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A critical review of fluoride removal from water by using different types of adsorbents

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Abstract. The water can be contaminated by natural sources or by industrial effluents. One such contaminant is fluoride. Fluoride contamination in the water environment due to natural and artificial activities has been recognized as one of the major problems worldwide. Among the commonly used treatment technologies applied for fluoride removal, the adsorption technique has been explored widely and offers a highly efficient simple and low-cost process for fluoride removal from water. This review paper the recent developments in fluoride removal from surface water by adsorption methods. Studies on fluoride removal from aqueous solutions using various carbon materials are reviewed. Various adsorbents with high fluoride removal capacity have been developed, however, there is still an urgent need to transfer the removal process to an industrial scale. Regeneration studies need to be performed to more extent to recover the adsorbent in field conditions, enhancing the economic feasibility of the process. Based on the review, technical strategies of the adsorption method including the Nano-surface effect, structural memory effect, anti-competitive adsorption and ionic sieve effect can be proposed. The design of adsorbents through these strategies can greatly improve the removal efficiency of fluoride in water and guide the development of new efficient methods for fluoride removal in the future. This paper describes brief discussions on various low-cost adsorbents used for the effective removal of fluoride from water.

Keywords: adsorbent; adsorption; contamination; fluoride removal; technical strategies

1. Introduction

The geological formation is the main source of fluoride in the groundwater. Fluoride is a naturally occurring compound derived from fluorine, the 13th most abundant element on Earth. It is found in rocks, soil, and fresh and ocean water. Fluoride occurs naturally in public water systems as a result of runoff from weathering of fluoride-containing rocks and soils and leaching from soil into groundwater. Atmospheric deposition of fluoride-containing emissions from coal-fired power plants and other industrial sources also contributes to amounts found in water, either by direct deposition or by deposition to soil and subsequent runoff into the water.

The major sources of fluoride in groundwater are fluoride bearing rocks such as fluorspar, cryolite, fluorapatite and hydroxylapatite. The fluoride content in the groundwater is a function of many factors such as the availability and solubility of fluoride minerals, the velocity of flowing

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Table 1 Inorganic Fluoride Emissions from Industries

Industries	Effluents tonnes per year
Non-Ferrous metal foundries	4000
Aluminium Industries	16000
Combustion of coal	16000
Phosphate fertilizer and processing	18700
Ceramics	21200
Steel	40100

water, pH, temperature, concentration of calcium and bicarbonate ions in water. Rao and Metre (2014) shows the other sources of fluoride occurrence in water are industrial discharge from aluminium industries, phosphate industries, coal plants as well as due to water, food, air, medicament and cosmetics. Inorganic fluoride effluents from different industries are given in Table 1.

According to current knowledge, a fluoride concentration of about 0.5 mg/L is beneficial in preventing dental caries during tooth development, while levels higher than 1.5 mg/L may result in fluorosis or other health problems. A maximum fluoride concentration of about 4 mg/L is considered adequate for the prevention of skeletal fluorosis. A secondary maximum contaminant level of 2 mg/L is recommended to minimize the cosmetic risk of dental fluorosis, which can occur when fluoride is incorporated into the enamel. The excessive presence of fluoride in potable water continues to be a serious public health concern in many parts of the world, including India. Adsorption has shown considerable potential in the defluoridation of wastewater. The viability of such a technique is greatly dependent on the development of suitable adsorptive materials. Bioremediation is recognized as a cost-effective and environmentally friendly option for the clean-up of contaminated water.

Bio-sorption method is a very effective/attractive technique for the removal of fluoride from water. This technique involves low-cost adsorbents (also called bio sorbents) such as rice husk, sawdust, moringa olifera extract, red mud and gooseberry etc. This review reports the recent developments in fluoride removal from the water environment by the adsorption method. Studies on fluoride removal using various carbon materials, natural minerals, polymers and resins, biomaterials and industrial by-products for fluoride are reviewed.

2. Various adsorbents for fluoride removal

2.1 Biomaterials

Given the low cost and environmental friendliness, a large number of natural biomaterials and modified biomaterials had been applied to remove fluoride from the water environment, like tea waste (Cai *et al.* 2015), algae (El-Said, El-Sadaawy and Aly-Eldeen 2018) and leaf (Dehghani *et al.* (2018)), husk (Gebrewold *et al.* 2019), etc. Babu *et al.* (2018) focused on fluoride removal by exhausted coffee grounds from the synthetic contaminated water and confirmed the potential as a successful biosorbent. The adsorption ability was found to be 9.05 mg/g for fluoride and removed 90% of fluoride from wastewater. The stem of Tecomella undulata was used as an adsorbent

Table 2 Fluoride Adsorption Capacity of the Tea Biosorbents

Tea Biosorbents	Adsorption Capacity (mg/g)
Original tea	3.83
Tea-Fe	10.47
Tea-Al	13.79
Tea-Al-Fe	18.52

by Brahman *et al.* (2016). The researchers studied the effect of pH, biomass dosage, analysis concentration, time, and temperature and determined an optimum reaction condition with a maximum adsorption capacity of 6.16 mg/g. Kazi *et al.* (2018) conducted defluoridation in the presence of ions of water using Cucumis pubescent. Manna *et al.* (2015) have selected grafted jute as a potential adsorbent for defluoridation. The fluoride accumulation of grafted jute powder was significantly higher than that of untreated jute powder. Salomon-Negrete *et al.* (2018) reported the synthesis of novel adsorbents for fluoride removal from water using avocado kernel seeds. Results showed that the adsorbent obtained via pyrolysis had the highest adsorption properties, while its counterpart obtained with CO_2 activation decreased its defluoridation performance where the carbonization temperature was the main synthesis variable. Mei *et al.* (2019) prepared a new type of high-efficiency adsorbent by treating tea dregs with the extrusion method. Extruded tea waste increased the surface pore size, which could provide more loading sites for zirconium, and improved the adsorption efficiency of tea-based biosorbents for removing fluoride in drinking water. The maximum fluoride adsorption capacity for the various tea bio sorbents is given in Table 2.

2.2 Natural minerals for fluoride removal

Natural minerals refer to the natural single substance or compound formed under the geological process, with a relatively fixed chemical composition. Natural minerals play a unique role in the field of pollution control and environmental remediation because of their obvious advantages in the scale, cost, operation and effect of pollution control. In this paper, natural minerals for fluoride removal are classified into these categories: clay, zeolite, calcium-based minerals, SiO_2 and other minerals.

2.2.1 Clay

Several clay materials with native and modified forms are tested on fluoride removal including clay minerals, bentonite, kaolinite, palygorskite, vermiculite and diatomite etc. Defluoridation by adsorption onto cost-effective natural materials was the most commonly utilized method. Ben Amor *et al.* (2018) investigated the capacity of raw Tunisian clays in the defluoridation of natural water. They found that kaolinite was more efficient at removing fluoride than smectite. The percentage of fluoride removal was 73% for kaolinite and 46% for smectite, with an initial fluoride concentration of 2 mg/L. Chemical modification of clay had also been reported by some researchers. Zhang *et al.* (2016) used natural clay modified by lanthanum and aluminium as fluoride ion adsorbent. Mudzielwana *et al.* (2017) synthesized an efficient fluoride adsorbent by coating Na-activated bentonite with MnO_2 through in-situ reduction of $KMnO_4$. Although the maximum adsorption of Na-activated bentonite with MnO_2 (2.40 mg/g) was lower than that of other adsorbents, its adsorption to fluoride was sufficient, with a fluoride removal percentage of more than 91% at all evaluated pH levels (2.0-12.0). Chao *et al.* (2019) obtained ceramist adsorbent with better defluoridation rate and mechanical strength by optimizing the mixing proportion of volcanic rock, bentonite, corn starch and aluminium sulphate.

2.2.2 Calcium based minerals

Calcium based materials are mainly composed of apatite, brushite and limestone. Apatite is a kind of calcium-containing phosphate mineral, commonly known as hydroxyapatite. He *et al.* (2016) developed the preparation of ultra-long HAP nanowires successfully. Chen *et al.* (2016) synthesized sulphate-doped hydroxyapatite hierarchical hollow microspheres. The prepared hydroxyapatite possessed an adsorption capacity of about 14.30 mg/g while the sulphate-doped hydroxyapatite showed enhanced fluoride removal performance with a defluoridation capacity of 28.30 mg/g. The adsorption data could be fitted better by the Freundlich than the Langmuir model and the adsorption kinetics followed the pseudo-second-order model. Chen *et al.* (2017) reported the controllable synthesis of petal-like brushite nanosheets using chitosan as a regulator. The addition of chitosan can prevent the agglomeration of calcium phosphate, thus controlling the size of trans calcium phosphate nanosheets. The nano-material exhibited an excellent fluoride adsorption capacity of 231.50 mg/g. Several studies about fluoride removal with limestone had been reported. Gogoi *et al.* (2015) reported that phosphoric acid-enhanced limestone was used to remove fluoride from groundwater. Wong and Stenstrom (2018) have studied calcium carbonate as an economical and effective adsorbent for on-site defluorinated drinking water systems. $CaCO_3$ can bring fluoridated water (below 10 mg/L) down to drinkable fluoride concentrations (below 1.5 mg/L) via physical adsorption, determined through D-R isotherm calculations. Vijayeeswarri *et al.* (2019) prepared surface-modified limestone with different amounts of $CaCl_2$ and NaH_2PO_4. The adsorbent was prepared using crystalline calcium carbonate, calcium chloride and monobasic sodium phosphate as the main ingredients. Surface and elemental analyses showed that fluoride constituted up to 3.8% of the surface of the saturated adsorbent. Kinetic data showed that the diffusional resistance was a rate limiting step to water defluoridation. Pilot scale operation of the process in a rural tenement with local help to prepare the adsorbent and treat 700 L of groundwater each day for 4 months was demonstrated. During this period the average fluoride concentration of the feed water was 7.1 ppm, and was reduced to 1.0 ppm by the treatment. They also show that the saturated adsorbent could be regenerated by acid wash followed by surface modification.

2.2.3 SiO_2

Several research groups have studied the adsorption of fluoride on diatomite and SiO_2. Akafu *et al.* (2019) modified diatomaceous earth (diatomite) provided locally in Ethiopia with an aluminium hydroxide solution. The maximum fluoride removal was observed to be 89.4% with an initial fluoride concentration of 10 mg/L. The Langmuir maximum adsorption capacity was 1.67 mg/g. Although diatomite was readily available in nature, and its use as an adsorbent made the process more economical, the lack of study on the regeneration capacity created confusion about its applicability. Therefore, the regenerative capacity of this kind of adsorbent needs more attention and research. Similarly, Zhang *et al.* (2018) modified mesoporous silica with cerium. Isothermal adsorption results showed that the fluoride ion adsorption process of Ms-Ce was fitted with the Langmuir isotherm adsorption model. The maximum adsorption capacity was 17.96 mg/g.

2.2.4 Other minerals

Chiavola *et al.* (2019) investigated the efficiency of three distinct iron-based adsorbent media in capturing arsenic, vanadium, and fluoride. These adsorbents differed in terms of particle size, iron content, and specific surface area. The study evaluated their performance in both single-contaminant and binary-contaminant solutions. The results demonstrated that all tested adsorbents effectively and rapidly removed arsenic and vanadium from both single-contaminant and binary-contaminant solutions. Vanadium exhibited a higher adsorption capacity compared to arsenic. However, the adsorbents showed limited success in reducing fluoride concentration significantly. Among the factors studied, particle size emerged as the most influential parameter affecting removal rates. Optimal kinetic and isotherm models, along with associated parameters, were identified for each experimental condition. In binary solutions, the presence of vanadium hindered the arsenic uptake, while fluoride had no substantial impact. Solanki *et al.* (2021) investigated the efficacy of various inorganic polymeric coagulants (IPC) named IPC-23, IPC-13, IPC-17, and alum for the purpose of removing fluoride from drinking water. The selection of IPC dosages was based on the Al2O3 content in the recommended alum dose outlined in the batch Nalgonda defluoridation technique. The research examined the impact of coagulant dosage (IPC) at different pH levels and initial fluoride concentrations on fluoride removal efficiency. Using synthetic water samples with fluoride concentrations ranging from 2 to 6 mg/L, the optimized dosage treatment led to residual fluoride levels decreasing to 1.0 to 1.2 ppm with IPC-17. The optimal pH for effective fluoride removal was found to be 6.5. Notably, the performance of IPC deteriorated when applied at both lower and higher pH values.

2.3 Polymers and resins for fluoride removal

Polymers and resins are an important class of adsorbents used to remove anionic and cationic pollutants from water and wastewater. Their irregular, macromolecular and three-dimensional framework structure of the hydrocarbon chain network makes them become good fluoride removal materials.

2.3.1 Polymers

Polymers can be modified their surface properties to improve the adsorption affinity of fluoride. The application of polymers in adsorption is because of their changeable surface properties, high surface activity, relatively low cost and useful properties for adsorbent synthesis. Hence, the application of polymers for fluoride removal in aqueous solutions has attracted much attention. Li *et al.* (2015) synthesized a conjugated microporous polymer (BCMP-3) from triarylboron by carbon-carbon coupling reaction. The BET specific surface area of the new three-dimensional conjugated framework can reach 950 m^2/g. The maximum adsorption capacity was up to 24 mg/g at equilibrium fluoride concentrations of 16 mg/L and a temperature of 298 K. Raghav and Kumar (2019) loaded the Fe-Al-Ni tri-metal oxides on two biopolymers, pectin and alginic, respectively. According to the Langmuir isotherm, the maximum adsorption capacity of Fe-Al-Ni/pectin and Fe-Al-Ni/alginate was 285 and 200 mg/g respectively, which indicated that the pectin had a higher adsorption capacity. Chen *et al.* (2017) studied the fluoride removal by PPy/TiO_2 composite. The characterization results showed that the composites had suitable specific surface areas and abundant positive charge nitrogen atoms. Experimental data were fitted to Langmuir isotherm with the fluoride maximum adsorption capacity of 33.18 mg/g. Wang *et al.* (2017) prepared a superparamagnetic electrochemically regenerable Fe_3O_4/polypyrene core-shell nanocomposite, which had a high adsorption capacity after 20 adsorption-regeneration cycles. Further, Aigbe *et al.* (2020) demonstrated that the removal of fluoride ions in an aqueous solution by PPy/Fe_3O_4 was improved under the action of a rotating magnetic field. Mukherjee *et al.* (2020) have synthesized cellulose nanofiber-polyaniline (PANI)- template ferrihydrite nanocomposite (CNPFH) for defluoridation. Sarkar *et al.* (2019) synthesized an efficient, three dimensional and porous alumino-silicate polymeric adsorbents using the steel plant Linz-Donawitz slag for effective removal of fluoride via adsorption from an aqueous solution. The Linz-Donawitz slag polymeric adsorbent (LDSGP) was modified by divalent metal ions Ni^{2+}, $Zn^{2+,}$ respectively. Sharma *et al.* (2019) has modified the synthesized poly(amidoxime) with iron metal. The study indicated that pectin-g-poly(amidoxime)- Fe complex had selectivity for fluoride ions even though the adsorption capacity (3.20 mg/g) was low.

2.3.2 Resins

Resins are also often used as adsorbents for fluoride removal due to good stability, high adsorption capacity and good flexibility in working conditions. Phillips *et al.* (2018) explored the effectiveness of Haix-Fe-Zr and Haix-Zr resin beads in the removal of fluoride. The results showed that Haix-Fe-Zr resin beads were more effective in removing fluoride from the spiked groundwater compared to Haix-Zr resin beads. Li *et al.* (2020) used modified chelating resin containing sulfonated monophosphonic acid bifunctional groups (S9570-Fe(III)) to remove fluoride from the water phase. Compared with the commonly used resins with monofunctional groups, S9570-Fe (III) resin with both monophosphonic-sulfonic acid bifunctional groups performed best for the fluoride removal from the aqueous solution. The study proved the effectiveness of phosphoric sulfonic acid bifunctional group chelating resin on fluoride removal, which provided a new method for the removal of fluoride.

2.4 Carbon-based materials for fluoride removal

They are widely used in adsorption, catalysis, sensing and other fields. The properties of porous carbon materials can be improved by modification and metal-doping. In this paper, carbon-based adsorbents for fluoride removal are classified into these categories: activated carbon, biochar and bone char and carbon nanotubes.

2.4.1 Activated carbon

An efficient adsorbent due to its high porosity, large surface area and high catalytic activity. Activated carbon has a relatively small adsorption capacity as well as a low affinity for inorganic pollutants, like fluoride. To overcome these difficulties, recent investigations have focused on modifying activated carbons with various chemical species. Choong *et al.* (2020) studied the adsorption of fluoride on palm shell activated carbon (PSAC) and magnesium silicate ($MgSiO_3$) modified PSAC. The authors found an interesting phenomenon that the $MgSiO_3$ impregnated layer changed the adsorption behaviour of fluoride from monolayer to heterogeneous multilayer based on the Langmuir and Freundlich isotherm models. PSAC and MPSAC followed pseudo-second-order kinetics. Roy *et al.* (2017) used calcium-impregnated activated charcoal for fluoride removal. The optimum removal efficiency was obtained as 99.68% within a contact time of 40 min. Mullick and Neogi (2018) studied zirconium-impregnated activated carbon, using ultrasound as the tool for synthesis and applying it for fluoride adsorption from water. A maximum fluoride removal of 94.4% was obtained for the optimum pH 4 within an equilibrium time of 180 min. The adsorption data were fitted most suitably to the Langmuir model with the maximum adsorption capacity obtained up to 5.40 mg/g. The adsorption kinetics followed the pseudo-second-order model. Saini *et al.* (2020) impregnated rice straw with alumina and then converted it into activated carbon. The maximum removal efficiency was more than 96% observed at 10 mg/L initial fluoride concentration. The kinetic model revealed the pseudo-second-order rate, and the adsorption data fitted the D-R and Temkin Isotherm models best. The maximum adsorption capacity obtained was 2.86 mg/g. Chiavola *et al.* (2022) The research encompassed an examination of six distinct adsorbents' ability to remove fluoride. These adsorbents included four commercial ones: titanium dioxide (TiO_2), ArsenXP^{np}-A33E, granular activated carbon (GAC), and granular ferric hydroxide (GFH), as well as two laboratory-designed media: nano-fine media and nano-granular media. The evaluation was carried out through batch experiments using synthetic and actual water samples containing arsenic and vanadium contaminants. Of the evaluated adsorbents, TiO_2 exhibited the highest fluoride adsorption capacity. It was also effective in reducing fluoride concentrations below drinking water limits without necessitating pH adjustments. Other adsorbents achieved similar fluoride reduction, though specifically under acidic pH conditions. The nano-sized laboratory media demonstrated a lower removal efficiency compared to TiO_2 but performed better than A33E, GAC, and GFH. Among the various factors analysed, adsorbent dosage and pH emerged as primary determinants influencing removal efficiency. The pseudo-second-order model was identified as the most suitable for describing kinetic experimental data across all media. The predicted maximum adsorption capacity, in a decreasing order, was TiO_2 > A33E > GAC > GFH according to this model. However, the presence of competing ions and unfavourable pH conditions significantly hampered the removal capabilities of all media.

2.4.2 Biochar and Bone char

Biochar is the product of pyrolysis of biomass energy. Biochar is widely used as an adsorbent for fluoride removal due to its easy availability and low price. Li *et al.* (2016) studied fluoride adsorption on poly pyrrole-grafted peanut shell biological carbon. The adsorbent was found to have a good fluoride removal efficiency of 91.2% for 11.5 mg/L fluoride solution and 10 g/L adsorbents. Bonyadi *et al.* (2019) synthesized activated carbon from the Populous alba tree (PAAC) under the assistance of ultrasonic and applied it to the removal of fluoride ions in synthetic wastewater and actual wastewater. The maximum removal efficiency of fluoride (93.37%) occurred under the fluoride concentration of 10 mg/L, and PAAC of 4 g/L. Yu *et al.* (2015) investigated the possibilities of an innovative lanthanum-modified carbon (LMC) adsorbent rooted in Sargasso sp. Almost 90% of fluoride adsorption occurred within the first 1 h. Dewage *et al.* (2018) prepared alpha- Fe_2O_3 and Fe_3O_4 on a high surface area of Douglas fire biochar, which was used to remove nitrate and fluoride ions from water rapidly. Adsorption was evaluated from 298 to 318 K using the Langmuir and Freundlich isotherm models. Langmuir adsorption capacity was 9 mg/g for fluoride. Saikia *et al.* (2019) used the harmful weed Akebia stem to produce high-quality carbon and modified it with AlOOH nanoparticles to effectively remove fluoride from drinking water. The per cent defluoridation increased from 80.1 to 97.1% on increasing the adsorbent dose from 2 to 10 g/L. The adsorption process was in good accord with the Freundlich model and pseudo-second-order kinetics. The adsorption capacity was found to be in the range of 46.55-53.71 mg/g for the temperature range of 30-50℃, which is better than many other similar adsorbents.

Bone charcoal is the activated carbon obtained by sealing, heating and degreasing animal bones. Rojas-Mayorga *et al.* (2015) studied the physicochemical characterization of metal-doped bone chars and their adsorption behaviour for water defluoridation. Results showed that the fluoride adsorption properties of bone chars can be enhanced up to 600% using aluminium sulphate for surface modification, showed an adsorption capacity of 31 mg/g. Langmuir isotherm and pseudo-second-order equations were proper for representing the adsorption performance. Medellin-Castillo *et al.* (2020) synthesized bone char from pleco fish and determined its adsorption capacity towards fluoride. The fluoride adsorption capacity of fish fins bones and fish backbones was enhanced by 4 and 16%, respectively after the carbonization process. The Langmuir isotherm best adjusted the adsorption equilibrium data.

Mukherjee *et al.* (2018) focused on remediating fluoride from synthetic water using steam-activated carbon derived from Aegle marmelos (bael shell/wood apple) (BAC) and Parthenium hysterophorus (PHAC) through batch sorption techniques. The investigation considered various parameters, including initial fluoride concentration (4-12 mg/L), time (0-5 h), temperature (293.15–333.15 K), adsorbent dosage (4-14 g/L), pH (4-9), and RPM (150-350). BAC achieved maximum fluoride removal of 89% under specific conditions: initial concentration of 10 mg/L, adsorbent dose of 6 g/L, pH 5, temperature 313.15 K, agitation speed of 250 rpm, and contact time of 9 h. In contrast, PHAC achieved a maximum removal of 78% with an initial concentration of 8 mg/L, adsorbent dose of 10 g/L, pH 4, temperature 313.15 K, and contact time of 12 h. Analytical techniques such as SEM, EDX, and FTIR confirmed the fluoride binding capability of the adsorbents. Economic feasibility was assessed by calculating the total costs of preparing 1 kg of adsorbent, resulting in 1.122 USD for BAC and 1.0615 USD for PHAC. These cost evaluations were crucial in determining the practical viability of these adsorbents for large-scale applications. Furthermore, the study observed the impact of fluoride solution on the growth of Chlorella Sorokiniana BTA 9031. Comparing the fluoride removal efficiencies of both adsorbents, it was concluded that BAC shell exhibited superior efficacy over PHAC for eliminating fluoride from aqueous solutions.

Wang *et al.* (2018) developed through a straightforward process: lanthanum-loaded pomelo peel biochar (PPBC-La). The study involved conducting batch adsorption experiments to evaluate the performance of the adsorbent. At 25℃ and pH 6.5, PPBC-La exhibited a maximum fluoride adsorption capacity of 19.86 mg/g. PPBC-La demonstrated effective performance within a wide pH range of 2.4-9.6, exhibiting a positive charge at pH values lower than 5.8. The presence of certain anions, such as $SO_4{}^{2-}$, Cl^-, and $NO_3{}^-$, had only a minor impact on fluoride uptake, while $HCO_3{}^-$ and $PO_4{}^{3-}$ displayed more significant effects. Real groundwater assessment confirmed that at a dosage of 1.0 g/L and pH 5.2, PPBC-La effectively removed 9.8 mg/L of fluoride. Importantly, the regeneration experiments demonstrated PPBC-La's capacity for reusability. Through FTIR, XPS analysis, and anion exchange experiments, it was established that the mechanism underlying fluoride adsorption by PPBC-La was primarily driven by the exchange of anions (such as $NO_3{}^-$ and OH^-) with fluoride ions.

2.4.3 Carbon nanotubes

Dehghani *et al.* (2016) Utilized both single- and multi-walled carbon nanotubes, researchers looked into the defluoridation of the liquid phase. Researchers discovered that the specific surface areas of single- and multi-walled carbon nanotubes were 700 and 270 m^2/g, respectively. For an initial fluoride concentration of 1 mg/L, the highest fluoride adsorption capacities of multi-walled carbon nanotubes and single-walled carbon nanotubes, respectively, were 2.83 and 2.40 mg/g. The adsorption data were described well by the Freundlich isotherm and followed pseudo-second-order kinetic. Roan's group used a simple in-situ sol-gel method to prepare a novel composite material, hydroxyapatite (HA)-multi-walled carbon nanotubes (MWCNTs), which were used for the first

Table 3 Removal of fluoride Percentage using Various Adsorbents

Sr. No.	Adsorbents	% Removal
1	Chalk powder	86
2	Concrete	53
3	Horse gram powder	75
4	Multhani mitti	56
5	Orange peel powder	79
6	Pine Apple peel powder	86
7	Ragi seed powder	65
8	Red mud	71

time to remove fluoride from water. The specific surface area of the synthesized HA-MWCNTs was 180.504 m^2/g, which resulted in a defluoridation capacity of 30.22 mg/g. It was worth noting that HA-MWCNTs were able to decrease the fluoride concentration of actual nuclear industry wastewater from 8.79 mg/L to about 0.25 mg/L with a removal efficiency of 97.15%. The fluoride adsorption data agreed well with both of the Langmuir isotherm model and the Freundlich isotherm model, and the adsorption kinetic data were fitted to a pseudo-second-order model.

2.5 Industrial by-products for fluoride removal

Many industrial by-products are wastes that need to be disposed of. Their rational use can save disposal costs, prevent pollution of the environment by the disposal site, and divert the disposal site to other uses. Several types of industrial by-products have been used for the adsorptive removal of pollutants including fluoride from water and exhibited excellent defluoridation performance. Kang *et al.* (2019) studied the fluoride removal performance of flue gas desulfurization gypsum (FGD). FGD removed 93.31% of fluoride from 109 to 7.3 mg/L. Kinetics analysis indicated that the theoretical fluoride capacity at 1 g/L FGD gypsum was 96.90 mg/g. Deng *et al.* (2016) prepared ferric modified chromium (III)-fibrous protein (Fe-CrFP) adsorbent from tanning leather waste through crosslinking reaction. Langmuir equation could describe the adsorption of fluoride with the maximum adsorption capacity of 14.12 mg/g. Zhou *et al.* (2020) prepared a novel bimetallic adsorbent by activation using zirconium immobilized alkali-active chrome-tanned leather particles. The adsorption of fluoride on zirconium immobilized alkali-active chrome-tanned leather particles was well described by the Langmuir equation with the fluoride removal capacity of 30.49 mg/g. The percentage removal of fluoride using various low-cost adsorbents is shown in Table 3.

2.6 Metals for fluoride removal

Zhu *et al.* (2015) employed a precipitation-calcination technique to synthesize a binary oxide of aluminum (Al^{3+}) and zirconium (Zr^{4+}), namely Al_2O_3-ZrO_2. This newly created adsorbent amalgamated the favorable attributes of both Al_2O_3 and ZrO_2. The adsorption isotherm behavior was effectively captured by the linear Langmuir model, yielding a maximal adsorption capacity of 114.54 mg/g. Saha *et al.* (2015) introduced β-cyclodextrin (β-CD) as a surface modifier for hydrous zirconium oxide (HZO). Their investigation revealed a remarkable increase in the concentration of surface sites on the modified HZO, denoted as CY-HZO. The surface site concentration surged substantially from 26 nm^{-2} to 6300 nm^{-2}, leading to a concurrent enhancement in fluoride adsorption capacity. Notably, the Langmuir adsorption capacity of CY-HZO stood at 31.45 mg/g, which was markedly superior to the 22.45 mg/g capacity exhibited by unmodified HZO. Kang *et al.* (2017) produced various forms of CeO_2, including nanorods, octahedrons, and nano cubes, each possessing distinct morphologies. The fluoride removal performance of these diverse CeO2 shapes varied noticeably. Theoretical calculations indicated that the adsorption capacities for fluoride were 71.50 mg/g for CeO_2 nanorods, 28.30 mg/g for octahedrons, and 7 mg/g for nanocubes, respectively. Notably, the CeO_2 nanorods demonstrated the highest fluoride adsorption capacity, whereas the CeO_2 nano cubes displayed the lowest capacity. This discrepancy can be attributed primarily to the distinct crystal surfaces exposed by the varied morphologies of CeO_2, resulting in differing levels of reaction activity. Raj *et al.* (2019) introduced a straightforward approach for creating a zirconium-loaded copolymer coating on aluminum, achieved through electro polymerization and electrodeposition methods. The resultant coating displayed remarkable corrosion protection for aluminum and was effectively employed as an adsorbent for eliminating fluoride from groundwater. The adsorption behavior aligned well with the Freundlich isotherm model, and the adsorption capacity was quantified at 4.95 mg/g. Wang *et al.* (2015) developed a novel composite, composed of magnesium (Mg), iron (Fe), and lanthanum (La), designed in a flaky configuration to enhance fluoride adsorption. The experimental findings indicated that the most effective adsorbent was obtained when the molar ratio of Mg/Fe/La was 25:1:4. This composite was synthesized at a temperature of 25℃ and subsequently calcined at 400℃, resulting in a remarkable adsorption capacity of 112.17 mg/g for fluoride ions. The adsorption mechanism was well-captured by the Langmuir isotherm model, and the kinetics were suitably described by the pseudo-second-order kinetic model. Dhillon *et al.* (2015) produced a hydrous hybrid oxide nanoadsorbent comprising iron (Fe), calcium (Ca), and zirconium (Zr). This nanoadsorbent exhibited an impressive capacity of 250 mg/g for fluoride adsorption. Furthermore, its appeal was augmented by its effectiveness in treating actual water samples possessing the pH of drinking water, without any instances of leaching effects. This attribute enhanced its attractiveness for the purpose of fluoride removal. Mouelhi *et al.* (2016) conducted an investigation into the competitive adsorption dynamics involving fluoride and natural organic matter (NOM) on activated alumina. The experimental outcomes indicated that the presence of humic acid in the system hindered the fluoride adsorption capability of activated alumina. This led to a reduction in the removal efficiency of fresh activated alumina, which decreased from 70.4% to 51%. In a separate study, Hafshejani and colleagues utilized acetone aluminum as a precursor, dissolved in methanol via flame spray pyrolysis (FSP) technology, to fabricate nanoparticles of aluminum oxide (Al_2O_3). The equilibrium adsorption data were effectively fitted to the Langmuir isotherm model, revealing a maximum adsorption capacity of 13.70 mg/g. Kanrar *et al.* (2020) produced a cost-effective bimetallic oxide composed of chromium (Cr III) and zirconium (Zr IV), denoted as CZ, and utilized it to eliminate fluoride from solutions. The fluoride removal process on CZ adhered to the kinetics of pseudo-second-order rate equations. Both the Freundlich and DR isotherm models were well-suited to describe the adsorption behavior, yielding a maximum adsorption capacity of 90.67 mg/g. Additionally, lanthanum (La), a harmless rare earth element with ample reserves, exhibited a notable attraction towards fluoride ions. Gao *et al.* (2020) innovatively prepared three-dimensional hierarchical flower-like microspheres consisting of a ternary metal oxide comprising zinc, magnesium, and aluminum (CZMA). Experimental results were effectively described by the Langmuir model, revealing a substantial maximum adsorption capacity of 84.24 mg/g at 298 K under neutral conditions. Furthermore, the utilization of rare earth metals such as lanthanum (La) and cerium (Ce) is a prevalent strategy to enhance the fluoride adsorption capacity. Wang *et al.* (2017) studied that a magnesium-aluminium-zirconium (Mg-Al-Zr) triple-metal composite was successfully synthesized via a straightforward co-precipitation technique for the purpose of fluoride removal. The outcomes of the study revealed that the uncalcined Mg-Al-Zr composite exhibited the most impressive fluoride removal capacity, measuring 22.9 mg/g based on the Langmuir isotherm model. The kinetics of the adsorption process adhered to the pseudo-second-order model, and the adsorption isotherm behaviour was best described by both the Langmuir and Freundlich isotherm models. Across a broad pH range spanning from 3 to 10, the Mg-Al-Zr composite showcased a relatively high fluoride adsorption capacity. The thermodynamic evaluation indicated that the fluoride adsorption onto the composite was an endothermic reaction. Remarkably, the as-prepared composite demonstrated exceptional fluoride removal performance when applied to both real groundwater and surface water samples. Based on the characterizations and analyses conducted, a mechanism for fluoride removal by the Mg-Al-Zr composite was proposed. This mechanism involves processes such as ion-exchange facilitated by hydroxyl groups and nitrate ions, along with complexation facilitated by hydroxyl groups.

2.7 Other methods for fluoride removal

López-Guzmán *et al.* (2019) focussed on assessing the electrocoagulation process's efficacy for the simultaneous removal of fluoride and arsenic from a well located in Durango, Mexico. The aim was to address the local contamination issue and establish a methodology with broader applicability. A series of tests were conducted, varying factors such as treatment duration, contaminant concentrations, initial pH levels, and electric current densities. Both iron and aluminum were used as electrode materials. In the simultaneous presence of both contaminants, the removal efficiencies were noteworthy, reaching 85.68% for fluoride and nearly complete removal (approximately 100%) for arsenic. Importantly, the final concentrations of both pollutants were found to be below the drinking water limits stipulated by the World Health Organization (WHO) and Mexican regulatory authorities. The optimal conditions for the electrocoagulation process were determined as follows: a current density of 4.5 mA/cm^2, an initial pH of 5, and a treatment duration of 15 minutes. These conditions were derived while considering initial concentrations of 5 mg/L for fluoride and 80 µg/L for arsenic. Das and Nandi (2019) investigated the concurrent removal of fluoride and Fe(II) ions from drinking water using the electrocoagulation (EC) process with aluminium electrodes, featuring a submerged electrode surface area of 116 cm2. Through a series of experiments, the impact of various factors, including pH, current density (Cd), inter-electrode distance (Id), and sodium chloride (NaCl) dosage (Csi), on the efficiency of fluoride and Fe(II) ion removal was examined. The findings pointed to optimal conditions for achieving the highest removal rates of fluoride and Fe(II) ions, which included a pH level of 7.0, a Cd of 4.31 mA cm^{-2}, an Id of 1.0 cm, and a Csi of 0.33 g L^{-1}. After 60 minutes of EC treatment, an impressive removal efficiency of 96% for fluoride ions and 98.88% for Fe(II) ions was observed. Interestingly, the study revealed a mutual enhancement effect: the presence of Fe(II) increased fluoride removal efficiency, and conversely, fluoride ions enhanced Fe(II) removal efficiency. Additionally, the treated water showed reductions in other impurities such as salinity, total dissolved solids (TDS), conductivity, and turbidity. Kinetic analysis indicated that, under the same operating conditions, the removal rate of Fe(II) ions ($k = 0.0766$ min^{-1}) was higher compared to that of fluoride ions ($k = 0.0535$ min^{-1}). In summary, this study affirmed that EC is an efficient method for simultaneously eliminating fluoride and Fe(II) ions, along with other impurities, with an energy consumption of 1.716 kWh m^{-3}.Pillai *et al.* (2020) described and reviewed, including coagulation-precipitation, ion exchange, membrane separation, and adsorption. In India, membrane and ion exchange methods are less commonly employed due to their cost and maintenance requirements. Instead, coagulation-precipitation and adsorption methods are predominantly utilized. One noteworthy technique used in India and other developing nations like Kenya, Senegal, Tanzania, and India for fluoride removal is the Nalgonda method. This method has gained popularity due to its effectiveness in mitigating fluoride contamination. Adsorption stands out as a widely adopted method for defluoridation in India and elsewhere. Its popularity can be attributed to its cost-effectiveness and high efficiency in removing fluoride from water. However, there is a pressing need to transition from research and development to practical implementation of these methods on a larger scale, particularly in commercial applications. Initiatives to address contamination control are urgently required to combat fluoride contamination effectively. Ye *et al.* (2016) studied that, the purification process involved several steps, including the preparation of a water-in-oil (W/O) emulsion, as well as extraction and demulsification procedures. The study aimed to elucidate the transport mechanism responsible for moving fluoride using an emulsion liquid membrane, with a primary amine known as LK-N21 serving as the fluoride carrier. Several extraction conditions were investigated, including the concentrations of surfactant and carrier, the type and concentration of precipitant, emulsification time and speed, the volume ratio of the internal phase to the organic membrane phase, external phase pH, and the volume ratio of the external phase to the W/O emulsion. These parameters were assessed for their effectiveness in purifying groundwater contaminated with fluoride.

3. Conclusions

Based on the literature reviewed, carbon materials had a large specific surface area, controllable pore structure and surface chemical properties. The common activated carbon was cheap, but the adsorption capacity of fluoride was poor. Natural minerals played unique roles in the field of pollution control and environmental remediation because of their obvious advantages in the scale, cost, operation and effect of pollution control. Though these materials had low fluoride adsorption capacity, they were cost-effective and therefore could potentially be used in developing countries where the cost of operation is a major factor in the choice of adsorbents. Polymers and resins were an important class of adsorbents used to remove anionic and cationic pollutants from water. These adsorbents were relatively expensive and therefore were useful only for water treatment in industries. Biomaterials and industrial by-products have the advantages of being non-toxic, easy to obtain and low cost, but their adsorption capacity is low, so it is necessary to use metal to modify them to improve their fluoride removal performance. Even though various adsorbents showed good performance on fluoride removal, more studies are needed to transfer the process to an industrial scale. Also, regeneration studies needed to be performed to more extent to recover the adsorbent, enhancing the economic feasibility of the process.

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