*Review Article*

# Fluoride in Drinking Water and Nanotechnological Approaches for Eliminating Excess Fluoride

**Ruwanthi W. Premathilaka** [ID][1] **and Nalinda D. Liyanagedera** [ID][2]

[1]*Post Graduate Institute of Science, University of Peradeniya, Sri Lanka*
[2]*Department of Computing & Information Systems, Wayamba University of Sri Lanka, Sri Lanka*

Correspondence should be addressed to Ruwanthi W. Premathilaka; ulrrwp019@gmail.com

Arising awareness of health hazards due to long-term exposure of fluoride has led researchers to seek for more innovative strategies to eliminate excess fluoride in drinking water. Fluoride-bearing chemicals in both natural and anthropogenic sources contaminate drinking water, which mainly cause for human fluoride ingestion. Hence, developing sustainable approaches toward alleviation is essential. Among many emerging techniques of defluoridation, nanotechnological approaches stand out owing to its high efficiency, and hence, as in many areas, nanotechnology for excess fluoride removal in water is gaining ground compared to other conventional adsorbents and process. The present review focuses on some of the advanced and recent nanoadsorbents including their strengths and shortcomings (e.g., CNT, LDH, graphene-based nanomaterials, and magnetic nanomaterials) and other processes involving nanotechnology while discussing basic aspects of hydrochemistry of fluoride and geological conditions leading for water fluoride contamination. Considering all the findings in survey, it is evident that developing more sustainable techniques is essential rather than conducting batch-type experiments solely.

## 1. Introduction

Being an integral need of human survival, the quality and safety of water, particularly drinking water, is thoroughly concerned. The chemical composition of water is one of the basic factors monitored to make sure the access to safe drinking water of any community. Chemical composition depends on both anthropogenic sources and geogenic sources. While there are several chemical factors governing the quality of water, the concern over maintaining optimum fluoride concentration is gaining its ground in today's world. Both developed countries and nondeveloped countries are now facing the repercussion of excess fluoride in drinking water. In developed countries, fluoride is deliberately added into drinking water systems to prevent dental carries and dental fluorosis; an issue which has been debatable for a long time since some authors have reported an opposite trend [1–5]. Furthermore, the origin of these artificial fluoridation sources has been found and reported as phosphate industrial waste products rather than of pharmaceutical grade [6]. In contrast, most of the other countries who do not practice the fluoridation experience undesirable consequences of water fluoridation due to prevailing hydrological conditions and certain undesirable practices of communities such as using low-grade aluminum utensils to boil water and cooking, especially acidic food [7, 8].

For many years, various types of methods have been studied for excess fluoride removal in water. A lot of research has been conducted on adsorbents while few studies have concentrated on filtration techniques as reverse osmosis and nanofiltration and electrochemical methods as capacitive deionization. The most traditional approach was the elimination through precipitation. However, all these methods have their own disadvantages and advantages when using in real-world applications.

Precipitation involves using aluminum sulphate and lime or calcium and phosphate compounds to precipitate out dissolved fluoride in water. Although it is widely used in community wise, the usage of high aluminum content is detrimental to human health. In addition, the efficiency of

this removal method is not that high (around 70%) [9]. In contrast, membrane processes of fluoride elimination such as reverse osmosis (RO), nanofiltration (NF), and electro-dialysis are highly efficient in water systems with low to medium level salinity [9], and they demand no chemicals. The working pH range is broader than other techniques. However, carrying out the operation of RO plants requires skilled labors and high cost [10].

The other most diversified method can be given as adsorption in which various kinds of innovative adsorbents have evolved until today. Enumeration can be given as oxide materials, carbonaceous materials, ion exchange resins, biopolymer-based materials, soils, clays, and other low-cost materials. Many researchers have reported on different strategical endeavors on excess fluoride removal in water. Adsorption can be defined as the accumulation of a substance or material at an interface between the solid surface and the bathing solution [11]. It is one of the mass transfer techniques which utilizes the surface of a solid to segregate out the desired compound (liquid or gas). Adsorption is more simple and cost effective compared to many methods. Potential for reuse and regeneration is another advantage. However, drawbacks can be illustrated as pH dependency, effect, and competition of other ions and disposal methods. Researchers have come up with various tactical approaches to overcome these drawbacks and have presented more innovative, sustainable solutions.

Porosity, surface area, and the nature of the surface are the governing factors of adsorption. Proper physical and chemical modifications enhance the adsorption capacity of many adsorbents. Nanotechnology plays its role in this regard, and immense research work has been reported on utilizing nanotechnology in water remediation including removal of excess fluoride. Thus, this paper discusses various types of novel nanotechnological endeavors and their basic physical, chemical parameters, and the degree of possibility to use those in real-world applications.

However, most of these adsorbents have been assessed in batch-type experiments, and only few have been assessed on continues type experiments. The batch experiments reveal the design parameters as adsorption rate constant, equilibrium constants, mass transfer coefficient, etc. To evaluate the industrial applicability of the adsorbents, carrying out continuous type methods as fixed-bed adsorption process is essential [12]. Batch type experiments examine the effect of initial adsorbate concentration, effect of the pH, contact time, adsorbent dosage, temperature, and particle size for the adsorption process. Conducting regeneration studies is crucial in assessing the economical and the extent of eco-friendliness of the adsorbent. In most of the reported studies, the simultaneous effect of all variables has been neglected, and instead, they have evaluated only one variable at a time, which should be modified without imitating the common trend. At the same time, this survey revealed that only few studies have been conducted in continuous fixed-bed-type mode to scale up the process economically. Mathematical models can be assisted in this regard. However, there are plenty of batch experiments conducted along with matching experimental data with existing kinetic and isotherm models [12–15].

## 2. Fluoride in Drinking Water

*2.1. Chemistry of Fluoride.* Fluorine, having nine protons in its nucleus, is the most electronegative and reactive element in the periodic table. Thus, this pale yellow-green, irritant, and odorous gas does not exist in its natural state but instead forms ionic states or compounds with other chemicals in minerals as fluorspar, fluorapatite, and cryolite. When focusing on the abundance on earth's surface, fluorine is ranked 13th [16, 17]. Fluoride is a naturally occurring ion found in varying amounts in minerals, rocks, and volcanic gases. Other than these naturally occurring fluorides, anthropogenic sources as coal-fired power plants, plastic factories, glass manufacturing process, phosphate manufacturing process, and brick and tile work also generate fluoride. Utilization of different kinds of fluoride salts can be seen in many industrial applications. Fluoride ion is a Lewis base, and therefore, its conjugated acid hydrogen fluoride is a weak acid in water. However, its acidity is higher than anhydrous acetic acid [16]. When compared with other halides, having a $pK_a$ value of 3.19, fluoride acts as a weak acid in spite of its high polarity [18]. Owing to the basicity of fluoride ions, aqueous media show basic characters. Based on the pH of the medium, fluoride forms water-soluble complexes with polyvalent metal ions such as $Mg^{2+}$, $Ca^{2+}$, $Al^{3+}$, and $Fe^{3+}$, which is why it differs from most of other halides [19]. Fluoride also significantly reacts with silicon-containing compounds, the reason why hydrofluoric acid is used in glass etching process. Many water soluble type of fluorides occur in nature, for instance, ammonium fluoride, antimony trifluoride, boron trifluoride, difluorophosphoric acid, fluorosilicic acid, fluorosulphonic acid, white acid, etc. These soluble fluoride salts can react slowly with water to form hydrofluoric acid which behaves in a slightly different way compared to other hydrogen halide acids owing to the higher reactivity of fluoride ion. Fluoride ions are highly solvated in protic solvents due to their smaller radius/charge ratio. Upon treatment with a standard acid, fluoride salts form hydrogen fluoride which can be doubly protonated to form $H_2F^+$ followed by formation of $HF^{2-}$, which is a form of homoconjugation and thus increases the acidity of the compound [20]. Fluorine can replace hydrogen whenever it encounters; thus, there are so many organic compounds in many industries [1]. However, in groundwater, fluoride ions appear to stay intact or as aqua complexes due to the lower percentage of other cations as aluminum and iron. In aprotic solvents, fluorides are relatively unsolvated and named as "naked" fluorides and easily react with Lewis acid to form strong adducts. Due to this low binding affinity of fluoride, these ions exist as free fluoride ions in groundwater and very few exist as major cation complexes [21, 22].

*2.2. Occurrence and Hydrogeochemistry.* While Sivasankar et al. [16] have reported the abundance of fluorine in earth's crust as 0.05–0.1% (500–1000 mg/kg), it has been reported as 300 mg/kg in Tebutt's study [23]. It is accounted as an incompatible lithophilic element by Faure 1991 [24]. Studies reported the concentration of fluorine may vary from hundred

to thousand mg/kg in the three rock types (igneous, sedimentary, and metamorphic rocks) [16]. Fluoride occurs in igneous and sedimentary rocks, particularly in carbonated-type sedimentary and phosphate beds of volcanic layers and shark teeth [25], and Deer et al. [26] reported that the occurrence is almost similar in these two types, which is evident in He et al.'s study in 2013 [27]. He reported the abundance values for sedimentary and igneous as 1175 mg per kg, and 1043 mg per kg, respectively. Geochemistry, mineralogical composition of rocks and extent of alteration of sediments govern the concentration of fluoride in groundwater [16]. A large variety of fluoride-containing minerals have been identified by today. Sellaite [$MgF_2$], fluorite or fluorspar [$CaF_2$], cryolite [$Na_3AlF_6$], fluorapatite [$3Ca_3(PO4)2Ca(F,Cl2)$], apatite [$CaF2.3-Ca3(PO4)$], topaz [$Al2SiO4(F,OH)2$], fluormica (phlogopite) [$KMg3(Si3Al)O10(F,OH)2$], biotite [$K(Mg,Fe)3AlSi3O10(F,OH)2$], epidote [$Ca2Al2(Fe3+; Al)(SiO4)(Si2O7)O(OH)$], amphibole such as tremolite [$Ca2Mg5Si8O22(OH)2$] and hornblende [$Ca2(Mg,Fe,Al)5(Al,Si)8O22(OH2)$], mica, clays, villuanite, and phosphorite can be given as prominent examples [16, 28–30].

Majority of research done on excess fluoride contamination in groundwater has suggested the corresponding factors as presence of fluorine-bearing minerals and rocks, circulation of water around rocks, withering of fluorine-rich rock fragments, long-time exposure, good depth, and other hydrological conditions as paleo groundwater circulation by fluoride-rich water near fault zones of granite terrain and upward flow of groundwaters revealed by isotope studies [31, 32]. Studies of Nagadu et al. [33] and Scaillet and Macdonald [34] reported the relationship between the fluoride and magma. Owing to the similarity in radius of $OH^-$ and $F^-$, the substitution of fluoride ions in place of hydroxide ions happens during magmatic differentiation. This has resulted in formation of crystallized rocks, pegmatite granites which are rich in fluorite, fluorapatite, and fluoride-enriched micas and/or amphiboles. Granite is a potent source of high fluoride content in groundwater according to many researchers [31]. Further, enhancement of dissolution due to alkalinity of granite deposits has resulted higher fluoride percentage [35]. Constant interaction of groundwater with fluoride bearing rocks is a contributing factor for high fluoride percentage in water, which is exemplified in the study of He et al. [27] in Hangjinhouqi area. The high fluoride content in groundwater was attributed to long-term water-rock interaction which facilitated the mobility of fluoride from the Yin Mountains. Metamorphic changes may lead to this consequence. The higher the depth of aquifer, the higher the percentage of dissolved ions since longer exposure time and slower water exchange. Fluoride behaves in the same manner with few exceptions due to other reasons as differences in the constructions of wells, their open intervals, and the type and structure of the opened rocks. Vertical infiltration during the discharge process of rainfall which leads to dissolution of soluble fluoride into groundwater can be verified via average concentration values of soluble fluoride in main three rock types in fluoride rich areas according to Sivasankar et al. [16].

## 2.3. Anthropogenic Sources.

Fluoride is released from various types of human-involved processes. Usage of fertilizers as NPK, potash, and superphosphate releases considerable amounts of fluoride into soil and water. Waste management in this industry and others including aluminum, copper, and nickel production also release fluoride into the environment. Controlled addition of fluoride to dental products, food products, and pharmaceutical products also contributes to accumulation of fluoride in the environment. Other than these sources, fluoride accumulation in the environment occurs due to various industries that utilize fluorine-containing compounds. Hydrogen fluoride is used in manufacturing of aluminum and chlorofluorocarbons. Other fields where fluorides are involved are electronic industries, cleaning glass, tanning leathers, brick and tile work, petroleum industry, and uranium isotopes separating. For drinking water fluoridation, sodium fluoride is widely used. Other than that, it is used as an insecticide. Sodium hexafluorosilicate is also used in fluoridation of drinking water supplies. Calcium fluoride, on the other hand, is used in glass, ceramics, and fluorescent lamp industry, and sulfurehexafluoride is used as a gaseous dielectric medium in the electrical industry.

## 2.4. Health Impact.

Fluoride can be a double-edged sword owing to both its beneficial and harmful impacts on human body. Fluoride is thought to reduce tooth decay although there are several controversial facts regarding the relationship between the level of fluoride and tooth decay. Research regarding the impact of fluoride on tooth decay suggests three ways of how fluoride mitigates the process of tooth decay. Development of the chemical structure of the enamel at the development stage, making the enamel more resistant to acid attacks, and enhancement of remineralization with an improved quality of crystals are the three proposed ways [36]. Some studies suggest that dental caries reduction is improved in the studied area after the fluoridation. Consuming the recommended level is very important in this scenario. Up to a certain level, fluorides in drinking water replace hydroxide ion from hydroxyapetite, the main constituent of teeth, and strengthen teeth and bones. However, some authors claim there is no significant effect of fluoride ingestion on preventing tooth decay [5, 6]. Long-time exposure and high dosage of fluoride makes the enamel and bones so hard and brittle rather than making it strong. Earlier stage can be visible as white spots on teeth and known as dental fluorosis where it spread further into the skeletal system which is known as skeletal fluorosis [29]. Strengthening of the bone structure is influenced by the interface of collagen and the bone surface. During the long-term exposure, the exchange between fluoride and hydroxyapatite becomes perpetual and irreversible reaction is prohibited. This triggers the synthesis of bone material, and ostesclerosis (hardening and classifying of bones) is induced. Many of the mechanical properties as bone matrix proteins and mineral-organic interfacial bonding are affected. Tensile strength of the bone decreases. It is widely accepted that fluoride causes fetal chronic kidney diseases

since fluoride excretion takes place in the kidney. Sri Lanka is no exception which is suggested by its high percentage of prevalence of chronic kidney disease of unknown etiology (CKDu), especially in North Central Province which is reported to contain the highest level of fluoride. The study of Illeperuma et al. [8] attributed the ingestion of high amount of fluoride into the human body to using low-quality aluminum vessels in cooking. Leaching of heavy metals as aluminum and lead happens in high-fluoride containing water and complexation of fluoride with metals amplifies the entry of toxins into the body. However, some studies revealed no significant correlation between fluoride and CKDu [37–39].

### 2.5. Standard Levels of Fluoride.

The WHO recommended value for fluoride content in drinking water is 1.5 mg/L while 1 mg/L is beneficial for human for preventing dental caries [40, 41]. Sri Lankan guideline value suggests the recommended level of fluoride for drinking water as maximum desirable level of 0.6 mg/L and maximum permissible level of 1.5 mg/L according to SLSI (Sri Lanka standards Institute) [42]. In Sri Lanka, the optimum level for caries prevention has been given as 0.6–0.9 mg/L by Warnakulasuriya et al. [43].

### 2.6. Fluoride in Groundwater: Sri Lanka.

Being situated in the tropical band, Sri Lanka is inherited mainly with three climatic zones comprised of a dry zone with an annual rainfall of less than 1500 per annum, a wet zone where it has been reported as more than 2500 per annum, and an intermediate zone. The tropical climate of the country facilitates leaching out of fluoride from fluorine bearing rocks due to intense withering. Although the types of rocks and minerals are nearly same in both dry and wet zones, notably different climatic conditions and hydrological conditions have resulted a higher percentage of fluoride reported in the dry zone [44]. Groundwater containing higher fluoride content in dry zone is suggested by its high occurrence of endemic fluorosis cases [7, 44, 45]. The abundance is attributed to high evopotranspotation and slow rate of groundwater movement in that area which is a common scenario in arid regions [7]. Wet zone, in contrast, contains groundwater with lower fluoride content owing to extensive leaching of its minerals and flushing out with heavy rains. Considering the types of minerals in the three major lithotectonic units (namely, Highland, Vijayan, and Highland), Sri Lanka comprises fluoride-bearing minerals such as hornblende, sphene, mica, and appetite which contribute to geochemical cycle of fluorine in the physical environment [44]. Previous studies have reported an amount of greater than 1.0 mg/L of fluoride in groundwater, which is exceeding the recommended level, in Kurunegala district (Nikawewa, Nikaweratiya, Polpithigama, and Abanpola). Around 80% of wells in some villages as Karawilagala, Horapola, and Olukarandara in Anuradhapura district have been reported as containing excess of fluoride [44]. The above study revealed Plonnaruwa district in the dry zone as containing high fluoride percentage in groundwater, which is further

suggested by its occurrence of high-fluoride containing charnokitic gnessis rocks as biotite and hornblend (Amphibole) in a later study of Dharmagunewardhena et al. [45]. The study further revealed higher occurrence and vulnerability for weathering of amphibole in the country rock could be a reason for the presence of high fluoride fluxes in the groundwater. Apatite has been reported in excess amounts in all the crystalline country rock samples, and this has been given a possible reason for uniform distribution of fluoride in groundwater.

## 3. Methods of Excess Fluoride Removal

### 3.1. Nanotechnological Approaches in Removing Excess Fluoride.

Among many methods documented in the literature, this paper targets for various kinds of possible nanotechnological approaches in removing excess fluoride in groundwater. Nanotechnology is a technology involving the manipulation of matter having at least one dimension in size range of 1 nm–100 nm. Due to their size, they are gifted with unusual chemical, physical, thermal, and electrical properties when compared to macro and microcounterparts. Principles such as high aspect ratio and quantum confinement are the underlying reasons for these discrepancies [46]. No exception, the reactivity also increases [47]. When moving on to water treatments applications, nanoparticles play an efficient role compared to its macrocounterpart [48].

### 3.2. Layered Double Hydroxides (LDHs).

Layered double hydroxides which are also known as hydrotalcite-like compounds comprise of two-dimensional brucite-like positively charged layers. Excess positive charge occurring on each layer is attributed to cation replacement and oxidation in octahedra. Between these kinds of two layers, exchangeable anions are located to compensate the effect of excessive positive charge on each layer and this arrangement gives its layered type nature. Depending upon the nature of cations and the ratio between divalent and trivalent cations, a variety of LDHs are created [49, 50]. Scientists have been working on exploiting this phenomenon in many fields including environmental remediation, thus excessive fluoride removal in drinking water. Furthermore, its unique structural properties such as distribution of different metal cations, surface hydroxyl groups, tunability, swelling properties, high thermal and chemical stability, intercalated anions with interlayer space, and high bio compatibility make LDHs more suitable in many applications [50]. Negligible toxicity is another advantage [51]. Synthesis of LDHs is mainly done using simple coprecipitaion method and other methods involve ion exchange rout and reconstruction rout [52]. Some instances report the usage of block copolymers to form a micella [53]. By monitoring the synthesis parameters such as nucleation, aging program, solid composition, and interlayer anion, size can be dramatically changed [51]. The most commonly used solvent is distilled water in preparation although in some instances methanol has been reported [54]. This layered structure has demonstrated the memory-effect in previous studies

[50, 55, 56]. Elhalil et al. [56] has shown this effect in calcined Mg/Al-layered double hydroxide in defluorination application in groundwater.

In the study of Elhalil et al. [56], water defluoridation had been carried out using both calcined Mg/Al-layered double hydroxide and its ordinary counterpart (macro size). The results showed that calcined LDHs had a greater potential of fluoride removal compared to noncalcined one (80% and 20%, respectively). According to the kinetic study of adsorption process, data best matched with pseudo-second-order kinetic model with adsorption coefficient 0.998 mg/g. Maximum absorption was reported at pH 6.85. Adsorption and ion exchange were the mechanisms reported. However, with further regeneration cycles (adsorption and calcination), the adsorption capacity had decreased, which the author attributed this low fluoride removal to decreasing of crystallinity with increasing number of cycles. Gao et al. [57] carried out a study to evaluate the fluoride removal potential of Mg-Al-LDHs nanoflake impregnated magnetic alginate beads (80–100 nm) and the author claimed its fluoride removal ability was astonishingly effective compared to most of other adsorbants ($32 \, mg \cdot g^{-1}$ at pH 5). According to authors, safety issues should be concerned and as a tactical approach, alginate beads, which are biodegradable and highly abundant, were used to immobilize potentially harmful nanoparticles. Magnetism was achieved by using $Fe_2O_3$ nanoparticles. Another study [58] incorporated Co into Mg/Al LDHs to synthesize rosette-layered structure, and the adsorption capacity was 58.82 mg/g at pH = 7(value almost similar to natural water bodies). A flower-like calcined Ca-Mg LDHs (588.97 nm in length and 64.56 nm in width) synthesized via a simple hydrothermal method showed the maximum adsorption values as 9.211 mg/g and 8.294 mg/g for first and fourth cycle, respectively [59]. Another study [60] deployed an electrosorption method (capacitive deionization) with NiAl LMO (nickel aluminum-layered metal oxide) in order to selectively remove excess fluoride ions from water. In this sophisticated method of fluoride removal, effective adsorption and regeneration via applying a reverse voltage of adsorbent is well ensured. The maximum adsorption capacity was 49.28 mg/g for fluoride ions, and the authors suggested the reason for high selectivity of $F^-$ is the highest negativity of ions and the complexation between fluoride and hydroxyl ammonium ions. Retention of 94.4% removal rate after ten cycles reveals the high durability of this electrosorption technique compared to many other techniques.

### 3.3. Magnetic Nanoparticles.

Magnetic nanoparticles, used for versatile functions in many industries, possess variety of unique properties. Electrons in orbitals of atoms possess unique magnetic moments, and it gives rise to different magnetic properties of different type of materials. While paramagnetic state exhibits a temporary magnetism in presence of an external magnetic field (a small net crystal magnetization), ferromagnetic and antiferromagnetic states exhibit magnetism owing to individual magnetic moments without an external magnetic field below Curie temperature (for antiferromagnetic, net magnetic moment is zero). Ferrimagnets also possess magnetization [61]. Applications in magnetic nanoparticles employ the effect exerted by particle magnetic moment on their properties in presence of a magnetic field [62]. When the size of a ferromagnet or a ferrimagnet is brought down to the nanosize range, it acts as a super paramagnet which acts almost similar to a paramagnet in an external magnetic field and thus prevents particle aggregation and ensures colloidal stability. In the nanorange, particles behave as single magnetic domain [63]. Tren and Webster have emphasized the toxic effect of pure metal magnets and hence the unsuitability for biomedical applications [64]. Synthesizing methods include size reduction (top down approach), chemical coprecipitation, sol-gel method, hydrothermal synthesis microemulsion, laser evaporation techniques, laser evaporation techniques (bottom up approach), and biomineralization processes [61, 65]. Ubiquitously used magnetic materials involve iron, cobalt, nickel, and its oxides (magnetite, maghemite, chromium dioxide, and cobalt ferrite) [66]. Several studies have been conducted to assess the suitability of using magnetic nanoparticles in $F^-$ removal [67–69].

Riahi et al. [70] synthesized $Fe_3O_4@ZrO_2$, a combination of superparamagnetic nanoparticles with Zirconium oxide which has been reported as having a high fluoride adsorption capacity in previous studies. Magnetic nanoparticles which ease the separation of magnetic material-target conjugate using an external field and the $Zr^{4+}$ solution were separately synthesized via a coprecipitate method, and then a freshly prepared $Zr^{4+}$ metal solution was added dropwise into the solution containing magnetic nanoparticles. Particle size of the resultant core-shell structure was 10 nm, and the zeta potential was −34.1 (±0.2) mV which was smaller than pure $Fe_2O_3$ nanoparticles and thus ensured lower particle aggregation probability. While adsorption data best fit with Langmuir model giving adsorption capacity $158.6 \, mg \cdot g^{-1}$ in pH 2.5, kinetic analysis matched the data with pseudo-second-order rate equation. Charge density of the surface which in turn depends on solution's pH determines the adsorption capacity. This adsorbent showed amphoteric properties (according to Brønsted–Lowry acid–base theory) depending on solution pH, and hence, ligand exchange or surface complexation may happen in fluoride sorption, VSM analysis revealed. Sahoo and Hota [71] have synthesized a new magnetic nanocomposite, a binary metal oxide ($MgO-MgFe_2O_4$/10 nm) attached on to graphene oxide via a simple hydrothermal method. MgO has shown excellent adsorbent capacity for fluoride [72] owing to the presence of several $OH^-$ groups, higher sorption capacity, nontoxicity, and environmental friendliness, and hence, the binary mixture of iron and MgO nanoparticles has shown promising results. According to authors, graphene oxide was used as a substrate to anchor nanoparticles so that it not only enhances the specific area for adsorption but also it ensures efficient recovery. Despite that nanoparticles are being used frequently for environmental remediation, due to their ultrafine size, these particles are hard to separate. This may pose other adverse health and environmental issues [73]. This kind of tactical approaches

eliminate such problems. Adsorption capacity was reported as $34 \, mg \cdot g^{-1}$, and kinetic study revealed that data fit with pseudo-second-order kinetic equation and obeys the Langmuir isotherm. Thermodynamically adsorption process was endothermic. Another study conducted by Dewage et al. [74] reported an adsorbent composed of Douglas fir biochar and $Fe_3O_4$ dispersed onto the biochar surface for acquiring magnetization, for rapid nitrate and fluoride removal. Since both biochar and $Fe_3O_4$ separately act as an adsorbent, this novel adsorbent is known as a magnetic hybrid biochar. Some octahedral $Fe_3O_4$ particles present in biochar were in the micro range ($0.5 \, \mu m$–$3.5 \, \mu m$), and others were roughly spherical with diameter $100 \, nm$–$300 \, nm$. Adsorption isotherm studies revealed that the data follow Langmuir adsorption isotherm with $9 \, mg/g$ adsorption capacity. Adsorption mechanism was depicted by electrostatic attraction between negative ions (both fluoride and nitrate) and amphoteric hydroxyl ions which are positively charged below PZC. Above pH 11, hydroxyl ions on surfaces of both iron oxide and biochar were deprotonated; hence, the adsorption capacity declined rapidly. According to Sig and Stumm [75], $Fe_3O_4$ surface contains 4–10 iron-bonded hydroxyl groups per $nm^2$. Study conducted by Zhao et al. [76] illustrated the fluoride removal potential of a nanocomposite constructed with hydrous $Al(OH)_3$ and $Fe_3O_4$ nanoparticles, having an adsorption capacity around $88.48 \, mg \, g^{-1}$ according to Langmuir equation.

An efficient and novel adsorbent (superparamagnetic Fe3O4@Polyprrrole) in an electromagnetic coupling system has been evaluated for defluoridation in Weng et al.'s study [77]. Electrochemical ion exchange (EIX) is a combination of ion exchange and electrochemistry in order to obtain a higher efficiency of separation than using either technique separately [78]. This method is widely used in water remediation especially in elimination of toxins. In conventional EIX, the electroacive substance is electrically (by applying a voltage) either reduced or oxidized in order to uptake and elute ions. However, due to concentration polarization and low electrical conductivity, the efficiency is hindered. To overcome the challenge, a novel "magnetic potential-responsive ion exchange nanomaterial "(21–23 nm) has been synthesized in this study so that the ion exchange resin can be magnetically separated after the ion exchange process. Further, if these novel nanoparticles can be adsorbed on an electrode by a magnet, adsorbed ions can be easily desorbed by applying a potential, which ensures the recoverability of the nanomaterial.

### 3.4. Carbon Nanotubes.
Carbon nanotubes (CNTs), an allotrope of carbon, possess unusual characteristics which are valuable in nanotechnology. Further, owing to their capability of being functionalized by other chemicals and one-dimensional periodic structure, properties of CNT can easily be manipulated. Carbon nanotubes are best described as structures having cylindrical graphene structures capped with fullerinoid endcaps [79]. CNTs exist as both single-wall and multiwall nanotubes composed of many coaxial and nested single-wall nanotubules. Typical dimensions are

reported as 2–20 nm for outer diameter, 1–3 nm for inner diameter, $1 \, \mu m$ for the length, and 340 pm for intertubular distance [80]. The arrangement of hexagons in graphene sheets with respect to the central axis determines whether the structure of the nanotube is arm chair, zigzag, or chiral one.

An adsorbent made by single-walled carbon nanotubes (SWCNTs) for excess fluoride removal was reported in a recent study [81]. The inner and outer diameters of CNT were 1–2 nm and 0.8–1.1 nm, respectively, and length was 5–15 $\mu m$. As many adsorbents, when increasing the adsorbent dosage, the adsorption capacity decreased due to agglomeration and overlapping of adsorbents with increasing adsorbent concentration. However, the removal percentage increased with increasing adsorbent dosage. The maximum adsorption capacity was 16.63 mg/g at pH 6.

Another study [82] describes the capability of hydroxyapatite (HA) nucleated and grown on multiwalled carbon nanotubes in excess fluoride removal in groundwater. Adsorption capacity was $39.22 \, mg \cdot g^{-1}$ at 323 K. Commercially available multiwalled nanotubes (MWCNTs) were functionalized to form carboxylic groups via a refluxing process with nitric acid followed by an in situ sol-gel polymerization method to form HA-MWCNT composite. Initially functionalized MWCNTs were sonicated with SDS (sodium dodecyl sulphate) so that SDS was fully adsorbed onto CNT tubes. Then $Ca(NO_3)_2$, $NaH_2PO_4$, and $NH_4OH$ were added systematically followed by an adjustment of pH. Finally, aging and calcination were performed to obtain HA-MWCNT powder. TEM (transmission electron microscopy) data suggested the formation of needle-like HA nanoparticles on the surface of the MWCNTs. Surface specific area was $180.504 \, m^2 \cdot g^{-1}$, and average pore size was 14.607 nm. Adsorption was an endothermic process. An almost similar study was carried out by Tang et al. [83] to obtain an adsorption capacity of $11.05 \, mg \cdot g^{-1}$. A comparison between SWCNTs and MWCNTs regarding the capability of fluoride removal is depicted in the study of Dehghani et al. [84]. BET studies showed the specific surface areas as 700 and 270 $m^2/g$ for SWCNTs and MWCNTs, respectively. Freundlich isotherm model best described the data and the best fit kinetic model was pseudo-second-order kinetics model. Adsorption capacity values were 2.83 and 2.4 mg/g for MWCNTs and SWCNTs, respectively, while the obvious discrepancy was attributed to the presence of higher internally available adsorption sites. The experiment conducted by Rostami et al. [85] evaluated the potential of multiwalled carbon nanotubes (MWCNTs) in mitigating excess fluoride problem, and further the study elaborated the toxic effect of fluoride-laden MWCNTs to aquatic systems by using *Daphnia magna* organism. They had studied the effect of initial fluoride concentration and optimum adsorbent dosage for the highest percentage removal. Results revealed that highest removal percentage (60.1%) was reported at 1 mg/L of initial fluoride concentration at pH 5 and at a dose of 0.5 mg/L of the adsorbent. The focus of this study was to evaluate the toxicity effect of fluoride-loaded MWCNT to water bodies, which should be addressed properly when using nanotechnology. Dose descriptors are given in terms of

TABLE 1: Summary of fluoride removal capacities by different adsorbents.

| No | Adsorbant | Special remarks | AC (mg/g) | Studies conducted | Ref |
|---|---|---|---|---|---|
| 1 | MgO-MgFe$_2$O$_3$ binary oxide anchored on to GO (graphene oxide) | Adsorption mechanism: Electrostatic interactions inner-sphere complexation (Mg$^{2+}$ -F$^-$) (anion exchange) H bonding hydrothermal method (precursor; PEG) Ave. diameter of binary oxide: 10 nm separation via an external magnetic field Highly stable and high specific area presence of CO$_3^{2-}$ and PO$_4^{3-}$ lowers the removal % | 34 at pH 6.0 (303.15 K) | Pseudo-second-order kinetic equation Langmuir isotherm model Endothermic and spontaneous process Saturation magnetization: 0.575 emg$^{-1}$ | [71] |
| 2 | rGO/ZrO2 (continuous fixed bed column study in upward flow mode) | Hydrothermal route Possible mechanisms: Surface reactions between ZrO$_2$ and F$^-$(ZrO2 exists as seven coordinated polyhedral species and hence it increases the adsorption capacity of rGO) Addition of F$^-$ happens via hydroxyl protonation Fluoride ion attack loss of water molecule Removal was affected by PO$_4^{3-}$ | 45.7 at pH 7 | Break through curve: Yoon–Nelson model (continuous bed type) | [95] |
| 3 | 3D yttrium based-graphene oxide-sodium alginate hydrogel | Macro structure adsorbent which involves graphene oxide. A sol-gel process was used GO sheets can be easily crosslinked with yttrium ion and sodium gel was used as the supporter medium. Mechanism: ion exchange Easy regeneration | 288.96 at pH 4.0 | Langmuir isotherm model Both pseudo-first-order and pseudo-second-order models are best matched. Column study: Thomas model. The removal rate in the column system (at relatively lower flow rate) >batch reactor | [96] |
| 4 | Hydrous iron (iii)-aluminum (iii) mixed oxide-graphene oxide composite (HIAGO) | Synthesized by a chemical precipitation method "Spindle liked" mixed oxides dispersed irregularly on GO backbone Mechanisms: Electrostatic interaction and ion exchange | 27.8 at pH 5 (318 K) | Best matched with Langmuir isotherm model and the pseudo-second-order kinetics endothermic reaction | [94] |
| 5 | Hierarchical AlOOH@ reduced graphene oxide hybrid | Supercritical carbon dioxide assisted synthesis (eco-friendly) Specific area: 513 m$^2$·g$^{-1}$ (mesoporous structure) AlOOH nanosheets were evenly spread (layer upon layer) on rGO and a hierarchical 3D structure was created Electrostatic interaction and ligand exchange adsorption process to form Al-F complexes Mean pore size; 8 nm | 118.7 at pH 6.5 (high AC at lower F$^-$ concentration) | Best matched with Langmuir isotherm model and the pseudo-second-order kinetics | [97] |
| 6 | Magnetic iron-aluminum oxide/graphene oxide nanoparticles | One step method of co -precipitation method Specific surface area; 349 m$^2$/g Mechanisms: Electrostatic interactions, anion exchange, and inner-sphere complexation Can be used in a wide pH range; 3–9 low residual ion and aluminum residual after defluoridation | 64.72 at pH 6.5 | Best matched with Langmuir isotherm model and the pseudo-second-order kinetics. Saturation magnetization: 7.5 emu/g (superparamagnetism) | [98] |
| 7 | Al$_2$O$_3$-Fe$_3$O$_4$-expanded graphite nano-sandwich structure | Coprecipitate method resulting 60–80 nm Fe$_3$O$_4$ cubes and 20–50 nm Al$_2$O$_3$ spread on graphite surface Fluoride removal efficiency: 96% at pH 4 After two cycles the efficiency: 91% Convenient separation via an external magnetic field Stability is higher | 2.19 at pH 2–10 | Best matched with Langmuir isotherm model and the pseudo-second-order kinetics. Saturation magnetization: 3.7 emu/g | [99] |
| 8 | Hydrous CeO2-Fe3O4 decorated polyaniline fibers nanocomposite | A coprecipitation deposition on pre-synthesized polyaniline fibers over a large pH range (3–10) the removal rate was nearly constant giving the maximum as 94% at pH 3 | 93.46–117.64 over a pH range 3–10 | Best matched with Langmuir isotherm model and the pseudo-second-order kinetics. Exothermic reaction. Spontaneous reaction | [100] |

TABLE 1: Continued.

| No | Adsorbant | Special remarks | AC (mg/g) | Studies conducted | Ref |
|---|---|---|---|---|---|
| 9 | Activated carbon@SnO2 (biosorption process) | Activated carbon was synthesized via pyrolysis of sawdust and activation with phosphoric acid. A mixture of activated C and stannous chloride was sonicated followed by $NH_3$ addition to obtain a gel like product. After washing the obtained product was calcined at 673 K for 2 hCrystal structure; rutile tetragonal tin oxide $SnO_2$ nanoparticles embedded on amorphous carbon matrix (12 nm) Mechanism; combination of strong electrostatic interaction between Sn4+ and arsenic/fluoride anions, followed by anion exchange process with hydroxylated surface of $SnO_2$-AC nanocomposite | 4.60 at pH 6.5 | Best matched with Langmuir isotherm model and the pseudo-first-order kinetics. Endothermic and spontaneous reaction. Chemisorption may happen. Greater regeneration capability (removal % remained around 90% after 3 consecutive cycles) Low production cost (cheaper than activated C solely according to the cost estimation study) | [101] |
| 10 | Magnesium oxide entrapped polypyrrole hybrid nanocomposite | MgO nanoparticles were synthesized with constant mechanical stirring (1000 rpm) using $MgCl_2$ and $NH_3$. Polymer nanocomposite was synthesized by chemical oxidative polymerization using $FeCl_3$ as an oxidant. | 4.32 | Best matched with Langmuir isotherm model fluoride removal is endothermic and spontaneous nature. Field study was conducted. (79% of fluoride was removed) | [102] |
| 11 | Mesoporous $\gamma$-ALOOH powder from coal-bearing kaolinite | Extraction of Al from kaolinite using sulfuric acid instead of hydrochloric acid. Synthesis of mesoporous $\gamma$AlOOH was performed in a hydrothermal synthesis using hexamethylenetetramine as the hydrolyzing agent The average crystallite size was estimates as 14.4 nm for as prepared material compared to commercial one in which the value is 37 nm. | Not given | BET surface area could be controlled from 6.3 to 192.5 $m^2 \cdot g^{-1}$ when varying reaction time and temperature. | [103] |
| 12 | Chitosan-Fe-Al-Mn metal oxyhydroxides composite | Hydrous mixed-metal oxyhydroxides, loaded chitosan composite was made using laterite clay and waste from steel (low-cost materials) industry via coprecipitation method Polymeric matrix prevents particle agglomeration 20–30 nm mixed-metal spheres were homogeneously spread on chitosan matrix (this ensures easy access of F-onto the porous outer surface of mixed-metal sphere) BET surface area is 41.6 $m^2$/g. Influence of other ions was not significant. Prevents strong electric double layer formation when the polymer barrier is present and thus it does not hinder the adsorption. can be used as a fluoride scavenging material in a household filter effective for broad pH range; 3.5–8.5 | 40.0 ± 0.5 at pH 6.7 | Best matched with Freundlich isotherm model (multilayer adsorption on heterogenous surface sites) and the pseudo-second-order kinetics with rapid adsorption (chemisorption is possible) Adsorption capacity of mixed-metal oxyhydroxides with chitosan > without chitosan | [104] |
| 13 | Highly efficient nano-adsorbent, Al(III)-Fe(III)-La(III) trimetallic oxide | Health risk of using Al solely has been eliminated by introducing $Fe^{3+}$ in this study (although $Fe^{3+}$ is widely used for fluoride adsorption some studies suggest low AC as 16.5 mg/g). $La^{3+}$ is an excellent fluoride adsorbent. The presence of $Fe^{3+}$ makes the separation easier via an external magnet Chemical rout was used and triethanolamine is the chelating agent Adsorption mechanism: Ligand exchange XRD pattern revealed the amorphousness of the structure which increase the surface area (22.14 $m^2$/g)Avrg. Particle size; 20 (±0.50) nm pore diameter 3.324 nm | Not given | Maximum fluoride could be removed up to 99.8% at pH 7.0, contact time: 60 min, adsorbent dose: 0.3 g/100 ml | [105] |

TABLE 1: Continued.

| No | Adsorbant | Special remarks | AC (mg/g) | Studies conducted | Ref |
|---|---|---|---|---|---|
| 14 | Hybrid Al2O3/Bio-TiO2 nanocomposite impregnated Thermoplastic polyurethane (TPU) nanofibrous membrane for fluoride removal | Titanium dioxide was synthesized using a bacteria *Bacillus licheniformis* and modified with alumina followed by impregnation of synthesized hybrid material on to eletrospun thermoplastic polyurethane nanofibers through silane functionalization Particle size of the nanocomposite: $50 \pm 6$ nm. Average diameter: $239 \pm 33$ nm. Titania was in the anatase phase having a body centered tetragonal crystal structure. Mechanism of $F^-$ adsorption: Formation of surface complexes | 1.9 | Both batch type and dip mode adsorption studies were carried out and, in both studies, adsorbent capacity decreased when the adsorbate concentration is increased. Best matched with Langmuir isotherm model and with second-order kinetic model. | [106] |
| 15 | Coconut-shell derived carbon/carbon nanotube composite | CNT were coated on coconut-shell charcoal using plasma enhanced chemical vapor deposition BET surface area: $358\,m^2 \cdot g^{-1}$ Low-cost adsorbents Removal percentage: 65% of the initial concentration of $4.4\,mg\,L^{-1}$ | 0.36 at pH 2 | Best matched with Langmuir isotherm model and the pseudo-second-order kinetics fluoride removal is endothermic and spontaneous nature. A field study was carried out to nalagonda water sample and obtained satisfactory results (initial adsorbent concentration is $10\,g\,L^{-1}$ and equilibrium contact time was 3.5 h) | [107] |
| 16 | Iron-oxide nanoparticles by green Synthesis. Method using *Moringa oleifera* leaf extract | Green synthesis (a solution of iron nitrate III was mixed with heated leaf extract under stirring and immediate color change from green to black indicates the nanoparticle formation) Plant extract acts as the reducing agent Pore diameter: 4.14 nm. Specific surface area: $99.79\,m^2 \cdot g^{-1}$ Spherical mesopores were present. There is no need to use chemicals, high temperatures, and pressure | 1.40 at pH 7 (higher than BGAC) | Study compared the removal percentage with granulated charcoal of bone (BGAC) Best matched with Langmuir isotherm model and the pseudo-first-order kinetics. Endothermic and spontaneous. Equilibrium time: 40 min at pH 7 for iron oxide while it was 180 min at pH 5for BGAC Repeated sorption regeneration cycles indicated reusability. | [108] |
| 17 | NaP : HAp nanocomposite | Hydroxyapatite was synthesized followed by composite making with NaP Zeolite Both cactus-like and diamond like morphology were observed Particles shaped hydroxyapatite were within the diameter of 40–70 nm BET surface area: $35.62\,m^2/g$ pore volume: $0.141\,cm^3/g$ | 66.66 mg/g | Analysis of several factors were carried out using the four factors box—Behnken design with three levels (optimum pH value was found to be 7 at 60 min with 5 mg/L of fluoride concentration and at 55°C) Optimum removal; 97.45% Best matched with Langmuir isotherm model. The adsorption is an endothermic process | [109] |
| 18 | Millisphere nanocomposite of La-Doped Li-Al layered double hydroxides supported by polymeric anion exchanger (LaLiAl-LDH@201) | Drawbacks of LDHs such as pressure drop and blockage were overcome by impregnating the LDHs into millimetric polystyrene anion exchanger Li/Al LDH was doped with high-valent metal Lanthanum Spherical nanoparticles with clean edges to irregular state. Stability over wide pH range; 3.5–12 Adsorption mechanism: Anion exchange between Cl– and F–, and the specific interaction between La and F Capability of *in situ* regeneration when NaOH, NaCl binary mixture was added An increase in adsorptive capacity in the presence of the competing anions was observed Negligible capacity loss, La leaching, or structure alteration was observed after five adsorption-regeneration cycles | 75.7 | The adsorption kinetics could be fitted with both pseudo-first-order and pseudo-second-order models with approximately identical coefficients of determination. Best matched with Freundlich isotherm model. Excellent fixed bed working capacity and regeneration ability. | [110] |

Table 1: Continued.

| No | Adsorbant | Special remarks | AC (mg/g) | Studies conducted | Ref |
|---|---|---|---|---|---|
| 19 | Tetraethylenep-entamine functionalized nanomagnetic composite | nFe3O4@TEPA was produced using a polyol-media one-pot solvothermal method. Adsorption capacity was independent from solution pH (2–11). The effect of HF at pH below 5 (pHpzc) has not affected the AC. Avg. diameter: 20 nm. Higher saturation magnetization compared to other nanomagnetic polymers. Adsorption mechanism: Electrostatic attraction and H bonding. The effect of coexisting ions were estimated by standard response surface methodology (RSM) design called box-behnken design (BBD) | 163.9 | Best matched with Langmuir isotherm model. Endothermic and spontaneous saturation magnetization: 48.2 emu/g. Better reusability (composite could be used for at least 10 cycles with a loss of less than 2.8% upon recovery on average) | [111] |
| 20 | Membrane capacitive deionization with nanoporous and microporous $Limonia$ $acidissima$ (wood apple) shell activated carbon electrode (LASAC) | Nanoporous-activated C was synthesized from $Limonia$ $acidissima$ using chemical and thermal modifications. For LASAC electrode preparation, LASAC powder, graphite powder, and polyvinylidene fluoride were mechanically stirred in N, N dimethylacetamide solvent to make a paste | 2.7554 at pH 7.2 Under 100 mg/L Feed concentration and 1.2 V | Best matched with Langmuir isotherm model and the pseudo-first-order kinetics | [112] |
| 21 | Electrically enhanced adsorption and green regeneration 1 for fluoride 2 removal using $Ti(OH)_4$-loaded activated carbon electrodes | Blending of electrosorption and adsorbent adsorption Membrane can be easily regenerated by applying -1.6 V Excellent regeneration capability and stability of removal % after reusage The adsorbent possesses high adsorption $F^-$ selectivity, high adsorption capacity, and clean regeneration without any chemicals Surface area: 1700 $m^2$/g Pore size: 1.5 nm and 2.35 nm Influence of other ions is negligible | 115.2 at +1.2 V | Best matched with Langmuir isotherm model | [113] |
| 22 | Millimeter-sized Mg-Al-LDH nanoflake impregnated magnetic alginate beads | Biobased sorbent Rhombohedral symmetry was there. Estimated thickness of the nano-LDH: 18 nm Multidispersed $Fe_2O_3$ particles with avg. diameter 20 nm surface adsorption, interparticle diffusion and intraparticle diffusion all contributing to the rate of adsorption | 32.4 at pH 5 | Best matched with Freundlich isotherm model and the pseudo-second-order kinetics with rapid adsorption | [57] |
| 23 | Metal organic framework (Uio-66) | $ZrCl_4$ $[Zr_6O_4(OH)_4(BDC)_6]_{21}$ and terephthalic acid were dissolved in DMF solution and heated in an autoclave to synthesis Uio-66 Avg. size: 153–213 nm. Optimum conditions according to RSM and central composite design analysis were pH: 7, fluoride ion concentration: 14.6 mg $L^{-1}$, Uio-66 dosage: 0.4 g l–1, contact time: 41.5 minute, removal efficiency of 80.21 percent, and a desirability of 1 | 31.09 pH range 6–9 | Best matched with Langmuir isotherm model and the pseudo-second-order kinetics. | [114] |

NOEC (no observed effect concentration). Results showed that NOEC-24 was 0.391 g/L, and accordingly, the authors claimed that the toxicity is negligible in aquatic environment.

3.5. Nanofiltration. When an external pressure is applied to counteract the osmotic pressure through a semipermeable membrane, it allows impurities (certain solutes) to retain (concentrate) and water (permeate) to pass through; this phenomenon is called reverse osmosis (molecular separation from aqueous medium). In nanofiltration (NF), the membrane possesses nanometer-sized pores (1–10 nm) which are larger than pores in membranes used for reverse osmosis (RO). It allows divalent ions to remain and monovalent ions to pass through. Ability of processing large volumes and producing high output are some of the benefits of using nanofiltration. Ayoob et al. [86] state that both methods (nanofiltration and reverse osmosis) are better in defluoridation compared to other conventional methods as precipitation and adsorption. In Sri Lanka, RO is used industrially to filter drinking water samples. Factors affecting for the retention of ions include Donnan effect owing to

electrostatic attraction between ions and the fixed charges of the membrane and the steric hindrance [87, 88]. Further elaborated theory has been put forward as SEDE model (steric, electric, and dielectric exclusion model) by Szymczyk and Fievet [87]. Removal efficiency of 82% at the flow rate of 0.4 L/min was obtained in another study of application of nanofilters [89].

*3.6. Graphene-Based Nanomaterials.* Graphene, a single layer of hexagonally arranged carbon allotrope ($SP^2$), is now being widely used to construct sensors, transistors, and catalysts and deployed in environment pollution management [90, 91]. This 2D, atomically thin graphene inherits unique mechanical, electrical, and thermal properties such as high room temperature charge carrier mobility (100,000 $cm^2 \cdot V^{-1} \cdot s^{-1}$), theoretically large surface area (2630 $m^2 \cdot g^{-1}$), optical transparency, excellent mechanical strength (2.4 _ 0.4 TPa), high thermal conductivity (2000 to 5000 $W \cdot m \cdot K^{-1}$), capacity of sustaining large electrical current density (108 $A \cdot cm^{-2}$), etc. [92, 93]. Graphene sheet acts as a supportive matrix for nanomaterials (nano-oxide materials) and give good dispersibility (retard agglomeration) and mechanical strength. Organic pollutants can be eliminated via Π-Π interactions [91]. Further, graphene oxide, the precursor of graphene, is prepared by Hummer's method, and it being associated with number of –COOH, -C=O, and –OH is an excellent scavenger of polar and ionic solutes from solvents [94]. Table 1 demonstrates the applicability of graphene in fluoride scavenging.

*3.7. Polymer-Based Nanomaterials.* Polymer grants intrigued qualities for nanocomposites and membranes. The greater flexibility, mechanical strength, selective transfer of chemicals, excellent film forming ability, high perm selectivity, and low cost are some of the properties that are beneficial in water purification applications [115]. Due to its high tailoring ability, when polymers are incorporated with nano-oxide materials, fouling can be retarded. Further, it enhances the membrane hydrophilicity as well. These polymer composites can also be used in ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) applications. Polymer nanocomposites can be categorized into two as blended nanocomposites and thin-film nanocomposite membranes. In blended form, both polymer and nanoparticles are dispersed in the casting solution prior to the casting process. In thin-film type, nanoparticles make a thin film on the polymer matrix by self-assembly, or the deposition of nanomaterials is done after the polymer membrane has been synthesized. Thin-film polymer nanocomposite drags the attention of researcher owing to its resistance to pH changes and high stability. To overcome the leakage problem in membranes due to high pressure, the surface of nanoparticles can be modified by chemical functionalization [116]. Recent studies of polymer nanocomposites on fluoride removal are mentioned in the table (Table 1) below.

*3.8. Other Novel and Green Approaches.* The stem of a weed variety, *Ipomoea carnea*, has been carbonized to form good-quality carbon followed by AlOOH nanoparticle deposition for defluordation in water. The study [117] claims the adsorption capacity as 46.55–53.71 mg g$^{-1}$ at pH 6 to 8 although the efficiency drops at real groundwater application. Moreover, the author suggests this method as an effective utilization of cumbrous weed and low-cost method in addition to commercially available methods (e.g., RO technique). Synthesis of different phases of titanium dioxide nanoparticles by using metal-resistant *Bacillus* NARW11 species was assessed by Suryiaraj et al. [118] to gain adsorption capacity of 0.85 mg/g (anatase phase, 47.26 ± 13.5 nm). Xia et al. [119] have reported facile defluoridation of drinking water by forming shell@fluorapatite nanoarray during boiling egg shells.

## 4. Conclusion

Various types of recent and novel fluoride removal techniques involving nanotechnology are summarized in this review. Further, contamination means have also been briefly elaborated. Focus has been given to novel adsorbents such as LDHs, magnetic nanoparticles, CNT, and other membrane techniques among many other possible techniques. However, given experimental results are valid under specific parameters including pH, other ions present, initial fluoride concentration, temperature, etc. Therefore, these methods should be tested in real-world application even though only few studies have succeeded so far. Other than that cost factor, simplicity and eco-friendliness of these nanomaterials should be evaluated in this regard.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

## References

[1] K. E. Heller, S. A. Eklund, and B. A. Burt, "Dental caries and dental fluorosis at varying water fluoride concentrations," *Journal of Public Health Dentistry*, vol. 57, no. 3, pp. 136–143, 1997.

[2] J. Lalumandier and R. G. Rozier, "The prevalence and risk factors of fluorosis among patients in a pediatric dental practice," *Pediatric Dentistry*, vol. 17, no. 1, pp. 19–25, 1995.

[3] L. Morgan, E. Allred, M. Tavares, D. Bellinger, and H. Needleman, "Investigation of the possible associations between fluorosis, fluoride exposure, and childhood behavior problems," *Pediatric Dentistry*, vol. 20, no. 4, pp. 244–252, 1998.

[4] J. E. Williams and J. D. Zwemer, "Community water fluoride levels, preschool dietary patterns, and the occurrence of fluoride enamel opacities," *Journal of Public Health Dentistry*, vol. 50, no. 4, pp. 276–281, 1990.

[5] P. Connett, "The absurdities of water fluoridation," 2002, http://fluoridefreesacramento.org.

[6] P. Connett, *The Case Against Fluoride*, ChelseaGreenPublishing, White River Junction, VT, USA, 2010.

[7] C. B. Dissanayake, "Water quality and dental health in the dry zone of Sri Lanka," *Geological Society, London, Special Publications*, vol. 113, no. 1, pp. 131–140, 1996.

[8] O. A. Ileperuma, H. A. Dharmagunawardhane, and K. P. R. P. Herath, "Dissolution of aluminium from substandard utensils under high fluoride stress: a possible risk factor for chronic renal failure in the North-Central Province," *Journal of the National Science Foundation of Sri Lanka*, vol. 37, no. 3, pp. 219–222, 2009.

[9] S. Jagtap, M. K. Yenkie, N. Labhsetwar, and S. Rayalu, "Fluoride in drinking water and defluoridation of water," *Chemical Reviews*, vol. 112, no. 4, pp. 2454–2466, 2012.

[10] M. Barathi, A. S. K. Kumar, and N. Rajesh, "Impact of fluoride in potable water - an outlook on the existing defluoridation strategies and the road ahead," *Coordination Chemistry Reviews*, vol. 387, pp. 121–128, 2019.

[11] D. L. Sparks, *Environmental Soil Chemistry*, Elsivier Science, Atlanta, GA, USA, 2nd edition, 2003.

[12] U. Maheshwari, *Removal of metal ions from wastewater using adsorption: experimental and theoretical studies*, Ph.D. thesis, Birla Institute of Technology and Science, Pilani, Rajasthan, India, 2015.

[13] E. Bazrafshan, D. Balarak, A. Panahi, H. Kamani, and A. Mahvi, "Fluoride removal from aqueous solutions by cupricoxide nanoparticles," *Fluoride*, vol. 49, pp. 233–244, 2016.

[14] M. Zazouli, A. Mahvi, Y. Mahdavi, and D. Balarak, "Isothermic and kinetic modeling of fluoride removal from water by means of the natural biosorbents sorghum and canola," *Fluoride*, vol. 48, no. 1, pp. 37–44, 2015.

[15] H. Akbari, F. Jorfi, A. Mahvi, M. Yousefi, and D. Balarak, "Adsorption of fluoride on chitosan in aqueous solutions: determination of adsorption kinetics," *Fluoride*, vol. 51, no. 4, pp. 319–327, 2018.

[16] V. Sivasankar, "A world ubiquitous compound, its chemistry, and ways of contamination," in *Surface Modified Carbons as Scavengers for Fluoride from Water—2016*, p. 5, Springer International Publishing, Cham, Switzerland, 2016.

[17] A. Adriano, "Fluorine," in *Trace Elements in the Terrestrial Environment*, p. 479, 1986.

[18] N. Wiberg, A. Holleman, and E. Wiberg, *Inorganic Chemistry*, Academic Press, New York, NY, USA, 2001.

[19] D. Nordstom and E. Jenn, "Fluorite solubility equilibria in selected geothermal waters," *Geochimica et Cosmochimica Acta*, vol. 41, pp. 175–188, 1977.

[20] C. Chambers and A. Holliday, *Modern Inorganic Chemistry (An Intermediate Text)*, Butterworth & Co, Paddington, Australia, 1975.

[21] W. Edmunds and P. Smedley, "Fluoride in natural waters," in *Essentials of Medical Geology: Revised Edition*, pp. 311–336, 2013.

[22] D. Oszwath, "Fluorides and environmental health: a review," *Reviews in Environmental Science and Biotechnology*, vol. 8, pp. 59–79, 2009.

[23] T. Tebutt, *Relationship between Natural Water Quality and Health*, United Nations Educational, Scientific and Cultural Organization, Paris, France, 1983.

[24] G. Faure, *Principles and Applications of Inorganic Geochemistry: A Comprehensive Textbook for Geology Students*, Macmillan Coll Div Publisher, New York, NY, USA, 1991.

[25] J. Fawell, K. Bailey, J. Chilton, E. Dahi, and L. Fewtrell, *Fluoride in Drinking-water*, IWA Publishing, London, UK, 2006.

[26] W. Deer, R. Howie, and J. Zussman, *An Introduction to the Rock-Forming Minerals*, Mineralogical Society of Great Britain and Ireland, London, UK, 2013.

[27] J. He, Y. An, and F. Zhang, "Geochemical characteristics and fluoride distribution in the groundwater of the Zhangye Basin in Northwestern China," *Journal of Geochemical Exploration*, vol. 135, pp. 22–30, 2013.

[28] P. S. Datta, D. L. Deb, and S. K. Tyagi, "Stable isotope (18O) investigations on the processes controlling fluoride contamination of groundwater," *Journal of Contaminant Hydrology*, vol. 24, no. 1, pp. 85–96, 1996.

[29] M. Mohapatra, S. Anand, B. K. Mishra, D. E. Giles, and P. Singh, "Review of fluoride removal from drinking water," *Journal of Environmental Management*, vol. 91, no. 1, pp. 67–77, 2009.

[30] M. C. Kundu and B. Mandal, "Assessment of potential hazards of fluoride contamination in drinking groundwater of an intensively cultivated district in West Bengal, India," *Environmental Monitoring and Assessment*, vol. 152, no. 1–4, pp. 97–103, 2009.

[31] K. Brindha and L. Elango, "Fluoride in groundwater: causes, implications and mitigation measures," in *Fluoride Properties, Applications and Environmental Management*, S. D. Monroy, Ed., pp. 111–136, 2011.

[32] K. Kim and G. Y. Jeong, "Factors influencing natural occurrence of fluoride-rich groundwaters: a case study in the southeastern part of the Korean Peninsula," *Chemosphere*, vol. 58, no. 10, pp. 1399–1408, 2005.

[33] B. Nagudi, C. Koeberl, and G. Kurat, "Petrography and geochemistry of the Singo granite, Uganda, and implications for its origin," *Journal of African Earth Sciences*, vol. 36, no. 1-2, pp. 73–87, 2003.

[34] B. Scaille and R. Macdonald, "Fluorite stability in silicic magmas," *Contributions to Mineralogy and Petrology*, vol. 147, no. 3, pp. 319–329, 2004.

[35] M. G. García, K. L. Lecomte, Y. Stupar et al., "Geochemistry and health aspects of F-rich mountainous streams and groundwaters from sierras Pampeanas de Cordoba, Argentina," *Environmental Earth Sciences*, vol. 65, no. 2, pp. 535–545, 2012.

[36] R. Ullah and M. Zafar, "Oral and dental delivery of fluoride: a review," *Fluoride*, vol. 48, no. 3, pp. 195–204, 2015.

[37] R. Chandrajith, C. B. Dissanayake, T. Ariyarathna, H. M. J. M. K. Herath, and J. P. Padmasiri, "Dose-dependent Na and Ca in fluoride-rich drinking water—Another major cause of chronic renal failure in tropical arid regions," *Science of the Total Environment*, vol. 409, no. 4, pp. 671–675, 2011.

[38] S. Nanayakkara, S. Senevirathna, T. Abeysekera et al., "An integrative study of the genetic, social and environmental determinants of chronic kidney disease characterized by tubulointerstitial damages in the North Central Region of Sri Lanka," *Journal of Occupational Health*, vol. 56, no. 1, pp. 28–38, 2014.

[39] S. Rajapakse, M. C. Shivanthan, and M. Selvarajah, "Chronic kidney disease of unknown etiology in Sri Lanka," *International Journal of Occupational and Environmental Health*, vol. 22, no. 3, pp. 259–264, 2016.

[40] J. Fawell, K. Fawell, J. Chilton, E. Dahi, L. Fewtrell, and Y. Magara, *Fluoride in Drinking Water*, World Health Organization, IWA Publishing, London, UK, 2006.

[41] WHO, *Guidelines for Drinking-water Quality*, WHO Press, World Health Organization, Geneva, Switzerland, 4th edition, 2011.

[42] R. Ellepola, *Fluoride Levels in the Ground Water of Some Selected Districts of Sri Lanka*, University of Colombo: UC(SCI), Colombo, Sri Lanka, 1988.

[43] K. A. A. S. Warnakulasuriya, S. Balasuriya, P. A. J. Perera, and L. C. L. Peiris, "Determining optimal levels of fluoride in drinking water for hot, dry climates -a case study in Sri Lanka," *Community Dentistry and Oral Epidemiology*, vol. 20, no. 6, pp. 364–367, 1992.

[44] R. Chandrajith, J. P. Padmasiri, C. B. Dissanayake, and K. M. Prematilaka, "Spatial distribution of fluoride in groundwater of Sri Lanka," *Journal of the National Science Foundation of Sri Lanka*, vol. 40, no. 4, pp. 303–309, 2012.

[45] H. A. Dharmagunawardhane, S. P. K. Malaviarachchi, and W. Burgess, "Fluoride content of minerals in gneissic rocks at an area of endemic dental fluorosis in Sri Lanka: estimates from combined petrographic and electron microprobe analysis," *Ceylon Journal of Science*, vol. 45, no. 1, pp. 57–66, 2016.

[46] S. J. Tesh and T. B. Scott, "Nano-composites for water re-mediation: a review," *Advanced Materials*, vol. 26, no. 35, pp. 6056–6068, 2014.

[47] R. K. Sharma, P. Sharma, and A. Maitra, "Size-dependent catalytic behavior of platinum nanoparticles on the hexacyanoferrate(III)/thiosulfate redox reaction," *Journal of Colloid and Interface Science*, vol. 265, no. 1, pp. 134–140, 2003.

[48] UNW-DPAC, "Water and industry in the green economy: information brief," UN Report, 2011.

[49] Z. Brigul and A. Ahmet, "Layered double hydrox-ides—multifunctional nanomaterials," *Chemical Papers-Solvak Academy of Science*, vol. 66, pp. 1–10, 2012.

[50] G. Mishra, B. Dash, and S. Pandey, "Layered double hy-droxides: a brief review from fundamentals to application as evolving biomaterials," *Applied Clay Science*, vol. 153, pp. 172–186, 2018.

[51] R. Rojas, D. Bedoya, C. Vasti, and C. Giacomelli, "LDH nanoparticles: synthesis, size control and applications in nanomedicine," in *Layered Double Hydroxides (LDHs): Synthesis, Characterization and Applications*, pp. 101–120, Nova Science Publishers Inc., New York, NY, USA, 2015.

[52] P. Nalawade, B. Aware, V. Kadam, and R. Hirlekar, "Layered double hydroxides: a review," *Journal of Scientific and In-dustrial Research*, vol. 68, pp. 267–272, 2009.

[53] N. Sanson, F. Bouyer, M. Destarac, M. In, and C. Gérardin, "Hybrid polyion complex micelles formed from double hydrophilic block copolymers and multivalent metal ions: size control and nanostructure," *Langmuir*, vol. 28, no. 8, pp. 3773–3782, 2012.

[54] H. Dong, H. S. Parekh, and Z. P. Xu, "Particle size- and number-dependent delivery to cells by layered double hy-droxide nanoparticles," *Journal of Colloid and Interface Science*, vol. 437, pp. 10–16, 2015.

[55] X. Y. Yo, T. Luo, Y. Jia, and C. Gao, "Three-dimensional hierarchical flower-like Mg–Al-layered double," *Nanoscale*, vol. 4, pp. 3466–3474, 2012.

[56] A. Elhalil, S. Qourzal, F. Z. Mahjoubi et al., "Defluoridation of groundwater by calcined Mg/Al layered double hydrox-ide," *Emerging Contaminants*, vol. 2, no. 1, pp. 42–48, 2016.

[57] C. Gao, X.-Y. Yu, T. Luo et al., "Millimeter-sized Mg-Al-LDH nanoflake impregnated magnetic alginate beads (LDH-n-MABs): a novel bio-based sorbent for the removal of fluoride in water," *Journal of Materials Chemistry A*, vol. 2, no. 7, pp. 2119–2128, 2014.

[58] M. Noorjahan, M. A. Khayyum, and K. G. Mangatayaru, "A novel cobalt modified layered double hydroxide for the ef-ficient removal of fluoride," *Materials Focus*, vol. 4, no. 4, pp. 283–289, 2015.

[59] L. Bo, Q. Li, Y. Wang, L. Gao, X. Hu, and J. Yang, "Ad-sorptive removal of fluoride using hierarchical flower-like calcined Mg–Al layered double hydroxides," *Environmental Progress and Sustainable Energy*, vol. 35, no. 5, pp. 1420–1429, 2016.

[60] Z. Bai, C. Hu, H. Liu, and J. Qu, "Selective adsorption of fluoride from drinking water using NiAl-layered metal oxide film electrode," *Journal of Colloid and Interface Science*, vol. 539, pp. 146–151, 2019.

[61] L. Mohammed, H. Gomma, D. Ragab, and J. Zhu, "Magnetic nanoparticles for environmental and biomedical applica-tions: Review," *Particuology*, vol. 30, no. 1, 2016.

[62] A. Silva, D. Corato, F. Gazeau, T. Pellegrino, and C. Wilhelm, "Mag-netophoresis at the nanoscale: tracking the magnetic targeting efficiency ofnanovectors," *Nanomedicine*, vol. 7, no. 11, pp. 1713–1723, 2012.

[63] T. Indira and P. Lakshmi, "Magnetic nanoparticles- a re-view," *International Journal of Pharmaceuitical Sciences and Nanotechnology*, vol. 3, no. 3, pp. 1035–1042, 2010.

[64] N. Tran and T. J. Webster, "Magnetic nanoparticles: bio-medical applications and challenges," *Journal of Materials Chemistry*, vol. 20, no. 40, pp. 8760–8767, 2010.

[65] M. Timko, M. Molcan, A. Hashim et al., "Hyperthermic effect in suspension of magnetosomes prepared by various methods," *IEEE Transactions on Magnetics*, vol. 49, no. 1, pp. 250–254, 2013.

[66] X. Yang, M. Liu, H. Zhu et al., "Preparation, characterization, Magnetic property and Mossbuuer Spectra of the beta FeOOh nanoparticles modified by nonionic surfactant," *Journal of Magnetism and Magnetic Materials*, vol. 320, pp. 132–136, 2008.

[67] L. Chai, Y. Wang, N. Zhao, W. Yang, and X. You, "Sulfate-doped Fe3O4/Al2O3 nanoparticles as a novel adsorbent for fluoride removal from drinking water," *Water Research*, vol. 47, no. 12, pp. 4040–4049, 2013.

[68] L. Chen, B.-Y. He, S. He, T.-J. Wang, C.-L. Su, and Y. Jin, "Fe—Ti oxide nano-adsorbent synthesized by co-precipitation for fluoride removal from drinking water and its adsorption mechanism," *Powder Technology*, vol. 227, pp. 3–8, 2012.

[69] C. Zhang, L. Chen, T.-J. Wang, C.-L. Su, and Y. Jin, "Syn-thesis and properties of a magnetic core-shell composite nano-adsorbent for fluoride removal from drinking water," *Applied Surface Science*, vol. 317, pp. 552–559, 2014.

[70] F. Riahi, M. Bagherzadeh, and Z. Hadizadeh, "Modification of Fe3O4 superparamagnetic nanoparticles with Zirconium oxide; preparation, characterization and its application to-ward fluoride removal," *RSC Advances*, vol. 5, no. 88, pp. 72058–72068, 2015.

[71] S. K. Sahoo and G. Hota, "Surface functionalization of GO with MgO/MgFe2O4 binary oxides: a novel magnetic nanoadsorbent for removal of fluoride ions," *Journal of Environmental Chemical Engineering*, vol. 6, no. 2, pp. 2918–2931, 2018.

[72] R. Nagarajah, K. T. Wong, G. Lee et al., "Synthesis of a unique nanostructured magnesium oxide coated magnetite cluster composite and its application for the removal of selected heavy metals," *Separation and Purification Tech-nology*, vol. 174, pp. 290–300, 2017.

[73] M. Liu, T. Wen, X. Wu et al., "Synthesis of porous Fe3O4 hollow microspheres/graphene oxide composite for Cr(VI) removal," *Dalton Transactions*, vol. 42, no. 41, pp. 14710–14717, 2013.

[74] N. Dewage, A. Liyanage, C. Pittman, D. Mohan, and T. Malsna, "Fast nitrate and fluoride adsorption and magnetic separation from water on α-Fe2O3 and Fe3O4 dispersed on Douglas fir biochar," *Bioresource Technology*, vol. 263, pp. 258–268, 2018.

[75] L. Sigg and W. Stumm, "The interaction of anions and weak acids with the hydrous goethite (α-FeOOH) surface," *Colloids and Surfaces*, vol. 2, no. 2, pp. 101–117, 1981.

[76] X. Zhao, J. Wang, F. Wu et al., "Removal of fluoride from aqueous media by Fe3O4@Al(OH)3 magnetic nanoparticles," *Journal of Hazardous Materials*, vol. 173, no. 1-3, pp. 102–109, 2010.

[77] M. Wang, W. Yan, W. Kong et al., "An electroactive and regenerable Fe3O4@Polypyrrole nanocomposite: fabrication and its defluorination in an electromagnetic coupling system," *Industrial and Engineering Chemistry Research*, vol. 56, no. 44, pp. 12738–12744, 2017.

[78] J. Sukamto, S. Rassat, R. Orth, and M. Lilga, *Electrochemical Ion Exchange*, Academic Press, Seattle, WA, USA, 2000.

[79] B. McEnaney, "Chapter 1—structure and bonding in carbon materials," in *Carbon Materials for Advanced Technologies*, pp. 1–33, Elsevier, Amsterdam, Netherlands, 1999.

[80] M. Endo, K. Takeuchi, S. Igarashi, K. Kobori, M. Shiraishi, and H. W. Kroto, "The production and structure of pyrolytic carbon nanotubes (PCNTs)," *Journal of Physics and Chemistry of Solids*, vol. 54, no. 12, pp. 1841–1848, 1993.

[81] D. Balarak, Y. Esfandyari, E. Bazrafshan, A. Mahvi, and Y. Esfandyari, "Adsorption of fluoride from aqueous solutions by carbon nanotubes: determination of equilibrium, kinetic and thermodynamic parameters," *Fluoride*, vol. 49, no. 1, pp. 71–83, 2016.

[82] Z. Ruan, Y. Tian, J. Ruan et al., "Synthesis of hydroxyapatite/multi-walled carbon nanotubes for the removal of fluoride ions from solution," *Applied Surface Science*, vol. 412, pp. 578–590, 2017.

[83] Q. Tang, T. Duan, P. Li, P. Zhang, and D. Wu, "Enhanced defluoridation capacity from aqueous media via hydroxyapatite decorated with carbon nanotube," *Frontiers in Chemistry*, vol. 6, p. 104, 2018.

[84] M. H. Dehghani, G. A. Haghighat, K. Yetilmezsoy et al., "Adsorptive removal of fluoride from aqueous solution using single- and multi-walled carbon nanotubes," *Journal of Molecular Liquids*, vol. 216, pp. 401–410, 2016.

[85] I. Rostami, A. Mahvi, M. Dehghani, A. Baghani, and R. Marandi, "Application of nano aluminum oxide and multi-walled carbon nanotube in fluoride removal," *Desalination and Water Treatment*, vol. 72, pp. 368–373, 2017.

[86] S. Ayoob, A. K. Gupta, and V. T. Bhat, "A conceptual overview on sustainable technologies for the defluoridation of drinking water," *Critical Reviews in Environmental Science and Technology*, vol. 38, no. 6, pp. 401–470, 2008.

[87] A. Szymczyk and P. Fievet, "Ion transport through nanofiltration membranes: the steric, electric and dielectric exclusion model," *Desalination*, vol. 200, no. 1–3, pp. 122–124, 2006.

[88] J. Shen and A. I. Schäfer, "Factors affecting fluoride and natural organic matter (NOM) removal from natural waters in Tanzania by nanofiltration/reverse osmosis," *Science of the Total Environment*, vol. 527-528, pp. 520–529, 2015.

[89] N. Yousefi, A. Fatehizedeh, K. Ghadiri, N. Mirzaei, S. D. Ashrafi, and A. Hossein Mahvi, "Application of nanofilter in removal of phosphate, fluoride and nitrite from groundwater," *Desalination and Water Treatment*, vol. 57, no. 25, pp. 11782–11788, 2015.
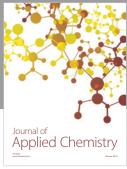
[90] M. Heidarizad and S. S. Şengör, "Synthesis of graphene oxide/magnesium oxide nanocomposites with high-rate adsorption of methylene blue," *Journal of Molecular Liquids*, vol. 224, pp. 607–617, 2016.

[91] R. K. Upadhyay, N. Soin, and S. S. Roy, "Role of graphene/metal oxide composites as photocatalysts, adsorbents and disinfectants in water treatment: a review," *RSC Advances*, vol. 4, no. 8, pp. 3823–3851, 2014.

[92] M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff, "Graphene-based ultracapacitors," *Nano Letters*, vol. 8, no. 10, pp. 3498–3502, 2008.

[93] J.-U. Lee, D. Yoon, and H. Cheong, "Estimation of os modulus of graphene by Raman spectroscopy," *Nano Letters*, vol. 12, no. 9, pp. 4444–4448, 2012.

[94] S. Kanrar, S. Debnath, P. De et al., "Preparation, characterization and evaluation of fluoride adsorption efficiency from water of iron-aluminium oxide-graphene oxide composite material," *Chemical Engineering Journal*, vol. 306, pp. 269–279, 2016.

[95] S. Mohan, D. K. Singh, V. Kumar, and S. H. Hasan, "Effective removal of Fluoride ions by rGO/ZrO2 nanocomposite from aqueous solution: fixed bed column adsorption modelling and its adsorption mechanism," *Journal of Fluorine Chemistry*, vol. 194, pp. 40–50, 2017.

[96] J. He, A. Cui, F. Ni, S. Deng, F. Shen, and G. Yang, "A novel 3D yttrium based-graphene oxide-sodium alginate hydrogel for remarkable adsorption of fluoride from water," *Journal of Colloid and Interface Science*, vol. 531, pp. 37–46, 2018.

[97] R. Sun, H.-B. Zhang, J. Qu, H. Yao, J. Yao, and Z.-Z. Yu, "Supercritical carbon dioxide fluid assisted synthesis of hierarchical AlOOH@reduced graphene oxide hybrids for efficient removal of fluoride ions," *Chemical Engineering Journal*, vol. 292, pp. 174–182, 2016.

[98] L. Liu, Z. Cui, Q. Ma, W. Cui, and X. Zhang, "One-step synthesis of magnetic iron-aluminum oxide/graphene oxide nanoparticles as a selective adsorbent for fluoride removal from aqueous solution," *RSC Advances*, vol. 6, no. 13, pp. 10783–10791, 2016.

[99] C. Xu, J. Li, F. He et al., "Al$_2$O$_3$-Fe$_3$O$_4$-Expanded graphite nano-sandwich structure for fluoride removal from aqueous solution," *RSC Advances*, vol. 6, no. 99, pp. 97376–97384, 2016.

[100] M. Chigondo, H. Kamdem Paumo, M. Bhaumik, K. Pillay, and A. Maity, "Hydrous CeO$_2$-Fe$_3$O$_4$ decorated polyaniline fibers nanocomposite for effective defluoridation of drinking water," *Journal of Colloid and Interface Science*, vol. 532, pp. 500–516, 2018.

[101] D. Mohanta and M. Ahmaruzzaman, "Bio-inspired adsorption of arsenite and fluoride from aqueous solutions using activated carbon@SnO$_2$ nanocomposites: isotherms, kinetics, thermodynamics, cost estimation and regeneration studies," *Journal of Environmental Chemical Engineering*, vol. 6, no. 1, pp. 356–366, 2018.

[102] A. Nagaraj, D. Govindaraj, and M. Rajan, "Magnesium oxide entrapped Polypyrrole hybrid nanocomposite as an efficient selective scavenger for fluoride ion in drinking water," *Emergent Materials*, vol. 1, no. 1-2, pp. 25–33, 2018.

[103] Q. L. Yin, S. Q. Zhao, and S. Asuha, "Novel approach for synthesis of mesoporous γ-AlOOH powder from coal-bearing kaolinite and its enhanced adsorption performance for Congo red and fluoride," *Solid State Phenomena*, vol. 288, pp. 79–86, 2019.

[104] M. Chaudhary, S. Rawat, N. Jain, A. Bhatnagar, and A. Maiti, "Chitosan-Fe-Al-Mn metal oxyhydroxides composite as highly efficient fluoride scavenger for aqueous medium," *Carbohydrate Polymers*, vol. 216, pp. 140–148, 2019.

[105] M. K. Adak, A. Sen, A. Mukherjee, S. Sen, and D. Dhak, "Removal of fluoride from drinking water using highly efficient nano-adsorbent, Al(III)-Fe(III)-La(III) trimetallic oxide prepared by chemical route," *Journal of Alloys and Compounds*, vol. 719, pp. 460–469, 2017.

[106] S. Suriyara, A. Bhattacharyya, and R. Selvakumar, "Hybrid Al2O3/Bio-TiO2 Nanocomposite impregnated thermoplastic polyurethane (TPU) nanofibrous membrane for Fluoride removal from aqueous solution," *RSC Advances*, vol. 5, no. 34, pp. 26905–26912, 2015.

[107] R. Araga, S. Kali, and C. Sharma, "Coconut-shell derived carbon/carbon nanotube composite for fluoride adsorption from aqueous solution," *Clean Soil and Water*, vol. 47, no. 5, article 1800286, 2019.

[108] C. Silveira, Q. L. Shimabuku, M. Fernandes Silva, and R. Bergamasco, "Iron-oxide nanoparticles by the green synthesis method using Moringa oleifera leaf extract for fluoride removal," *Environmental Technology*, vol. 39, no. 22, pp. 2926–2936, 2018.

[109] M. Zendehdel, B. Shoshtari-Yeganeh, H. Khanmohamadi, and G. Cruciani, "Removal of fluoride from aqueous solution by adsorption on NaP:HAp nanocomposite using response surface methodology," *Process Safety and Environmental Protection*, vol. 109, pp. 172–191, 2017.

[110] J. Cai, Y. Zhang, Y. Qian, C. Shan, and B. Pan, "Enhanced defluoridation using novel millisphere nanocomposite of La-doped Li-Al layered double hydroxides supported by polymeric anion exchanger," *Scientific Reports*, vol. 8, 2018.

[111] M. Hu, H. Shen, S. Ye, Y. Wang, J. Zhang, and S. Lv, "Facile preparation of a tetraethylenepentamine-functionalized nano magnetic composite material and its adsorption mechanism to anions: competition or cooperation," *RSC Advances*, vol. 8, no. 19, pp. 10686–10697, 2018.

[112] M. S. Gaikwad and C. Balomajumder, "Removal of Cr(VI) and fluoride by membrane capacitive deionization with nanoporous and microporous Limonia acidissima (wood apple) shell activated carbon electrode," *Separation and Purification Technology*, vol. 195, pp. 305–313, 2018.

[113] Y. Li, C. Zhang, Y. Jiang, and T.-J. Wang, "Electrically enhanced adsorption and green regeneration for fluoride removal using Ti(OH)4-loaded activated carbon electrodes," *Chemosphere*, vol. 200, pp. 554–560, 2018.

[114] M. Massoudinejad, A. Shahsavani, B. Kamarehie et al., "Highly efficient adsorption of fluoride from aqueous solutions by metal organic frameworks: modeling, isotherms, and kinetics," *Fluoride*, vol. 51, no. 4, pp. 313–323, 2018.

[115] M. Zahid, A. Rashid, S. Akram, Z. Rehan, and W. Razzaq, "A comprehensive review on polymeric nano-composite membranes for water treatment," *Journal of Membrane Science and Technology*, vol. 8, no. 1, 2018.

[116] M. Zargar, Y. Hartanto, B. Jin, and S. Dai, "Understanding functionalized silica nanoparticles incorporation in thin film composite membranes: interactions and desalination performance," *Journal of Membrane Science*, vol. 521, pp. 53–64, 2017.

[117] J. Saikia, S. Sarmah, P. Saikia, and R. L. Goswamee, "Harmful weed to prospective adsorbent: low-temperature-carbonized Ipomoea carnea stem carbon coated with aluminum oxyhydroxide nanoparticles for defluoridation," *Environmental Science and Pollution Research*, vol. 26, no. 1, pp. 721–737, 2019.

[118] S. P. Suriyaraj, T. Vijayaraghavan, P. Biji, and R. Selvakumar, "Adsorption of fluoride from aqueous solution using different phases of microbially synthesized TiO2 nanoparticles," *Journal of Environmental Chemical Engineering*, vol. 2, no. 1, pp. 444–454, 2014.

[119] Y. Xia, X. Huang, W. Li, Y. Zhang, and Z. Li, "Facile defluoridation of drinking water by forming shell@fluorapatite nanoarray during boiling egg shell," *Journal of Hazardous Materials*, vol. 361, pp. 321–328, 2019.

The Scientific
World Journal

Journal of
Applied Chemistry

Journal of
Nanomaterials

Scientifica

International Journal of
Polymer Science

Advances in
Chemistry

Advances in
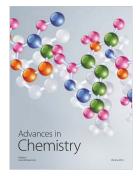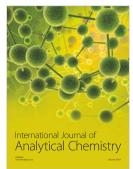Physical Chemistry

International Journal of
Analytical Chemistry

Hindawi

Submit your manuscripts at
www.hindawi.com

Advances in
Condensed Matter Physics

Journal of
Chemistry

International Journal of
Biomaterials

Advances in
High Energy Physics

Journal of
Engineering

Journal of
Nanotechnology

International Journal of
Corrosion

Journal of
Materials

BioMed
Research International

Advances in
Tribology

Advances in
Materials Science and Engineering