water purification for microelectronics and medical uses, because it rejects all dissolved solids. The factors that usually influence the membrane selection are the cost, recovery, rejection, water characteristics to treat, temperature, and pressure, among others. Defluoridation using reverse osmosis systems is running successfully in many developed countries [24].

Arora et al., [25] evaluated the potential of a reverse osmosis membrane for fluoride removal of underground water samples from India, at concentrations between 2.5 to 10 mg L$^{-1}$. The results indicated that reverse osmosis membranes removed up to 95% of F$^-$, and there was no need to remineralize the water. Besides, at pH >7 the efficiency decreased, but in acidic pH the performance of the membrane was affected and needed to be replaced, on the other hand, Ndiaye et al., [26] studied fluoride removal from effluents of the electronic industry using reverse osmosis. The results showed that the rejection of fluoride was typically higher than 98%, considering that the membranes used in the study were fully regenerated.
after each set of experiments. For industrial effluents, the process developed in this research allowed the reduction of the treated volume from 6 to 0.36 m$^3$ d$^{-1}$ without any pretreatment. Taking into account that membranes are sensitive to the polarization phenomena, and that they tend to forward biological fouling due to natural organic matter and microorganisms; mineral fouling can also occur when salts exceed and tend to precipitate [24]. In this respect Nicolas et al., [27] optimized the softening pretreatment, by sodium carbonate, of brackish water contaminated with high concentration of fluoride (\(> 5\) mg L$^{-1}$) in order to obtain purified water by reverse osmosis in a second stage: the calculated optimal amount of softening chemical was 15 mmol L$^{-1}$ of Na. Additionally, the pretreatment allowed not only an almost total removal of calcium but also a partial elimination of magnesium and fluoride.

### 2.2.2 Dialysis and Electrodialysis

Dialysis and electrodialysis are similar to reverse osmosis. In the case of dialysis, one or more solutes are transferred from one solution, called the feed, to another solution called the dialysate, through a membrane due to a concentration gradient. In electrodialysis, the separation of components of an ionic solution occurs in a cell consisting of a series of anion and cation-exchange membranes. These are arranged in an alternate manner between an anode and a cathode to form individual electro-dialysis cells. During the process of electrodialysis, there is an increase in the ion concentration of one type in one type of component and it is accompanied by a simultaneous decrease in the concentration of the other type of component (see Figure 2) [28].

Hichour et al., [29] used contaminated water samples from Africa (Maghreb, Senegal), to study the removal of fluoride with the Donnan dialysis process in a counter flow system. To maintain the fluoride concentration below the acceptable values (1.5 mg L$^{-1}$) at the outlet of the feed compartment, the extracted fluoride ions were complexed by adding Al$^{3+}$ into the receiver solution. Lounici et al., [30] also studied the fluoride removal by using electrodialysis. Their results showed that desorption of fluoride from activated alumina is a rapid process, within 6-15 min. Also, a study of adsorption-regeneration cycles showed that the electrochemical technique was more efficient than commercial caustic soda with 95% of fluoride removal. Following the same Donnan analysis, Germes et al., [31] also applied a hybrid process that combines adsorption on aluminum (Al$_2$O$_3$) and zirconium oxide (ZrO$_2$) to treat groundwater with 4 mg L$^{-1}$ of fluoride concentration resulting from phosphate mining in Morocco. It was found that the fluoride equilibrium concentration was attained more quickly and higher with ZrO$_2$ than with Al$_2$O$_3$. The mineralization of the treated groundwater was not modified. The cation composition remained unchanged, whereas anions (except chloride) were partially eliminated and substituted by Cl$^-$. The above lead to a fluoride concentration below 1.5 mg L$^{-1}$.

An interesting study by Annouar et al., [32] reported the elimination of fluorides from underground water by adsorption on chitosan followed by electrodialysis with the help of CMX-ACS membranes. Both
methodologies approached a safe limit of fluoride concentration. Following the same route, Sahli et al., [33] studied the defluoridation of brackish groundwater in Morocco by electrodialysis. This research group demonstrated that this methodology can defluorinate water with 3000 mg L\(^{-1}\) of total dissolved salts and 3 mg L\(^{-1}\) of fluoride. Recently, Elazhar et al., [34] compared the performance of nanofiltration and electrodialysis in fluoride removal from Moroccan groundwater. Although the performances are comparable in both technologies, the study revealed that electrodialysis has the advantage of flexibility with respect to the seasonal variation of fluoride content, and the final salt concentration can be adjusted. Nevertheless, nanofiltration can be used for small-scale applications.

2.2.3 Nanofiltration

Nanofiltration is not often used in water treatment, but can compete with reverse osmosis and electrodialysis for defluoridation of water supplies. The membranes that use this technology have narrower pores than those used for reverse osmosis, and offer less resistance when the solutes pass through them. As a consequence, the pressure required is much lower, less energy requirements, removal of the solute is much less exhaustive, and flows are faster. Nanofiltration is generally used to remove divalent ions such \(\text{SO}_4^{2-}\) and \(\text{Ca}^{2+}\), but it also can remove \(\text{F}^-\) from aqueous solutions despite being a very small anion. Moreover, fluoride removal with this technique is possible due to its high charge density that makes it a more strongly hydrated ion than others, and thus, it is more strongly retained in nanofiltration membranes by steric effects. The selectivity of nanofiltration in comparison with reverse osmosis is also an advantage due to the low cost of membrane materials that contributes to its actual spread. Furthermore, nanofiltration (as well as electrodialysis) is more suitable for producing drinking water directly without the need of remineralization. The main difference between nanofiltration and electrodialysis is that the second one requires regeneration of ion-exchange membranes thus making its use more expensive than nanofiltration.

As reported by Mohapatra et al., [35], several studies have been carried out using nanofiltration for demineralization of water, especially in the defluoridation of brackish water and wastewater treatment processes. Elazhar et al., [36] evaluated the use of nanofiltration to remove fluoride of 2400 m\(^3\) d\(^{-1}\) of water from a rural location in Morocco. The recovery rate obtained with this methodology was 84% of water and a fluoride rejection of 97.8%. Recently, Nasr et al., [37] applied nanofiltration for defluoridation of groundwaters. This study used commercial nanofiltration membranes and evaluated, among fluoride removal, the influence of chloride, sulfate and calcium that usually co-exist in groundwater. The results indicated that it is important to select an appropriate membrane in order to maintain \(\text{Cl}^-\) concentration in acceptable levels without losing the selective ability to remove \(\text{F}^-\), mixing with groundwater or remineralization is obligatory to produce water with a satisfactory composition.
2.3 Ion exchange technologies

Looking back in time it can be seen how synthetic resins, anionic and cationic, are compared in fluoride removal. An example is given by Ku et al., [38], who found that anionic resins are more easily interfered by the presence of foreign ions and are more difficult to be regenerated than cationic resins. The experiments were performed with Amberlite IR-120 which fluoride removal efficiency was highly affected by a pH increase. Essentially, the ion exchange technologies remain unchanged in terms of advantages and disadvantages; although they have high removal efficiency their cost is always high. Also the efficiency in fluoride removal decreases in the presence of other anions, in some cases pH changes and the process is very dependent on the concentration of the ion of interest, in this case, F ion (Singh et al.) [39].

In many cases the type of material for the membrane or resin is organic with a certain nature (cationic or anionic) and it can function as a matrix for other ions. There are a lot of studies where materials are employed as enhancers for defluoridation capacity over a certain type of membrane or resin. Classical materials in water treatment as zeolite or activated carbon have been employed as ion exchangers. Furthermore, in the case of zeolite due to its large internal surface area and active sites for fluoride adsorption by exchanging Na⁺ bound zeolite with Al³⁺ or La³⁺ ions, as reported by Onyango et al. [40].

A new strategy seems to be the inclusion of metals in certain matrixes to increase the efficiency and selectivity toward fluoride ions. One example is reported by Pan et al., [41], who synthesized a polystyrene anion exchanger that supported hydrous zirconium oxide nanoparticles. Another example is a chemically modified resin with Na⁺ and Al³⁺ (Viswanathan and S. Meenakshi [42]), that increased two times the fluoride uptake.

2.4 Adsorption process

As previously mentioned, ion exchange, electrodialysis and membrane processes are effective and can remove fluoride to a suitable level, however, they are considered a high cost water treatment method and require frequent regeneration and cleaning of the scaling fouling [43,44]. Some advantages and shortcomings of the water treatment techniques usually implemented to remove fluoride from water are reported in Table 1. Adsorption is widely used, especially in developing countries. Industrialized countries generally use more efficient but more costly adsorption media including synthetic ion resins or composite materials combined with reverse osmosis and electrodialysis, while developing countries exploit inexpensive locally available adsorptive media like clays, muds or agro-waste materials [13, 45]. As can been seen, adsorption greatly dependent on the development of adsorptive materials, where the efficiency of this technique mainly depends on adsorbents.
Recent attention of scientists has been devoted to the study of low cost, but effective conventional and non-conventional materials. A large number of adsorbent materials have been tested, such as amorphous alumina [46], activated alumina [47], activated carbon [48], calcite [49], clay [50], and rare earth oxides [51, 52]. Besides, some adsorbents can only work at a certain acid pH value, such as activated carbon which is only effective for fluoride removal at pH less than 3 [53].

Many researchers have developed synthetic sorbents using single or multi-metal oxides/hydroxides for fluoride removal from water, as it will be discussed in the following sections. This review has been focused on the potential of metal oxides/hydroxides/oxyhydroxides, and mixed metal oxides for water defluoridation. The following sections, will present a summary of relevant research in this field in terms of adsorption capacities and kinetics.

2.4.1 Metallic based adsorbents

These kinds of adsorbents have attracted more attention in recent years due to their high efficiency in almost all of the cases that these were tested for fluoride removal. One of the main obstacles for their implementation is their cost, however, it has been proven that small amounts of metals supported on cheaper materials significantly increase fluoride removal.

2.4.1.1 Monometallic based adsorbents

The basic reason for using metallic compounds as adsorbents for fluoride removal is based on the nature of these materials. Metallic elements have tendencies to give valence electrons and acquire positive charge that attract negatively charged fluoride ions. The literature shows that the number of publications on monometallic based adsorbents has increased in recent years. The adsorbents based on one metal are relatively few: about 15 different metals have been used for preparing adsorbents for multiple applications. One of the reasons is that many metals have not been used due to their toxicity.

From the first row of the periodic table (lithium, sodium, potassium, rubidium, cesium and francium), lithium is the only metal that has been studied to remove fluoride, but has not been reported as the principal element in the adsorbent, due to its relative high cost. The rest of alkali elements are excluded for the purpose of fluoride removal from water as adsorbents. Sodium could be used to remove fluoride via precipitation. On the other hand, alkali metals have the lowest electronegativity that results in a high affinity to form bonds of covalent predominance. With regard to alkali, the most studied earth metals are calcium and magnesium, which are the most abundant elements in earth’s crust.

Islam and Patel [54] proposed that among various technologies, fluoride adsorption by using quick lime appeared to be an interesting process. The use of quick lime as adsorbent to remove fluoride has not been clarified, so this study was directed to understanding the adsorption process in a better way. The
inconvenience of this adsorbent is that results in chemisorption along with precipitation of fluoride. Removal efficiency was found to be maximum when the initial fluoride concentration was high (>10 mg L⁻¹). Therefore, the removal of fluoride using quick lime cannot be used for domestic purpose, since it cannot bring fluoride concentration within permissible limit, and also increases the pH of the treated water. Nath and Dutta [55] reported acid-enhanced limestone defluoridation in a column reactor. Ca²⁺ ions, formed due to dissolution of limestone by oxalic acid, precipitate calcium fluoride along with precipitation of calcium oxalate. A good fluoride removal ability, low residual oxalate, acceptable final pH, low-cost and the simplicity of the process make the acid-enhanced limestone defluoridation process with oxalic acid a potential method for defluoridation of groundwater. There are some other works where the acid used is HCl, H₂SO₄, HNO₃, acetic acid or citric acid. When using strong acids, the remains in the water are Cl⁻, SO₄²⁻ and NO₃⁻ which are undesirable, while acetic and citric acid permit the enhancement of fluoride removal. The tests with oxalic acid were in search for a more suitable acid keeping in mind that being a stronger acid it should increase the concentration of Ca²⁺. Moreover, very little oxalate should remain in the treated water due to low solubility of calcium oxalate and high concentration of calcium ions produced in the column. They concluded that the precipitation process is rapid whereas the adsorption is slow and continues beyond 6 h. The adsorption is significant with fresh limestone but decreases with repeated use of the limestone.

Another mineral of calcium used for fluoride removal is hydroxyapatite. Badillo-Almaraz et al., [56] reported the use of commercial synthetic hydroxyapatite BIO-RAD and the best physicochemical condition for removing the biggest quantity of fluoride present in drinking water. It is reported that the retention of fluoride in the synthetic hydroxyapatite BIO-RAD diminishes notably as the pH rises. Another study by Gao et al., [57] reported an interesting article named size-dependent defluoridation properties of synthetic hydroxyapatite, where the results showed that the better performances in fluoride removal were obtained with the smaller particle size and the efficiency was better at a low pH. On the other hand, Poinern et al., [58] combined ultrasonic and microwave processes to produce nanoparticles of hydroxyapatite, which allowed to control the size and morphology varying the experimental conditions that regulate the particle nucleation and growth. The particles that were produced had a relatively low fluoride adsorption capacity compared with some materials related to the precipitation process such as quick lime, but these have the advantage that the equilibrium pH was 6.6, meaning that it would not be necessary to readjust pH in water for human consumption. Moreover, Wang et al., [59] worked with nanoparticles of hydroxyapatite and added low molecular-weight organic acids to improve fluoride removal. They found that the acids formed new active sites for fluoride adsorption at low pH where acids present a protonated state, and these organic acid anions could be exchanged with fluoride on the surface of hydroxyapatite nanoparticles.
Regarding other monometallic-based adsorbents, Nagappa and Chandrappa [60] synthesized mesoporous and nanocrystalline oxide manganese based adsorbents. These were prepared through combustion route and the comparative study for fluoride removal capacity (in standard fluoride solution 10 ppm) showed an adsorption uptake of 97%, while the regenerated material reduced the uptake to 76%. Maliyekkal et al., [61] also used synthesized MgO nanoparticles, but employed a cheaper synthesis method than combustion with similar results in fluoride adsorption capacity. It was also reported that phosphate ions affect the fluoride removal. With respect to the methods of synthesis of magnesium oxides, Sasaki et al., [62] found that sorption of fluoride increased when the adsorbent was synthesized at calcination temperatures that are lower than 873 K for 1h. The authors also reported that the process involved co-precipitation of F⁻ with magnesium hydroxide.

In addition, the interest of rare earth metals like adsorbents came from the particular properties that most of them exhibit, like multivalence behavior and the selectivity towards fluoride ions. Scandium and yttrium elements behave more like rare earth metals than transitional ones, and since these are extracted from minerals of rare earth metals they could be considered herein. Lanthanum has been studied to remove fluoride from water, for instance, Na and Park [63] used lanthanum hydroxide which showed a defluoridation capacity of 242.2 mg g⁻¹ at pH 7.5, and 24.8 mg g⁻¹ at pH 10. This material presented a sorption energy close to chemical sorption, and the regeneration percentage was 24.9 and 89.7% for 0.1 M NaOH and 2.0 M NaOH solutions, respectively. Rao and Karthikeyan [64] also studied the use of lanthanum oxide for fluoride removal and reported that the sorption capacity ranges from 0.5 to 2.5 mg g⁻¹, depending upon initial concentration and a higher sorption capacity was accomplished at low pH values. The energy of sorbent-sorbate bonding was found to be strong, which indicated a chemisorption process; and alum was a more effective regenerant than HCl and NaOH.

Transition metals have much more interest for fluoride removal by adsorption than alkaline and alkaline earth metals, because of their multivalent behavior and more “places” for the fluoride ion to interact. The transferring electron interactions between these metals and fluoride ions are slightly weak due to the higher electronegativity than alkaline and alkaline earth metals (with the exceptions of Mg and Be) that tend to precipitate fluoride.

The elements mainly used for water treatment are iron, zirconium, titanium and manganese. More than half of the reported studies related to monometallic compounds to remove fluoride use iron compounds. Tang et al., [65] used goethite to simultaneously adsorb arsenic and fluoride, being less favorable for fluoride. Granular ferric hydroxide was studied by Kumar et al., 2009 [66] and Tang et al. [67]. Both coincided that certain anions reduce the fluoride removal in the next order H₂PO₄⁻ >HCO₃⁻ >SO₄²⁻. The first study found that the maximum fluoride removal was 7.0 mg g⁻¹ at 25°C and optimal pH range between 4 and 8. The study of Tang et al., (2009) indicated that maximum fluoride adsorption was
achieved between pH 3 and 6.5, whereas the XPS results showed an inner-sphere complexation when fluoride was adsorbed by iron in the granular hydroxide. Iron oxide nanomaterials were studied by Mohapatra et al., [68] and found that this material, composed of different phases of iron oxides, had the best adsorption at pH of 5.75 and that it was severely affected by sulfate and chloride anions. Zirconium adsorbent in form of zirconium oxide showed a maximum fluoride adsorption capacity of 68 mg g$^{-1}$ at pH 7, and it was concluded that hydrous zirconium oxide was superior to most Zr-containing adsorbents (Dou et al. [69]). Moreover, Swain et al., [70] studied meso-structured zirconium phosphate and reported a maximum adsorption of fluoride at pH 6. Although the process showed bonding energy related to ion exchange, the material was used and regenerated up to five times.

Titanium dioxide has also been studied to remove fluoride, such is the case of Babaeivelni and Khodadoust [9] who reported a maximum fluoride adsorption at a pH range of 2-5. It was also reported that the presence of bicarbonate ion has a negative effect on fluoride uptake, but the selectivity of the material was for fluoride over bicarbonate, sulfate and calcium ions. Wajima et al., [71] reported another adsorbent for fluoride removal, titanium oxysulfate (TiOSO$_4$$\cdot$$x$H$_2$O), which showed a maximum fluoride adsorption at pH 3.

The p-block of the periodic table contains the elements Al, Ga, In, Sn, Tl, Pb and Bi. From these, Al, Sn and Bi have been reported as adsorbents for fluoride contained in aqueous solutions. Historically aluminum compounds are the best typical helper material in removal of contaminants from water and have been extensively studied. The research for defluoridation with alumina (Al$_2$O$_3$) shows different kinds of compounds which include different treatments to give it specific characteristics. Gong et al., [72] worked with five types of alumina that were poorly crystallized and their anion exchange capacity and point of zero charge varied for each one. Besides, acidic alumina exhibited higher ion exchange capacity with a more positively charged surface and better defluoridation performance (higher adsorption capacity and quicker removal of fluoride) than basic alumina. According to Goswami and Purkait [73], acidic alumina followed the Langmuir model with an adsorption capacity of 8.4 mg g$^{-1}$ and 94% of fluoride adsorbed at pH 4.4. There are other kinds of alumina used for defluoridation processes, like one reported by Kamble et al., [74] who used alumina of alkoxide, which is a gamma alumina that contains a small amount of Fe$_2$O$_3$, SiO$_2$ and has activated carbon in its pores. Kumar et al., [75] worked with nano-alumina, and the maximum fluoride sorption capacity reported was 14.0 mg g$^{-1}$ at 25 °C and pH 6.15. Liu et al., [76] and Mulugeta et al., [77] have also studied alumina hydroxides to remove fluoride. According to Liu et al., [76], the maximum fluoride adsorption capacity was 110 mg g$^{-1}$ in a pH range from 5.0 to 7.2, where the characteristics of low particle diameter, high surface area, and surface reactivity of the amorphous Al$_2$O$_3$$\cdot$$x$H$_2$O enable its high removal. The study presented by Mulugeta et al., [77] involved an adsorbent based of aluminum hydroxide with 90% of Al(OH)$_2$$\cdot$8(SO$_4$)$_{0.1}$ and 10.7% of aluminum sulfate and 10% of
sodium sulfate with impurities. The fluoride adsorption capacity (for continuous packed column experiments at a flow rate of 100 empty bed volumes per day) was 26.2 mg F\textsuperscript{−} g\textsuperscript{−1}. Additionally, Wang et al., [78] concluded that nano-AlOOH possesses a maximum fluoride removal of 3.2×10\textsuperscript{−3} mg g\textsuperscript{−1}, which is comparable with the activated alumina, and has a maximum adsorption around pH 7. On the other hand, Srivastav et al., [79] synthesized three forms of bismuth trioxide (Bi\textsubscript{2}O\textsubscript{3}) that were examined for defluoridation of aqueous solutions. Those three additional bismuth hydro(oxides) (HBOs) were synthesized from Bi\textsubscript{2}O\textsubscript{3}, HCl and NaOH. The highest removal percentage presented in this work for those materials was ∼65% at 10 mg/L of initial fluoride concentration, while commercially available Bi\textsubscript{2}O\textsubscript{3} powder removed approximately only 6% of fluoride. Table 2 shows the comparison of some monometallic adsorbents and their performance for fluoride removal from water.

2.4.1.2 Bimetallic based adsorbents

In an effort to improve the fluoride adsorption capacity of single metal oxides, researchers have developed bimetallic materials.

To enhance the alumina efficacy of fluoride removal, Liu et al., [80] studied the removal of this anion using an Al-based material modified with Ce, Ti, La or Zr. The hybrid Al-La and Al-Zr increased their adsorption capacity around 6.6 and 33%, respectively. Al-Ce possessed the highest adsorption capacity (62 mg g\textsuperscript{−1}) with a Ce/Al molar ratio of 1:4, at pH 6 and 25 °C. The preparation of the hybrid adsorbent Ce-Al by co-precipitation with NaOH and a drying temperature of 80 °C, allowed the formation of nanoparticles. SEM and XRD results showed that the bimetallic adsorbent possessed an amorphous structure with some aggregated nanoparticles. The point of zero charge at pH 9.6 showed that fluoride is attracted by electrostatic interactions with −OH exchange from the adsorbent surface. On the other hand, Maliyekkal et al., [81] modified alumina with manganese oxide to prepare a Mn-Al adsorbent, and applied it to defluoridation of drinking water. The optimal pH range for fluoride removal was 4-7, and the maximum adsorption capacity reached with this adsorbent was 2.65 times higher than activated alumina (2.851 mg g\textsuperscript{−1}). Moreover, the adsorption kinetics demonstrated that the manganese-oxide-coated alumina was faster than activated alumina, which can be regenerated with 2.5% NaOH.

On the other hand, Tripathy and Raichur [82] also studied the effect of manganese dioxide coating on activated alumina in the removal of fluoride. The authors found that the maximum adsorption capacity reported by the Langmuir model was 0.16 mg g\textsuperscript{−1}, and the kinetic studies revealed that the adsorption followed second-order rate kinetics, up to 0.2 mg L\textsuperscript{−1}, at pH 7 in 3 h and at 25°C. In this case, the fluoride adsorption was attributed to physical adsorption.

Bansiwal et al., [83] modified mesoporous alumina with copper oxide to improve fluoride removal from water. The adsorption capacity of the Cu-Al material obtained from the Langmuir model was 7.22
mg g⁻¹. The enhancement in the fluoride adsorption capacity was attributed to the increase in zeta potential to more positive values. A decrease in sorption capacities was reported at pH above 8, and might be due to the presence of OH⁻ ions that compete for the same adsorption sites. No leaching of copper occurred when fluoride was adsorbed by the bimetallic material.

Following the co-precipitation methodology, Deng et al., [84] developed a Mn-Ce adsorbent. The highest adsorption capacity was achieved at a Ce/Mn ratio of 1:1, at pH 6 and 25°C. In equilibrium concentrations of 1 mg L⁻¹, the sorption capacity was 79.5 mg g⁻¹ for the powder adsorbent and 45.5 mg g⁻¹ for the granular one. Furthermore, kinetics studies showed that the adsorption process took place in the first hour, when the granular form of the adsorbent required 3 h to reach equilibrium, while the powder accomplished it at 8 h.

Fe-Ti, another bimetallic oxide, was studied for water defluoridation by Lin et al. [85]. The optimized Fe-Ti ratio was 2:1 with an adsorption capacity of 29.85 mg g⁻¹ at 25°C. It was found that the hydroxyl groups and Fe-O-Ti bonds on the adsorbent surface which provided active sites for adsorption: a Fe-O-F bond is formed after F⁻ removal. Biswas et al., [86] incorporated Sn(IV) to iron(III) oxide, and the maximum fluoride adsorption capacity was 10.50 mg g⁻¹ in a pH range 5.0-7.5. This trend was presumably due to the neutral or near neutral surface of the solid. The hybrid adsorbent can be regenerated up to a level of 75 % with a bicarbonate solution, at pH 13. Previously, the same group developed a crystalline and hydrous Fe(III)-Zr(IV) hybrid oxide for fluoride removal [87]. The optimum Fe/Zr ratio was 9:1, and the pH range for F⁻ uptake was between 4.0 and 7.0. The pH_{ZPC} determined for the oxide was 7.1-7.2, and the maximum adsorption capacity was 7.51 mg g⁻¹ at 20 °C and pH 6.8. The kinetic data obtained for fluoride removal described both the pseudo-first and the reversible first order equations. The kinetics also demonstrated that the fluoride adsorption took place with a boundary layer diffusion. The external mass transport with intra-particle diffusion phenomena governed the rate, limiting the process. Duo et al., [88] developed another Zr-Fe adsorbent using an extrusion method that was composed of amorphous and nano-scale oxide particles. The optimum Zr/Fe ratio was around 2.3, and the adsorption capacity reached with this material was 9.80 mg g⁻¹ under an equilibrium concentration of 10 mg L⁻¹ at pH 7. Moreover, it had an excellent mechanical stability and high crushing strength. The fluoride adsorption followed a pseudo-second-order kinetics, and the presences of Cl⁻, NO₃⁻ and SiO₄²⁻ did not inhibit the fluoride uptake, except for HCO₃⁻, PO₄³⁻ and AsO₄³⁻. The authors tested the granular bimetallic adsorbent in columns using real water and the results showed that it has high potential for fluoride removal.

Ti-Ce and Ti-La were prepared by Zhijian et al., [89] to enhance the fluoride adsorption capacity, in which the doping Ce and La oxides increased the points of zero charge in the zeta potentials of the hybrid adsorbents. At their points of zero charge, Ti-La and Ti-Ce (pH_{ZPC}= 6.8 and 6.2) adsorbed 18.7 and 22.6 mg g⁻¹, respectively, at a fluoride initial concentration of 10 mg L⁻¹. The sorption equilibrium was
achieved in 4 h where the pseudo-second order model described the sorption kinetics, besides, the nonspecific electrostatic attraction and the specific anion exchange with hydroxyl groups were mainly responsible for fluoride adsorption in the bimetallic adsorbents.

An iron-doped titanium oxide adsorbent was developed by Lin et al., [90]. This adsorbent had a maximum fluoride adsorption capacity of 53.22 mg g\(^{-1}\) at pH 7 and 25 °C, obtained by fitting the experimental data with the Langmuir isotherm model. The adsorption of fluoride followed a second-order kinetic. The authors prepared the adsorbent with an initial feed Fe/Ti molar ratio of 1, but a 0.35 molar ratio was used during the optimization because the Ti ions precipitated faster and earlier than Fe ions during the titration procedure used. It was found that the Fe doped into Ti oxide promoted the formation of active hydroxyl groups on the adsorbent surface, and it increased the fluoride adsorption capacity. The difference between the previous work by the same research group [85] and this study is that the feed molar ratio of Fe/Ti and the pH were lower, and the washed process included just water instead of ethanol. Thus, the differences in the synthesis process gave the iron-doped titanium oxide adsorbent a higher adsorption capacity than Fe-Ti bimetallic oxide.

Following the mixed oxides, Biswas et al., [91] synthesized an iron(III)-aluminum(III) adsorbent for fluoride removal from water. The results demonstrated that the optimum Fe/Al ratio was 1, and the maximum adsorption capacity was 17.73 mg g\(^{-1}\) at pH 6.9, and 28 °C. The authors established that this mixed oxides could be a better adsorbent than either of the pure oxides. The equilibrium data were fitted reasonably with the Langmuir and Redlich-Peterson models, and the equilibrium was reached in 1.5 h. Moreover, the pseudo-second-order model described the adsorption kinetics, and the adsorption rate was controlled by multistage diffusion.

Iron has also been used as an active agent in nanotechnology and this nanosized form has been studied for defluoridation of water since several years ago. For instance, a material composed by aluminum oxide embedded with Fe\(_2\)O\(_3\) nanoparticles (Fe\(_2\)O\(_3@\)Al(OH)\(_3\)) was prepared by Zhao et al., for fluoride removal from aqueous solutions [92]. The adsorbent, in the range of 240-340 nm, presented magnetic properties which can be an advantage for the easy separation from sample solutions by the application of an external magnetic field. The optimal ratio Fe\(_2\)O\(_3/\)Al(OH)\(_3\) was 2:5, and the adsorption capacity calculated by the Langmuir model was 88.49 mg g\(^{-1}\) at pH 6.5 and 25°C. The authors reported a residual fluoride concentration of 0.3 mg L\(^{-1}\) when using Fe\(_2\)O\(_3@\)Al(OH)\(_3\) nanoparticles, with an initial concentration of 20 mg L\(^{-1}\), which met the standard of the World Health Organization (WHO) for safe drinking water quality. Recently, Chai et al., [93] also developed sulfate-doped Fe\(_2\)O\(_3/\)Al(OH)\(_3\) magnetic nanoparticles for fluoride removal from water. The authors reported a maximum fluoride adsorption capacity of 70.4 mg g\(^{-1}\) at pH 7 and 25°C, where the fluoride sorption process can be achieved within 20 min with a 90% of F\(^-\) removal. SO\(_4^{2-}\) was released steadily from the nanoparticles with simultaneous
fluoride adsorption, indicating that an anion exchange mechanism took place during the fluoride removal. The difference between this research and that conducted by Zhao et al., [92] is that the pH range for fluoride adsorption was from 4.0 to 10.0, indicating the applicability of this developed nanoadsorbent for water defluoridation.

The rare earth oxides occur as a mixture of various oxides, Raichur et al., [52] used these elements as mixed rare earth oxides to remove fluoride from aqueous solutions. The chemical material composition was a mixture of La$_2$O$_3$ (44%), CeO$_2$ (2%), Pr$_6$O$_{11}$ (10.5%), Nd$_2$O$_3$ (36.5%), Sm$_2$O$_3$ (5%), among others in trace amounts. The maximum fluoride adsorption capacity was 196.08 mg g$^{-1}$ at pH 6.5 and 29 °C, where most of the adsorption took place in the first 10 min. The adsorption followed the Langmuir isotherm model and it was found that sulfate and nitrate, up to 100 mg L$^{-1}$, did not greatly affect the fluoride uptake. Adsorption studies demonstrated that fluoride can be desorbed at pH 12. However, the adsorption efficiency decreased from 98 to 91% after the first regeneration.

Several layered double hydroxides (LDH) have been developed in order to make efficient fluoride removal from water supplies. These mixtures are a family of lamellar compounds containing anions in the interlayer space and have been recently focused on the synthesis of new hybrid materials for fluoride removal from water. A recent study carried out by Kim et al., [94] demonstrated that the removal of high fluoride concentrations by Mg/Al layered double hydroxides can be useful. Batch experiments demonstrated that the optimal adsorbent was performed calcinating the Mg/Al LDH at 700 °C, while the X-ray analyses indicated a chemical composition of mixed metal oxides (Al$_8$O$_3$N$_6$+Mg$_{0.44}$Al$_{0.55}$) and magnesium oxide (MgO), respectively. Batch experiments showed that the fluoride sorption capacity was 1.7-2.9 times greater than Mg/Al calcined at a temperature less to 300°C, and the adsorption capacity was 91.4 mg g$^{-1}$. The kinetic data showed that the fluoride sorption arrived at equilibrium after 12 h. Moreover, fluoride sorption decreased considerably in the presences of anions such as phosphate, sulfate and carbonate.

Following the modification of adsorbents that contain Magnesium, Kang et al., [95] evaluated the calcinated Mg/Fe layered double hydroxide (Mg/Fe-CLDH) as a material for fluoride and arsenate removal from aqueous solutions. The adsorbent was synthesized by a co-precipitation method and the optimal Mg/Fe ratio was 5, calcinated at 400 °C, and the maximum adsorption capacity reached with this material was 50.91 mg g$^{-1}$ at pH 7. Data of equilibrium experiments were fitted by the Langmuir isotherm model and pseudo-second order kinetic. The fluoride adsorption mechanism involved surface adsorption, ion exchange interaction and the original layered double hydroxide (LDH) structure was reconstructed by rehydration of mixed metal oxides and the intercalation of F ions into the interlayer region.

MgAl-CO$_3$ was developed by Luv et al., [96] to treat high fluoride concentration solutions (5-2500 mg L$^{-1}$). The adsorbent was prepared by a co-precipitation method as well, and the maximum adsorption
capacity of this LDH containing carbonate, where the data was fitted with the Langmuir-Freundlich model, was 319.8 mg g\(^{-1}\) at pH 6 and 30°C. The kinetic experiments showed that the fluoride adsorption involves a rapid first order step and a slow second order step, and suggested that the second step was controlled by diffusion. It was found that the fluoride removal decreased in presence of other anions in the order of HCO\(_3\)->Cl>-H\(_2\)PO\(_4\)>SO\(_4\)\(^{2-}\), and the interlayer CO\(_3\)\(^{2-}\) of the LDH can be partially removed under acidic conditions, with concomitant incorporation of fluoride in the interlayer galleries of the LDH's.

Batistella et al., [97] also tested MgAl containing CO\(_3\)\(^{2-}\) layered double hydroxide activated in acidic conditions like HCl and HCOOH as reducing and complexing agents, respectively. The adsorption assays showed that an enhancement in adsorption was verified at pH 3.5 and a temperature of 50 °C. The high adsorption capacity reached with these conditions was 303.54 mg g\(^{-1}\) within 10 min of contact time and 0.19 M HCOOH, which was slightly higher than what was reported previously [91].

Recently, Zhang et al., [98] tested a lamellar compound named CeO\(_2\)/Mg-Fe layered double hydroxide composite for fluoride removal from water. In order to improve the fluoride removal efficiency, non-thermal plasma (NTP) was used to modify the surface of these composites. The optimum Ce/Fe mol ratio was 3/5 at 420 °C. The experimental results indicated that the adsorption was 52.4 mg g\(^{-1}\) at pH 6-7 and 25 °C. The kinetic adsorption data was found to fit the pseudo-second order model, while the equilibrium data was described by the Langmuir model. Also, the same research group developed another layered double oxide composed (Li-Al-LDH) by a co-precipitation method [99]. The results indicated that the maximum adsorption capacity reached with this adsorbent increased from 34.77 to 42.43 mg g\(^{-1}\) as the temperature increased from 10 to 40 °C, at pH 7. Besides, the adsorption kinetics of fluoride were represented by the pseudo-second-order model and the experimental data were fitted by the Freundlich isotherm model. It was also stated that from the kinetics analysis, chemisorption may be involved in the adsorption process and can be inferred that an ion-exchange was implicated in a second adsorption stage.

### 2.4.1.3 Trimetallic based adsorbents

It has been presumed that multimetal mixed oxides may be good for filtering materials and for scavenging high fluoride concentrations from contaminated water. Furthermore, it has been assumed that multimetal mixed oxides may be the natural key material in scavenging fluoride from the fluoride-rich percolated water [100].

In this context, Wu et al., [101] used a Fe-Al-Ce trimetal oxide in order to improve the adsorption capacity of the Fe-Ce bimetal oxide. The results of their study show that the maximum fluoride removal (95%) was achieved with an adsorbent calcined at 300 °C, achieving a fluoride adsorption capacity of 178 mg g\(^{-1}\) at pH 7. The one-site and two-site Langmuir isotherm models were applied to fit the isotherm. The experimental data were better fitted by the two-site Langmuir isotherm (R\(^2\) = 0.992 and Q\(_{\text{max}}\) = 229 mg
g^{-1}), suggesting that there might exist two adsorption sites with different adsorption energies on the adsorbent surface. The optimum pH for fluoride uptake was 6.0-6.5. However, the adsorbent also showed a high adsorption capacity over a relatively wide pH range of 5.5-7.0, were the pH_{ZPC} of this adsorbent was 7.5. The adsorption kinetic constant values of the first order rate (k) was determined as 0.002 and 0.0029 min^{-1}, respectively; and for concentrations of 10 mg L^{-1} and 50 mg L^{-1} the correlation coefficients (r^2) were 0.978 and 0.982, respectively. Adsorption fluoride was partially inhibited by high concentrations of phosphate or arsenate, and was not affected by the presence of chloride, sulfate, or nitrate. Desorption results and column experiments further indicated the practicality of trimetal oxide Fe-Al-Ce to remove fluoride for water.

The same group, Wu et al., [102], reported that increasing the initial fluoride concentration, the zeta potential becomes more negative in the range of pH 4-10. To elucidate the fluoride adsorption mechanism by Fe-Al-Ce, XPS and 19F Mass-NMR were used in combination to identify the adsorption of F^- on Al-Fe-Ce. They found a ligand exchange relationship between hydroxyl groups and metal-ions F^- -OH groups had contributed to adsorption of F^-, and although the Fe-Al-Ce contains a low proportion of Ce, Ce-OH was the preferred site for adsorption at low loads of F^- Al-F became the most abundant kind of complex at higher load, which could be related to the high molar ratio of Al in the adsorbent. Al_x-F, Ce_x-F_y, -F and Al; Fe-F were identified as fluorinated species after the adsorption process.

On the other hand, Biswas et al., [103] studied the fluoride removal efficiency of trimetal mixed oxide (HIACMO) synthetic hydrated iron(III)-aluminum(III)-chromium(III) from an aqueous solution. The HIACMO was synthesized by a simple chemical precipitation method. The HIACMO optimal pH for fluoride adsorption was observed in a range of 4.0-7.0. The time required to reach the equilibrium was 1.5 h, and the kinetic data followed the equation of pseudo-second order. Equilibrium data were described by the Langmuir isotherm model, and the maximum adsorption capacity reported was 31.8 mg g^{-1}.

Furthermore, Raichur and Basu [52] studied the efficacy of mixed rare earth oxides in the fluoride adsorption synthetic solutions. Likewise, they studied the adsorption kinetics, the pH effect, the initial fluoride concentration, the adsorbent dose and the presence of other anions in the fluoride adsorption efficiency. The characterization results showed that the adsorbent’s particle size was of 4.34 µm, which had a surface area of 6.75 m^2 g^{-1}. The adsorption kinetics results demonstrated that during the first 5 minutes, the higher amount of fluoride was adsorbed. They found that the adsorption capacity was 12 mg g^{-1}. Also, a dose of 8 g L^{-1} of adsorbent (at pH 6.5 and fluoride concentration of 50 mg L^{-1}) gave 98.5% of fluoride elimination. The maximum fluoride adsorption was held in the range of 6 to 6.5 with an adsorption capacity of 12.5 mg g^{-1}, which corresponded to the Langmuir model. Anions such as nitrate and sulfate affected fluoride uptake. They also reported that desorption of fluoride occurs at pH 12 and
that the adsorption efficiency decreased from 98 to 91% after the first regeneration. Table 3 shows the adsorption capacity of selected multimetallic adsorbents for fluoride removal from aqueous solutions.

2.4.2 Metal-impregnated based adsorbents

2.4.2.1 Carbon based adsorbents

Although carbon based adsorbents poorly remove fluoride from water, their carbonaceous matrix provides a high surface area and inhibits metal sintering in their pore structure. These properties allow modifying the carbons surface with metals to increase their fluoride adsorption capacity.

Cerium dispersed in carbon was reported by V. Sivasankar et al., [104]. This material was prepared by a carbonization of ammonium cerium sulfate impregnated with starch. The maximum fluoride uptake was determined to be 52 mg g\(^{-1}\) at a pH value of 8. Hernandez-Montoya et al., [105] also developed an activated carbon by modifying nutshell with a calcium solution derived from an eggshell. The authors reported an adsorption capacity of 2.3 mg g\(^{-1}\) at 30°C, and found that the calcium chemical species on the carbon surface were more important than the carbon textural parameters in the fluoride adsorption process.

The presence of sulfate and hydrogencarbonate decreased the adsorption capacity, showing that both limit the selectivity of Ca-impregnated activated carbon.

Another research group by Tchomgui-Kamga et al., [106] developed activated carbons that were impregnated with 1M mixture of Al and Fe salts, followed by carbonization at temperatures between 500-900 °C. The optimum adsorbent was carbonized at 650 °C. It was found that the maximum adsorption capacity was 13.64 mg g\(^{-1}\) at 28°C, and more than 92% removal of fluoride was achieved within 24 h at pH 7 with a 10 mg L\(^{-1}\) of F\(^-\) initial concentration. The kinetic data showed that the adsorption process followed a pseudo-second order model at neutral pH, it was possible to find a residual amount of Al and Fe of 0.67 and 1.8 mg L\(^{-1}\), respectively. These materials showed the presence of crystallized CaCO\(_3\) and CaO. Despite this content, all the charcoals showed acidic surface properties and points of zero charge (pH\(_{PZC}\)) values between 7.4–7.7. The fluoride removal was not modified by the presence of NO\(_3^−\), SO\(_4^{2−}\) and PO\(_4^{3−}\), while HCO\(_3^−\) and Cl\(^-\) slightly affected the defluoridation capacity. Leyva et al., [48] also synthesized aluminum-impregnated carbon with 3 to 5 times higher fluoride adsorption capacity. It was reported by Ma et al., [107] that granular activated carbon (GAC) coated with manganese oxides like MnO\(_2\) and Mn\(_3\)O\(_4\) improved the fluoride removal by at least three times. This material presented amorphous characteristics and the predominant valence on manganese was 4.

Materials including zirconium are the most studied to remove fluoride from water. Janardhana et al., [108] investigated the potential of a zirconium-impregnated activated charcoal. This material showed a fluoride adsorption capacity of 3–5 times higher than plain activated charcoal. Zirconium impregnated coconut fiber charcoal (ZICFC) was developed by Sathish et al., [109] and showed a maximum fluoride
uptake followed by groundnut shell and coconut shell charcoals. Regeneration of ZICFC was conducted by an elution of 0.02 M NaOH solution. Carbon nut shell carbon was also impregnated with zirconium by Alagumuthu and Rajan [110] who found that the optimum conditions to remove fluoride from water (1.83 mg g\(^{-1}\)) were pH 7, particle size of 53 µm and room temperature (303K). This adsorbent could be regenerated 96.2% with 2.5% sodium hydroxide in 180 min. Moreover, the equilibrium sorption data agreed reasonably well with the Langmuir isotherm model, and the sorption dynamic study revealed that the sorption process followed the pseudo-second-order equation; the sorption process was complex, both at the boundary of liquid film and intra-particular diffusion contributed to the rate-determining step. On the other hand, Li et al., [111] synthesized a manganese oxide coated graphene oxide that presented 8.34 times more fluoride removal than graphene oxide. The maximum adsorption capacity was 11.93 mg g\(^{-1}\) and the optimum removal of fluoride occurred in a pH range of 5.5–6.7.

Our research group has tailored an activated carbon modified with Zr(IV) and oxalic acid [112], that presented 3 times higher fluoride adsorption capacity (5.94 mg g\(^{-1}\)) than both Zr-impregnated coconut fiber carbon [109] and Ca-impregnated nutshell carbons [106], at pH 7, Ce= 40 mg L\(^{-1}\) and 25°C. We also found that without the presence of the organic acid, the adsorption capacity increased by only 32%, and the kinetics studies revealed that the Zr-impregnated activated carbon removed 71% of the initial fluoride concentration in the first 15 minutes, reaching equilibrium in 50 min. Table 4 shows the comparison of some carbon based adsorbents and their performance for fluoride removal from water.

2.4.2.2 Biosorbents and natural materials (clays, zeolites, minerals, mud) modified with metals

Biosorbents normally refer to naturally occurring biomasses or spent biomasses that passively bind to organic molecules or metal ions by a phenomenon commonly referred to as biosorption [113-115]. It was reported in the literature that the presence of chemical functional groups such as hydroxyl, carbonyl, carboxyl, sulfhydryl, theioether, sulfonate, amine amide, imidazole, phosphonate and phosphodiester present on the biosorbents surface contribute to biosorption [115-116]. Applications of biosorbent/biomass from various microbial sources, leaf-based adsorbents and water hyacinth have been reported by various investigators [117-123]. Moreover, biosorbents have been modified with metal ions to improve their natural adsorption capacity.

In this subject, Yao et al., [124] used neodymium-modified chitosan for defluoridation of water. The treatment conditions were optimized at pH 7, 323 K and a particle size of 0.10 µm. The equilibrium sorption data were also fitted reasonably well by the Langmuir isotherm model. The maximum equilibrium sorption was 22.38 mg g\(^{-1}\) at 303 K. Sorption dynamic studies revealed that the sorption process followed a pseudo-second-order equation; and showed that the sorption process was complex where the boundary of liquid film and intra-particle diffusion contributed to the rate-determining step. The
used adsorbents were regenerated with 4 g L\(^{-1}\) of NaOH during 24 h. Following this theme, Sundaram et al., [125] used a bioinorganic composite named nano-hydroxyapatite/chitosan (n-HApC) composite which could be employed for water defluoridation. It was observed that there was a slight enhancement in the defluoridation capacity of n-HApC composite (1.56 mg g\(^{-1}\)) compared to nano-hydroxyapatite (n-HAp), which showed a fluoride uptake of 1.29 mg F\(^{-1}\) g\(^{-1}\). Other contributions by Sundaram et al., [126-127] reported that nano-hydroxyapatite/chitosan composites, showed an increase in fluoride adsorption capacity from 1.29 mg g\(^{-1}\) to 1.56 mg g\(^{-1}\), and concluded that the use of chitosan is justified by its biocompatibility.

Jagtap et al., [128] also studied a modified chitosan-based adsorbent for defluoridation of water. The authors showed that when keeping constant the adsorbent dose of 1 mg L\(^{-1}\), pH 7.03, 150 rpm and a contact time of 24 h, an increase of initial fluoride concentration decreased the percentage of removal of fluoride, while the adsorption capacity increased (9 mg g\(^{-1}\)). This was attributed to the amount of fluoride ions available for adsorption as the concentration increases. Another study that involved biopolymers is that by Kamble et al., [129] who studied the applicability of chitin, chitosan and 20%-lanthanum incorporated chitosan (20% La-chitosan) as adsorbents for fluoride removal from drinking water. The effects of physico-chemical parameters such as pH, adsorbent dose, initial fluoride concentration and the presence of interfering ions during the adsorption were studied. The authors observed that the maximum fluoride uptake was 3.1 mg g\(^{-1}\) at pH 6.7 and an adsorbent dose of 1.5 g L\(^{-1}\). The equilibrium adsorption data were fitted reasonably well with the Freundlich isotherm model, and the presence of chloride, sulfate, carbonate and bicarbonate ions in drinking water greatly affected the fluoride uptake. These results indicated that the anions compete with sorption of fluoride on 20% La-chitosan. The adsorption rate was considered rapid, and the maximum fluoride uptake was attained within 20 min. Following with chitosan as biosorbent, Bansiwal et al., [130] used lanthanum incorporated chitosan beads (LCB) to remove fluoride from water. The equilibrium adsorption data was fitted by the Langmuir isotherm model and showed a maximum fluoride adsorption capacity of 4.7 mg g\(^{-1}\) at pH 5 with negligible lanthanum release. Additionally, kinetic studies revealed that fluoride uptake was fast, and follows a pseudo-first-order kinetics, whereas the presence of sulphate, nitrate and chloride marginally affected the removal efficiency, however, drastic reduction in fluoride uptake was observed in the presence of carbonate and bicarbonate. Thakre et al., [131] and Bansiwal et al., [130] agreed that the optimum loading of lanthanum was 10% and that the maximum fluoride adsorption capacity of lanthanum incorporated in chitosan beds is 4.7 mg g\(^{-1}\).

Chitosan flakes impregnated with lanthanum were studied by Jagtap et al., [132] in which the loading of lanthanum was 20% and found a maximum adsorption capacity of 1.27 mg g\(^{-1}\). They mentioned that the advantage of using chitosan over other supports like cellulose, activated carbon and alumina is that chitosan contains amino groups that have the ability to bind with the metal ions by forming complexes.
Following with modified chitosan for fluoride removal, Viswanathan and Meenakshi [133] developed a chitosan doped with Fe and they found that the fluoride adsorption capacity rose from 0.052 to 4.23 mg F\(^{-1}\) g\(^{-1}\). In addition, the same group (Viswanathan and Meenakshi [134]) doped chitosan with Zr(IV), as well as Liu et al., [136] who loaded Zr(IV) in carboxylated chitosan beads. The first authors compared the defluoridation capacity of Zirconium modified chitosan (4.85 mg g\(^{-1}\)) with carboxylated chitosan beads and raw chitosan beads which adsorbed 1.385 and 0.052 mg F\(^{-1}\) g\(^{-1}\), respectively. Liu et al., [135] synthesized a bio-based Zr(IV) impregnated dithiocarbamate modified chitosan bead material and found a defluoridation capacity of about 4.58 mg F\(^{-1}\) g\(^{-1}\) at pH 7.0, 30 °C and 40 min. With respect to impregnated chitosan with aluminum, Swain et al., [136] found that the percentage of fluoride adsorption was 84% for the first cycle operating batch study, with an initial concentration of 10 mg L\(^{-1}\), and had a good desorption capacity of 92% at pH 12. Furthermore, Viswanathan and Meenakshi [137] developed an alumina/chitosan composite for defluoridation and found an enhanced capacity of 3.81 mg g\(^{-1}\) in comparison with alumina and chitosan that showed an adsorption capacity of 1.56 and 52 mg g\(^{-1}\), respectively. Neodymium-modified chitosan was employed for defluoridation by Yao et al., [124] where the maximum sorption equilibrium was between 11.41–22.38 mg g\(^{-1}\), depending on the temperature (283–323 K), pH (5–9), adsorbent dose (0.2–2.0 g L\(^{-1}\)), particle size (0.10–0.50 mm) and presence of co-anions (NO\(_3\)\(^{-}\), Cl\(^{-}\) and SO\(_4\)\(^{2-}\)). Moreover, the adsorbents could be regenerated in 24 h by 4 g L\(^{-1}\) of sodium hydroxide.

Some other biosorbents have also been evaluated to remove fluoride from water. Ramanaiah et al., [138] used waste fungus (Pleurotus ostreatus 1804 SP) and reported that the fluoride–fungal interaction fit a pseudo-first-order rate equation. The amount of fluoride adsorbed per unit mass of fungus showed an increasing trend up to 20 mg L\(^{-1}\), and the experimental data fitted well the Langmuir's adsorption isotherm model with an adsorption capacity of 1.27 mg g\(^{-1}\) at pH 7 and 30 °C. Desorption was more evident in an inorganic solution and distilled water. Besides, the effect of temperature on the degradation of the fluoride-loaded biosorbent was also studied for its disposal ability. On the other hand, Mohan et al., [120] employed algal Spirogyra 101, and showed its ability to remove fluoride from aqueous phase. Batch sorption studies performed on the algal–fluoride system indicated an adsorption capacity of 1.272 mg g\(^{-1}\), which was more effective with a low pH (2 to 5). The initial high uptake of fluoride was attributed to chemisorption interactions, and the fluoride–algal interactions were corroborated with the pseudo-first-order rate equation.

Cellulose is the most abundant renewable biopolymer on earth, and has a low cost and is a promising raw material to synthesize adsorbents for defluoridation of aqueous solutions. Yu et al., [139] found that the agglomeration of nano-size hydroxyapatite (HA) can be avoided by using cellulose as a template to disperse nano-size HA in the cellulose matrix. This adsorbent combines the advantages of
cellulose and HA for fluoride removal, moreover, the composite materials showed a higher adsorption capacity than the nano-size HA. It was also reported that the residual fluoride concentration in drinking water could meet the drinking water standard established by the World Health Organization (WHO) by using more than 3 g L$^{-1}$ of adsorbent in the initial fluoride concentration of 10 mg L$^{-1}$. Another composite, Fe(III)-loaded ligand exchanged cotton cellulose adsorbent (Fe(III)LECCA), was synthesized by Zhao et al. [140]. This matrix was selected for being an inexpensive and biodegradable carrier, and a macroporous cellulose material with high surface area while Fe(III) was considered due to its strong affinity towards fluoride anions, environmental safety and low cost. The adsorption followed a first-order rate reaction and the adsorption capacity was 18.6 mg g$^{-1}$ at 25 °C. The leakage of Fe(III) from the adsorbent was just below 0.3 mg L$^{-1}$ due to the strong complex action between phosphonomethy amino group of LECCA and the chelating center Fe(III). On the other hand, in column experiments, with 20 mg L$^{-1}$ influent fluoride at 26 BV h$^{-1}$ flow rate under 25 °C, the column gained 5.6 mg g$^{-1}$ breakthrough adsorption capacity and NaOH regeneration was effective in up to 8 adsorption-desorption cycles.

Among natural adsorbents, Suzuki et al., [141] and Xu et al., [142] developed a defluoridation water-kaolinite-MgO system and magnesia-loaded fly ash cenospheres (MLC), constituted with silica and alumina, respectively. The modified MgO was proposed with the final objective of evaluating the use of commercial-grade MgO as a fluoride immobilization agent in soils. The studies of sorption with enough MgO added to the water-kaolinite (soil model) system worked better for defluoridation and it was considered as a reliable immobilizer for fluoride ions. Commercial-grade MgO had a fluoride adsorption capacity of 64 mg g$^{-1}$ at pH 11.5, and the fluoride adsorption mechanism was attributed to its incorporation into the Mg(OH)$_2$ by –OH substitution. Furthermore, the dominant fluoride immobilization agent for soils was kaolinite. In addition, a series of fluoride leaching tests showed that kaolinite without MgO is vulnerable to an alkali attack, and the fluoride desorption from the contaminated kaolinite took around 3-4 days. On the other hand, magnesia-loaded fly ash cenospheres [142] had a maximum fluoride adsorption capacity of 6 mg g$^{-1}$ at pH 3 and 45 °C. The coexisting ions had a large impact (phosphate>nitrate>sulfate) on the fluoride sorption on MLC, and the experimental data fitted well the pseudo-second order kinetic model and followed the Langmuir isotherm.

Orange waste, and its modification with metal ions, has also been studied for water defluoridation. For instance, Zr(IV) was loaded on a dried orange juice residue (Zr(IV)-DOJR) by Paudyal et al., [143]. The optimal parameter in the fixed bed column for Zr(IV)-DOJR that removed 13.9 mg g$^{-1}$ were 14.3 mg L$^{-1}$ of influent fluoride concentration, 1.2 cm of bed depth and 2.55 ml min$^{-1}$ of flow rate. The breakthrough time was 50 min., and the breakthrough curve model showed that Thomas and the Bed Depth Service Time (BDST) models were in agreement. Furthermore, dilute alkali (0.1 NaOH) solution was effective to desorbed fluoride from the loaded column. The same authors [144] prepared an adsorbent
with rare earth metal ions and orange waste with a saponification reaction using lime for water defluoridation. The maximum adsorption capacity for fluoride was reported at 0.60, 0.92, 1.06 and 1.22 mmol g\(^{-1}\) for Sc (III), Ho (III), La (III) and Sm (III) loaded adsorbent, respectively. They concluded that the La(III)- and Sm(III)- saponified orange juice residue (SOJR) had stronger interaction with fluoride ions even with a trace concentration, suggesting that these materials can be employed as effective adsorbents for the treatment of industrial effluents containing a trace concentration of fluoride ions.

Rice husk ashes and aerobic granules were also evaluated to remove fluoride from water, as reported by Ganvir and Das [145] and Wang et al., [146], respectively. In the first study, the authors coated the biosorbent with aluminum hydroxide and found a high fluoride adsorption capacity of 19 mg g\(^{-1}\). On the other hand, the aerobic granules, self-aggregation of microorganisms, were modified with Ce(III). Those granules showed a fluoride adsorption capacity of 45.80 mg g\(^{-1}\) at a neutral pH, that corresponded to an increase of 359 % compared to the pristine aerobic granules. Also the highest adsorption capacity occurred in the pH range of 3.0 to 5.0.

Alginate beads doped with Fe(III) or La(III) were studied by Sujana et al., [147] and Huo et al., [148], respectively. Hydrous ferric oxide doped alginate beads [149] worked better between pH 3.5 and 5, although their adsorption capacity was significant (45-55%) around neutral pH. The beads were 0.8-0.9 mm size and contained 32-33 % Fe(III), and showed a specific surface area of 25.8 m\(^2\) g\(^{-1}\) and a pH\(_{PZC}\) of 5.15. Modified beads showed a Langmuir F\(^{-}\) adsorption capacity of 8.9 mg g\(^{-1}\) at pH 7 and the adsorption kinetics were described by the pseudo-second order kinetic model followed by an intraparticle diffusion as the rate-determining step. Moreover, lanthanum alginate beads [148] showed that the fluoride adsorption isotherm was well fitted by the Langmuir model, and the maximum adsorption capacity was 197.2 mg g\(^{-1}\) at pH 4. The amount of La(III) in the alginate beds was 25 % with a specific surface of 4.05 m\(^2\) g\(^{-1}\). Also, the mechanism involved in fluoride adsorption by lanthanum alginate beads was an ion-exchange between F\(^{-}\) and Cl\(^{-}\) or OH\(^{-}\). Another research group by Zhou et al., [149] reported that the La\(^{3+}\)-impregnated cross-linked gelatin exhibited the maximum adsorption capacity of 98.8 % with a pH range of 5-7 (21.28 mg g\(^{-1}\)) while the adsorption followed a first-order reaction. Moreover, the adsorption capacity decreased to 82.3% after the adsorbent was regenerated three times with 1 M NaOH. Table 5 shows the adsorption capacity of modified biosorbents and natural materials for fluoride removal from aqueous solutions.

### 2.4.2.2.1 Synthetic resins, ceramics and polymers

Chen et al., [150] developed an iron-impregnated granular ceramic for water defluoridation. This material was prepared with Kanuma mud, zeolite and starch, with FeSO\(_4\)•7H\(_2\)O or Fe\(_2\)O\(_3\). It was found that the granular ceramic with FeSO\(_4\) was more effective for fluoride removal than the one that contained Fe\(_2\)O\(_3\). The maximum fluoride adsorption on ceramic-FeSO\(_4\) at pH 7 was 94.2 %, and the equilibrium data
was well fitted by both Langmuir and Freundlich models. Kinetics were governed by intraparticle diffusion and followed a second-order kinetics model. The particle size was around 3-5 mm, which would not block the sewer and could be easily separated from water. On the other hand, a hybrid sorbent of Zr(IV)-ethylenediamine was synthesized by Swain et al., [151] where the combination of zirconium(IV) and ethylenediamine reaction lead to the formation of a kind of gel material. The maximum fluoride removal (37.03 mg g\(^{-1}\)) was performed at pH 7, while the adsorption process followed a pseudo-second order kinetic model. The fluoride adsorption mechanism onto Zr(IV)-ethylenediamine adsorbent suggested an ion exchange mechanism fluoride –OH groups. Moreover, the presence of NO\(_3^-\), Cl\(^-\) or SO\(_4^{2-}\) did not have significant impact on fluoride removal.

Polystyrene has also been doped by Zr(IV), as reported by Samatya et al. [152]. This adsorbent material had the higher fluoride adsorption capacity, 6.14 mg g\(^{-1}\), between pH 2 and 4. The performance of this adsorbent was also studied in packed columns, which showed an optimum fluoride breakthrough capacity of 5.52 mg g\(^{-1}\), with an elution efficiency of 83% by 0.1M NaOH.

The wetness impregnation-coprecipitation of a material containing silicon (SiMCM-41) with Cerium (IV) oxide was studied by Xu et al., [153], who reported a fluoride adsorption capacity between 5-6 mmol F g\(^{-1}\) at 20 °C and initial fluoride concentration of 2 mmol L\(^{-1}\). Even thorium, a radioactive chemical element, has been used to synthesize a hybrid thorium phosphate composite, Islam et al., [154] that consisted of polycinnamamide thorium (IV) phosphate. The removal of fluoride by this composite was 87.6% and the adsorption capacity, calculated from the Langmuir isotherm, was found to be 4.74 mg g\(^{-1}\). The authors explained that the main advantage of the polymeric composite resides in the possibility of combining the physical properties of the constituents to obtain new structural or functional properties that can be shaped into any desired form (beads, candles and membranes).

Lanthanum (III) is another element that has been loaded in polymeric matrices, Fang et al. [155]. These authors concluded that the different chemical composition and chemical structure of the polymer matrix play the most important role in fluoride adsorption, and that the strongly acidic adsorbents are more effective on fluoride removal in a neutral pH than weak acidic adsorbents, and finally that in the neutral pH range of 4.5–8.0, the 200CT resin loaded with La would be the most appropriate adsorbent for small amounts of fluoride existing in hot spring water.

Recently, Chen et al., [156] reported the development of a Fe-Al impregnated granular ceramic for fluoride removal from an aqueous solution. It was found that the maximum adsorption capacity was 3.56 mg g\(^{-1}\) according to the Langmuir model, and the adsorption process was explained with the pseudo-second-order and pore diffusion models. The authors found that more than 96% of F\(^-\) adsorption was performed within 48 h from a 10 mg L\(^{-1}\) initial fluoride solution at pH 7. Also, the presence of CO\(_3^{2-}\) and PO\(_4^{3-}\) significantly reduced the fluoride removal efficiency. Furthermore, Wu et al., [157] immobilized Fe-
Al-Ce on a porous matrix of polyvinyl alcohol (PVA) by crosslinking with boric acid. The 3-5 mm size-
granules gave high hydraulic conductivity in packed beds for the removal of fluoride from drinking water.
The trimetallic oxide and PVA were found to form chemical bonds, which made the oxide heavily loaded
in the porous structure of PVA. Moreover, the trimetallic oxide concentration was higher than the PVA
concentration (7.5%) which produced a higher adsorption capacity in the granules; achieving an
adsorption capacity of fluoride ions of 4.46 mg g\(^{-1}\) at pH 6.5, at an initial fluoride concentration of 19 mg
L\(^{-1}\). Table 6 shows the fluoride adsorption capacity of some modified synthetic resins, ceramics and
polymers.

3. Final remarks

It is evident that the presence of fluoride in water supplies in many countries around the world is
still a problem to be solved. As shown in this review, different processes can be used to remove fluoride
from water. However, the adsorption process is generally considered more attractive because of its
effectiveness, convenience, ease of operation, simplicity of design, and for economic and environmental
reasons. Moreover, the improvement of different organic and inorganic adsorbents is progressing with the
support of nanotechnology and advanced characterization techniques. Metal
oxides/hydroxides/oxihydroxides and mixed metal oxides have shown a high potential to remove fluoride
from water, however, it is important to consider that the efficiency, selectivity, chemical and physical
stability, and cost are still drawbacks that have to be improved. Additionally, there is the need to validate
through adsorption-desorption cycles the use of the many adsorbent materials, reported in the literature, in
continuous systems at laboratory and pilot scale before these materials may be applied in water treatment
systems to meet the water regulations. Finally, it is evident that more research is needed to develop
adsorbent materials that provide suitable and economical solutions to remove fluoride from water,
especially for those communities in third world countries that do not have access to safe drinking water.

4. Acknowledgments

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assistance in the English writing of this manuscript.

5. References

1. Gosh, A., Mukherjee, K., Gosh S.K., Saha B., 2013. Sources and toxicity of fluoride in the


<table>
<thead>
<tr>
<th>No.</th>
<th>Reference</th>
<th>Details</th>
</tr>
</thead>
</table>


Table 1. Summary of the most common water treatment technologies for fluoride removal [8, 13, 45].

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coagulation/Precipitation</td>
<td>Widely used, high efficiency, commercially available technique</td>
<td>Could be expensive due to the large amounts of chemical required, efficiency depends of pH and presence of co-ions in water to be treat, adjustment and readjustment of pH is required. Formation of toxic sludge that requires it disposal. Low effectiveness (cannot remove F below 5 mg L(^{-1})).</td>
</tr>
<tr>
<td>Membrane processes:</td>
<td>High efficiency, remove other contaminants. No chemicals required.</td>
<td>High capital investment due to the operational (energy) and maintenance cost. Toxic waste water is produced due to F concentrated residue. No ion selectivity. Some membranes are pH sensitive. Clogging, scaling and fouling problems.</td>
</tr>
<tr>
<td>reverse osmosis, nanofiltration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrochemical treatments:</td>
<td>High efficiency and selectivity. No chemical required. No waste production</td>
<td>High cost during installation, operation (energy) and maintenance. No ion selectivity. Skilled labor required. Polarization problems.</td>
</tr>
<tr>
<td>dialysis, electrodialysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion exchange</td>
<td>High efficiency, simplicity and flexibility of design.</td>
<td>Expensive due to the resins, vulnerable to interfering ions (sulfate, phosphate, chloride, bicarbonate, etc.). Replacement of media after multiple regenerations, produces toxic liquid waste, and the efficiency is highly pH-dependent.</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Greater accessibility and low cost due to the wide range of adsorbents, simple operation.</td>
<td>High efficiency often demands adjustment and readjustment of pH, some water ions can interfere in fluoride adsorption. Replacement of media after multiple regenerations. Disposal of used adsorbent.</td>
</tr>
</tbody>
</table>
Table 2. Adsorption capacities and other parameters for the removal of fluoride by selected monometallic adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Fluoride adsorption capacity/ mg g⁻¹</th>
<th>Optimal pH</th>
<th>Temperature/°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum hydroxide</td>
<td>242.2</td>
<td>7.5</td>
<td>25</td>
<td>[63]</td>
</tr>
<tr>
<td>Granular ferric hydroxide</td>
<td>7.0</td>
<td>4-8</td>
<td>25</td>
<td>[66]</td>
</tr>
<tr>
<td>Zirconium oxide</td>
<td>68</td>
<td>7</td>
<td>25</td>
<td>[69]</td>
</tr>
<tr>
<td>Alumina hydroxide</td>
<td>110</td>
<td>5.0-7.2</td>
<td>25</td>
<td>[76]</td>
</tr>
<tr>
<td>Nano-AlOOH</td>
<td>3.26</td>
<td>7</td>
<td>---</td>
<td>[78]</td>
</tr>
</tbody>
</table>
Table 3. Adsorption capacities and other parameters for the removal of fluoride by selected multimetallic impregnated adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Fluoride adsorption capacity/ mg g⁻¹</th>
<th>Optimal pH</th>
<th>Temperature/°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-based material modified with Ce</td>
<td>62</td>
<td>6</td>
<td>25</td>
<td>[80]</td>
</tr>
<tr>
<td>Al-Mn hybrid material</td>
<td>2.852</td>
<td>4-7</td>
<td>30</td>
<td>[81]</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.16</td>
<td>7</td>
<td>25</td>
<td>[82]</td>
</tr>
<tr>
<td>Powder Mn-Ce material mixed with pseudo-bohemite (AlOOH)</td>
<td>79.5</td>
<td>6</td>
<td>25</td>
<td>[84]</td>
</tr>
<tr>
<td>Hydrous Fe(III)-Zr(IV) hybrid oxide</td>
<td>7.51</td>
<td>6.8</td>
<td>20</td>
<td>[87]</td>
</tr>
<tr>
<td>Iron doped Ti(IV)</td>
<td>53.22</td>
<td>7</td>
<td>25</td>
<td>[90]</td>
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<tr>
<td>Fe(III)-Al(III)</td>
<td>17.73</td>
<td>6.9</td>
<td>28</td>
<td>[91]</td>
</tr>
<tr>
<td>Fe₂O₃/Al(OH)₃ nanoparticles</td>
<td>88.49</td>
<td>6.5</td>
<td>25</td>
<td>[92]</td>
</tr>
<tr>
<td>Sulfate doped Fe₂O₃/Al(OH)₃</td>
<td>70.4</td>
<td>7</td>
<td>25</td>
<td>[93]</td>
</tr>
<tr>
<td>MgAl-CO₃</td>
<td>319.8</td>
<td>6</td>
<td>30</td>
<td>[96]</td>
</tr>
<tr>
<td>CeO₂/Mg-Fe layered double hydroxide composite</td>
<td>52.4</td>
<td>6-7</td>
<td>25</td>
<td>[98]</td>
</tr>
<tr>
<td>Li-Al double hydroxide composite</td>
<td>42.43</td>
<td>7</td>
<td>40</td>
<td>[99]</td>
</tr>
<tr>
<td>Synthetic hydrated iron(III)-aluminum(III)-chromium(III) ternary mixed oxide</td>
<td>31.88</td>
<td>4-7</td>
<td>30</td>
<td>[103]</td>
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</table>
Table 4. Adsorption capacities and other parameters for the removal of fluoride by carbon based adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Fluoride adsorption capacity/ mg g(^{-1})</th>
<th>Optimal pH</th>
<th>Temperature/°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerium dispersed in carbon</td>
<td>52</td>
<td>8</td>
<td>25</td>
<td>[104]</td>
</tr>
<tr>
<td>CMPNS-4</td>
<td>2.3</td>
<td>7</td>
<td>30</td>
<td>[105]</td>
</tr>
<tr>
<td>Al-Fe impregnated activated carbon</td>
<td>13.64</td>
<td>7</td>
<td>28 ± 2</td>
<td>[106]</td>
</tr>
<tr>
<td>Granular activated carbons coated with manganese oxides</td>
<td>2.24</td>
<td>5.2</td>
<td>28</td>
<td>[107]</td>
</tr>
<tr>
<td>Zirconium impregnated coconut fiber carbon</td>
<td>20.109</td>
<td>8</td>
<td>rt*</td>
<td>[109]</td>
</tr>
<tr>
<td>Zirconium impregnated cashew nut shell carbon</td>
<td>1.83</td>
<td>7</td>
<td>30</td>
<td>[110]</td>
</tr>
<tr>
<td>Manganese oxide coated graphene oxide</td>
<td>11.93</td>
<td>5.5-6.7</td>
<td>---</td>
<td>[111]</td>
</tr>
<tr>
<td>Zirconium-carbon hybrid sorbent</td>
<td>5.94</td>
<td>7</td>
<td>25</td>
<td>[110]</td>
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</table>

*room temperature
<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Fluoride adsorption capacity/ mg g(^{-1})</th>
<th>Optimal pH</th>
<th>Temperature/°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>neodymium-modified chitosan</td>
<td>22.38</td>
<td>7</td>
<td>50</td>
<td>[124]</td>
</tr>
<tr>
<td>Nano-hydroxyapatite/chitosan</td>
<td>1.56</td>
<td>7</td>
<td>30</td>
<td>[125]</td>
</tr>
<tr>
<td>Magnesia/chitosan composite</td>
<td>11.236</td>
<td>10.1-10.4</td>
<td>30</td>
<td>[126]</td>
</tr>
<tr>
<td>Magnesia/chitin composite</td>
<td>2.840</td>
<td>7</td>
<td>30</td>
<td>[127]</td>
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<tr>
<td>Modified chitosan-based adsorbent</td>
<td>9.0</td>
<td>7.03</td>
<td>30±2</td>
<td>[128]</td>
</tr>
<tr>
<td>Lanthanum-modified chitosan</td>
<td>3.1</td>
<td>6.7</td>
<td>30±2</td>
<td>[129]</td>
</tr>
<tr>
<td>Lanthanum incorporated chitosan beads</td>
<td>4.7</td>
<td>5</td>
<td>30±1</td>
<td>[130]</td>
</tr>
<tr>
<td>La-incorporated chitosan beads</td>
<td>4.7</td>
<td>---</td>
<td>30±1</td>
<td>[131]</td>
</tr>
<tr>
<td>Lanthanum impregnated chitosan flakes</td>
<td>1.27</td>
<td>---</td>
<td>---</td>
<td>[132]</td>
</tr>
<tr>
<td>La(III)-incorporated carboxylated chitosan beads</td>
<td>4.711</td>
<td>Neutral pH</td>
<td>30</td>
<td>[133]</td>
</tr>
<tr>
<td>Zr(IV) entrapped chitosan polymeric matrix</td>
<td>4.850</td>
<td>Neutral pH</td>
<td>30</td>
<td>[134]</td>
</tr>
<tr>
<td>Zr(IV) impregnated dithiocarbonate modified chitosan beads</td>
<td>4.58</td>
<td>7</td>
<td>30</td>
<td>[135]</td>
</tr>
<tr>
<td>Aluminum-Impregnated Chitosan Biopolymer</td>
<td>1.73</td>
<td>6.7</td>
<td>25±2</td>
<td>[136]</td>
</tr>
<tr>
<td>Alumina/chitosan composite</td>
<td>3.81</td>
<td>Neutral pH</td>
<td>30</td>
<td>[137]</td>
</tr>
</tbody>
</table>
Table 5. Adsorption capacities and other parameters for the removal of fluoride by biosorbents and natural materials modified with metals. *(Continuation)*

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Fluoride adsorption capacity/ mg g(^{-1})</th>
<th>Optimal pH</th>
<th>Temperature/°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fungal Pleurotus osteatus 1804 SP as biosorbents</td>
<td>1.27</td>
<td>7</td>
<td>30</td>
<td>[138]</td>
</tr>
<tr>
<td>cellulose@hydroxyapatite nanocomposites</td>
<td>4.22</td>
<td>6.5</td>
<td>25±1</td>
<td>[139]</td>
</tr>
<tr>
<td>Fe(III)-loaded ligand exchange cotton cellulose adsorbent</td>
<td>18.6</td>
<td>5.6</td>
<td>25</td>
<td>[140]</td>
</tr>
<tr>
<td>Magnesia-loaded fly ash cenospheres</td>
<td>6.0</td>
<td>3</td>
<td>45</td>
<td>[142]</td>
</tr>
<tr>
<td>Zr(IV) loaded dried orange juice residue</td>
<td>13.9</td>
<td>4</td>
<td>rt*</td>
<td>[143]</td>
</tr>
<tr>
<td>Sc-Saponified orange juice residue</td>
<td>0.6 (mmol/g)</td>
<td>4</td>
<td>30</td>
<td>[144]</td>
</tr>
<tr>
<td>Jm- Saponified orange juice residue</td>
<td>1.22 (mmol/g)</td>
<td>5</td>
<td>30</td>
<td>[144]</td>
</tr>
<tr>
<td>La- Saponified orange juice residue</td>
<td>1.06 (mmol/g)</td>
<td>4</td>
<td>30</td>
<td>[144]</td>
</tr>
<tr>
<td>Ho- Saponified orange juice residue</td>
<td>0.92 (mmol/g)</td>
<td>4</td>
<td>30</td>
<td>[144]</td>
</tr>
<tr>
<td>Aluminum hydroxide coated rice husk ash</td>
<td>15</td>
<td>5</td>
<td>27±1</td>
<td>[145]</td>
</tr>
<tr>
<td>Carboxylated aerobic granules containing Ce(III)</td>
<td>45.80</td>
<td>Neutral pH</td>
<td>25±1</td>
<td>[146]</td>
</tr>
<tr>
<td>Hydrous ferric oxide doped alginate beads b</td>
<td>8.9</td>
<td>7</td>
<td>29</td>
<td>[147]</td>
</tr>
<tr>
<td>Lanthanum Alginated Beads</td>
<td>197.2</td>
<td>4</td>
<td>25</td>
<td>[148]</td>
</tr>
<tr>
<td>La(^{3+})-impregnated cross-linked gelatin</td>
<td>21.28</td>
<td>5-7</td>
<td>29</td>
<td>[149]</td>
</tr>
</tbody>
</table>

*room temperature*
Table 6. Adsorption capacities and other parameters for the removal of fluoride by modified synthetic resins, ceramics and polymers.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Fluoride adsorption capacity/ mg g⁻¹</th>
<th>Optimal pH</th>
<th>Temperature/°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSO₄·7H₂O impregnated granular ceramics</td>
<td>2.157</td>
<td>6.9±0.1</td>
<td>30</td>
<td>[20]</td>
</tr>
<tr>
<td>Fe₂O₃ impregnated granular ceramics</td>
<td>1.699</td>
<td>6.9±0.1</td>
<td>30</td>
<td>[150]</td>
</tr>
<tr>
<td>Zr(IV)-ethylenediamine</td>
<td>37.03</td>
<td>7</td>
<td>25±2</td>
<td>[151]</td>
</tr>
<tr>
<td>Zr(IV) surface immobilized</td>
<td>5.52</td>
<td>---</td>
<td>30</td>
<td>[152]</td>
</tr>
<tr>
<td>Activated Cerium(IV) oxide/SiMCM-41</td>
<td>5-6 (mmol/g)</td>
<td>---</td>
<td>20</td>
<td>[153]</td>
</tr>
<tr>
<td>Thorium phosphate composite</td>
<td>4.74</td>
<td>Neutral pH</td>
<td>25±2</td>
<td>[154]</td>
</tr>
<tr>
<td>200CT resin loaded with lanthanum</td>
<td>1.34</td>
<td>6</td>
<td>30</td>
<td>[155]</td>
</tr>
<tr>
<td>Fe-Al-impregnated granular ceramic adsorbent</td>
<td>3.56</td>
<td>6.9±0.1</td>
<td>25±1</td>
<td>[156]</td>
</tr>
<tr>
<td>Fe-Al-CE hydroxide nanoadsorbent-polyvinyl alcahol</td>
<td>4.46</td>
<td>6.5</td>
<td>25</td>
<td>[157]</td>
</tr>
</tbody>
</table>
Figure 1. Schematic representation of reverse osmosis.

Figure 2. Schematic representation of electrodialysis.
Highlights

- Efforts to reduce fluoride from drinking water to acceptable limits are essential.
- More efficient and cost-effective materials are needed for water defluoridation.
- Adsorption is an important process to remove fluoride from water.
- Metal oxyhydroxides have a high potential for water defluoridation.