Review of fluoride removal technology from wastewater environment

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ABSTRACT

Industrial production is the main reason for excessive fluoride content in wastewater, and it is necessary to adopt economical and effective fluoride removal methods. Therefore, be aware of the existing form of fluorine and the formation mechanism of fluoride pollution, and based on the water purification agents, environmental functions, and material innovation, this overview focuses on the defluoridation mechanism, the advantages and disadvantages of precipitation and coagulation, adsorption, electrochemical technology, and membrane separation technology. In the actual process of treating fluoride-containing wastewater, appropriate methods should be adopted according to the different characteristics of the wastewater. This review describes the research progress of fluoride removal methods for fluoride-containing wastewater at home and abroad in recent years, further analyzes the advantages and technical bottlenecks of these methods, and looks ahead at the major development trends in the future to provide a reference for further research on treatment technology of wastewater with a high fluoride content.

Keywords: Fluoride-containing wastewater; Precipitation; Adsorption; Electrochemical technology; Membrane separation

1. Introduction

As one of the most common trace elements in the earth’s crust, the fluorine content in the earth’s crust is 625 mg/kg. It is widespread in nature and plays a vital role in ecological stability [1]. The natural source of fluorine is mainly the weathering and dissolution of fluoride-containing minerals [2], and the primary forms are magnesite (MgF₂), fluorspar (CaF₂), fluorapatite (Na₃AlF₆) and fluorapatite [3Ca₃(PO₄)₂Ca(FC1₂)] [3]. High levels of fluoride are found in groundwater in many parts of the world, in part due to the gradual release of fluoride ions into groundwater as fluoride-bearing rock slowly dissolves. These fluorinated ores can also release fluoride ions into surface water and lead to fluoride contamination of surface water. In addition, the global fluoride industry, such as electroplating, semiconductor, steel, and aluminum smelting, produces a large number of fluoride-containing wastewater. China’s spatial distribution of water resources is uneven, especially in arid and semi-arid areas, which are mainly dependent on groundwater for agriculture, industry, and domestic water supply [4]. However, rapid urbanization and industrialization have led to increased pollution of groundwater resources in many areas [5]. According to statistics, hundreds of millions of people in more than 30 countries, including China drink water with high-fluoride content. China and India are among the countries most affected by fluoride, with groundwater fluoride concentrations of up to 48 mg/L [6]. At the same time, the trace element fluorine also has a dual effect on the human body. An appropriate amount of fluorine plays an essential role in the development of the human skeleton, nervous system, and reproductive system [7]. Still, too little or too much intake is not conducive to human health. Chronic fluorosis is likely to occur when the human body takes in.

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excessive amounts of fluoride over a long period of time, which is likely to cause damage to hard tissues such as bones and teeth. In severe cases, bone fluorosis and dental fluorosis will occur. In addition, it will also have adverse effects on the human immune system, kidney, and gastrointestinal tract, even increasing the risk of cancer [8]. And studies have confirmed that excessive intake of fluorine has an effect on children’s IQ [9]. Therefore, defluoridation of wastewater is an urgent and challenging task for scholars.

Water is essential to the life of organisms on Earth, but intensified water pollution is an important area that needs attention. Excessive accumulation of fluoride in water endangers ecological stability and human health [10]. Compared to surface water, groundwater is the primary water source affected by fluoride pollution. This is due to the influence of natural factors. The pH value of groundwater, the solubility of fluoride-containing minerals, and the groundwater rusted water ions are factors that affect the migration and enrichment of fluoride in groundwater [11]. Weak restoration conditions and poor groundwater exchange also increased the fluoride content [12]. Moreover, human activities have an important influence on the migration and enrichment of fluoride in groundwater. In recent years, the development of industrial products such as aluminum, semiconductors, iron and steel, pesticides, and agricultural chemical fertilizers has greatly increased fluoride pollution in water [13]. From this, it can be concluded that fluoride pollution is serious and inevitable and that ensuring safe and clean drinking water is also a global challenge [14]. Therefore, fluoride pollution is gradually becoming a significant environmental and public health problem [15]. The World Health Organization (WHO) states that the best concentration range for fluoride in drinking water is 0.5 ~ 1.5 mg/L [16]. In this regard, China strictly limits the concentration of fluoride in the water. Drinking Water Quality Standards (GB 5749-2022) stipulates that the upper limit of fluoride concentration in drinking water is 1.0 mg/L [17]. In addition, the Integrated Wastewater Discharge Standard (GB 8978-2002) states that the maximum allowable concentration of fluoride in wastewater is 10 mg/L. For the wastewater discharged from inorganic chemical companies, the emission standards of pollutants from inorganic chemical industry (GB 31573-2015) require that the fluoride concentration be below 6 mg/L [18]. The emission limit of fluoride is 1.5 mg/L in the emission standard of pollutants for municipal wastewater treatment plants (DB32/4440-2022), a local environmental protection standard of Jiangsu Province organized by the Department of Ecology and Environment of Jiangsu Province.

The above current situation shows the necessity and urgency to speed up the treatment of fluoride-containing wastewater. At present, there are a large number of application studies of wastewater defluoridation technology in the world, and considerable advances in defluoridation theory, process, technology, etc. have been made. So far, the commonly used fluoride removal methods include precipitation, adsorption, electrochemical technology, membrane separation technology, and so on. Among them, the principle and operation of the precipitation method are straightforward [19]. However, due to the addition of chemical agents, the cost increases and fluoride ions in the water after fluoride removal exceed the emission standards of pollutants for the inorganic chemical industry (GB 31573-2015). The adsorption method has the advantages of many kinds of adsorbents, good selection performance, fast rate, and few pollution products [20], but the environment and its factors (pH, coexisting ions, temperature, the adsorbent pore size, etc.) will significantly affect the results of fluoride removal [21]. The electrochemical method has a high rate of fluoride removal, but there are problems of high equipment installation and maintenance costs [22]; Membrane filtration has the advantage of high effluent quality in fluoride removal, but it is prone to membrane fouling, high energy consumption and high cost [23]. The fluoride content in industrial effluents ranges from about 250 to 1,500 mg/L and, in some extreme cases may reach 10,000 mg/L [24]. Because of its strong electronegativity, fluorine basically coexists with other elements in the form of fluorine-containing compounds [25]. Fluoride in wastewater containing fluorine is mainly present in the form of hydrofluoric acid, fluorosilicic acid, or fluoride. Fluoride-containing wastewater contains a variety of pollutants, such as soluble inorganic salts, organic matter, heavy metals, and radioactive substances, leading to increased difficulties in wastewater treatment, more complex technological processes, and more additives. At the same time, fluoride is a kind of utilisable resource, the recycling of which can not only eliminate pollution and achieve environmental benefits, but also can achieve certain economic benefits. Fluoride is widely used in metallurgy, chemical industry and other industries. The recycling of fluoride in wastewater can effectively promote the recycling of fluoride resources. Adding sodium carbonate, sodium sulfate and other sodium compounds produces sodium ion effect, without evaporation concentration, sodium fluoride can be separated and recovered directly. Therefore, in order to protect the environment and human development in the long-term, it is necessary to find a simpler, more effective, and more economical method for removing fluoride from the fluoride-containing wastewater. In this paper, the mechanism of action, the performance of defluoridation, and the latest research results of the above techniques are analyzed in detail to provide theoretical support for follow-up research and practical application as well as and future treatment technologies of fluoridated wastewater, summarized and prospect.

2. Precipitation

2.1. Chemical precipitation

At present, the most widely used method in the fluoride removal process is chemical precipitation, which is generally suitable for the treatment of large-scale, high concentration fluoride-containing wastewater. Defluoridation by chemical precipitation means that a certain amount of precipitating agent is added to fluoride-containing wastewater to react with fluorine ions, and the reaction product is a fluoride-containing precipitate or fluoride-containing complex. Then the precipitate is removed by filtration to achieve the purpose of defluoridation. Table 1 shows the solubility product constant \(K_{sp}\) of fluoride-containing insoluble substances formed by chemical reactions. The solubility product constant \(K_{sp}\) of calcium fluoride is \(2.7 \times 10^{-11}\), indicating that calcium salt has an excellent defluoridation effect, relatively
low price, simple operation, and apparent defluoridation
effect, so it is generally suitable for the treatment of large-
scale high concentration fluoride-containing wastewater.
Commonly used chemical precipitators are lime (CaO), cal-
cium salt (CaCl₂, CaSO₄, etc.), calcium carbide slag (Ca(OH)₂),
etc. The main chemical reaction formula is:

\[
\text{Ca}^{2+} + \text{F}^- \rightarrow \text{CaF}_2
\]

However, calcium fluoride is soluble to a certain extent
and is dissolved together with calcium hydroxide, often
resulting in the fluoride content of the treated wastewater
still being 10 ~ 20 mg/L, which poses a challenge to meet
the maximum allowable discharge limit of 10 mg/L for
wastewater. Huang et al. [26] used chemical precipitation
to simultaneously remove total ammonia nitrogen, phos-
phate, and fluoride from the semiconductor wastewater. The
experimental results show that magnesium salt, as a pre-
cipitator, has a superior sedimentation property in remov-
ing fluoride compared with a calcium salt. The two-stage
precipitation method is economically feasible and highly
successful in eliminating phosphate and fluoride (97% and
91% removal rates, respectively) from semiconductor waste-
water. There are some problems in removing fluoride by
chemical precipitation, such as a large amount of sludge,
high moisture content, slow sedimentation rate, and severe
secondary pollution. Moreover, the removal of fluoride by
calcium salt precipitation method cannot reach the standard
at one time, so it must be used together with other meth-
ods. Secondary or even multiple wastewater treatments are
often required to meet discharge requirements.

2.2. Coagulation

At present, the commonly used coagulants are divided
into three categories: inorganic, organic, and microbial coag-
ulants. Iron salt and aluminum salt are common inorganic
coaigulants, and acrylamide (PAM) is the leading organic
coaigulant. One of the most commonly used is aluminum salt.
Aluminum salt is complexed with fluoride ion in the form
of \( \text{Al}^{3+} \) as a coagulant. Fluoride ions are removed by ligand
exchange, physical adsorption and leaching of the alumi-
num brine hydrolysis intermediate and the final aluminum
hydroxide \([\text{Al(OH)}_3]\) alum bloom. In particular, polyalumi-
num chloride has the advantages of large flocs, low dosage,
high coagulation efficiency, fast precipitation rate, and a
wide range of applications. It contains different aluminum
species, which has obvious advantages in the treatment of
wastewater with high fluoride concentration [27]. Fig. 1
shows the main mechanisms involved in fluoride removal
by different aluminum species. The aluminum salt coag-
ulation has a remarkable effect because of its low dosage,
a large amount of wastewater that can be treated, and can meet
the national discharge standard after one treatment. Dubey
et al. [28] examined the effects of aluminum sulfate (alum)
and polyaluminum chloride (PACl) on fluoride removal.
They found that the formation of soluble colloid Al-F com-
plex between aluminum and fluoride would lead to a decline
in fluoride removal performance. In contrast, in the case of
PACl, only a tiny amount of Al-F complex is formed, con-
firming the better fluoride removal performance of PACl in
the case of low residual aluminum.

It is found that the treatment effect of adding a single
coagulant to high fluoride water is not noticeable enough,
so it is necessary to use two or more coagulants together
or in combination with other methods in the treatment

<table>
<thead>
<tr>
<th>Insoluble compound</th>
<th>( K_{sp} )</th>
<th>( pK_{sp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF₂</td>
<td>( 2.7 \times 10^{-11} )</td>
<td>10.57</td>
</tr>
<tr>
<td>MgF₂</td>
<td>( 6.5 \times 10^{-9} )</td>
<td>8.19</td>
</tr>
<tr>
<td>PbF₂</td>
<td>( 2.7 \times 10^{-8} )</td>
<td>7.57</td>
</tr>
<tr>
<td>BaF₂</td>
<td>( 1.7 \times 10^{-6} )</td>
<td>5.77</td>
</tr>
<tr>
<td>MnF₂</td>
<td>( 1.3 \times 10^{-3} )</td>
<td>2.87</td>
</tr>
</tbody>
</table>

Table 1: Solubility product constants of insoluble fluoride

Fig. 1. Mechanism diagram of fluoride removal by different Al species.
process. Xiang et al. [29] also carried out a study of fluoride removal by algae cells and found that when 40.0 mg/L algae cells were added to the system, the fluoride removal rate increased from 22.75% to 72.99% because the algae cells significantly increased the distribution of Al(OH)$_3$ in the flocs. In addition, Xuefeng et al. [30] reduced the high content of fluoride in wastewater by coagulation with an added calcium source and found that the content of fluoride ions decreased significantly. After adopting three-stage series enhanced coagulation process for fluoride removal, the mass concentration of fluoride ion in the effluent of the sewage station was stable at less than 10 mg/L, which met the requirements of industrial first-class discharge standards. Although precipitation technology has been widely used to treat fluoride in water, it still has some limitations. For example, the flocculant price used is high, and the effect of fluoride removal is greatly affected by operating factors such as mixing conditions, sedimentation time, and anions such as SO$_4^{2–}$ and Cl$^{–}$ in water. In the coagulation process, the fluorinated precipitates formed on the surface of the coagulant will quickly cover the surface of the coagulant, block the surface gap, hinder the transfer of fluoride ions, and decrease the efficiency of fluoride removal.

### 3. Adsorption

#### 3.1. Metal based materials

Metal adsorbents at the current stage mainly include aluminum-based, iron-based, rare earth, and other metals (including calcium, magnesium, titanium, zirconium, etc.). Metal-based adsorbents have a fast adsorption rate, high adsorption capacity, and strong affinity for anions, and a good fluoride removal effect can be achieved by a small number of metal oxides or hydroxides, but the cost is high for rare earth metal-based adsorbents. The adsorption mechanisms of metal adsorbents are mainly ion exchange, electrostatic attraction, and complexation. The adsorption properties of different metal adsorbents for fluoride under other conditions are shown in Table 2. Among them, activated alumina is one of the most widely used fluoride adsorption materials, which has a large specific surface area and good chemical stability. F$^{–}$ ion can be adsorbed to the surface by electrostatic adsorption and then exchanged with hydroxyl groups in alumina to remove fluoride. The mechanism of defluoridation is shown in Fig. 2. However, the adsorption capacity is deficient, the adsorption speed is slow, and the fluoride removal efficiency is easily affected by the pH of the wastewater.

**Table 2** Comparison of fluoride adsorption properties of different metal adsorbents under different conditions

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg/g)</th>
<th>Concentration range (mg/L)</th>
<th>Contact time</th>
<th>pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous aluminum hydroxide</td>
<td>63.94</td>
<td>5–200</td>
<td>10 min</td>
<td>7</td>
<td>[32]</td>
</tr>
<tr>
<td>Cr(III)-incorporated Zr(IV) bimetallic oxide</td>
<td>90.67</td>
<td>10.5</td>
<td>360 min</td>
<td>5–7</td>
<td>[33]</td>
</tr>
<tr>
<td>FeOOH-graphene oxide nanocomposites</td>
<td>19.82</td>
<td>10–150</td>
<td>60 min</td>
<td>2–10</td>
<td>[34]</td>
</tr>
<tr>
<td>Lanthanum perovskite aluminate</td>
<td>40.8</td>
<td>5–30</td>
<td>0–60 min</td>
<td>7</td>
<td>[35]</td>
</tr>
<tr>
<td>Al(OH)$_3$ nanoparticles modified hydroxyapatite (Al-HAP)</td>
<td>93.84</td>
<td>200</td>
<td>24 h</td>
<td>7</td>
<td>[36]</td>
</tr>
</tbody>
</table>

**Fig. 2.** Mechanism diagram of fluoride adsorption on acid activated alumina.

*Al$^{3+}$: active adsorbent site of acid activated alumina adsorbent.
The formation of $\text{AlF}_3^+$ and $\text{AlF}_4^-$ complexes is accelerated when pH is too low, resulting in poor F$^-$ ion removal performance in solution and the fluoride removal efficiency of activated alumina is not good when pH is high, since the surface of the adsorbent is negatively charged under alkaline conditions, leading to electrostatic repulsion with F$^-$ ions and competitive adsorption between OH$^-$ and F$^-$ ions [31].

Because of the low adsorption capacity for fluoride, the surface of activated alumina is usually modified to make it acidic, and acid-activated alumina has potential application in fluoride ion contaminated industrial wastewater. In order to improve the efficiency of fluoride removal, Singh et al. [37] prepared two kinds of modified activated alumina from calcium and magnesium. It is found that the modified activated alumina has higher adsorption capacity and fluoride removal capacity in the broader pH range (4–9), which is more beneficial to the defluoridation of wastewater. In addition, increasing the density of active surface sites and increasing the specific surface area of adsorbents is also one of the means to improve adsorption efficiency or capacity. However, the use of aluminum-based adsorbents often leads to residual aluminum ions in the solution, which affects human health, and increases the pH and total dissolved solids of the treated solution, which increases the difficulty of follow-up treatment. Therefore, the combination of rare metals and natural materials can overcome these difficulties. Zhang et al. [38] produced a kind of zirconium-based chitosan-graphene oxide (Zr-CTS/GO) membrane with a good fluoride removal effect, and the membrane can effectively remove fluoride in a wide pH range (3–11), and the adsorption capacity is 29.06 mg/g. In summary, there are plentiful metal-based adsorbents, and the effect of removing fluoride is relatively good, but the content of metal in nature is limited. In order to reduce the influence of environmental factors on the performance of fluoride removal and ensure the efficiency of eliminating fluoride, we can focus on reducing metal content, preparing composite adsorbent, improving the performance of adsorbent, and improving the selectivity of adsorbent to specific pollutants (F$^-$ ion) in the future. It is necessary to develop metal-based adsorbents with higher performance and lower prices to reduce cost and save resources, which may become an essential direction of metal-based adsorbents research.

### 3.2. Carbon-based materials

Carbon-based materials have controllable pore structure and surface chemical properties, widely used in adsorption, catalysis, sensing, and other fields. The properties of porous carbon materials can be improved by modification and metal doping. The commonly used carbon-based adsorbents for fluoride removal are activated carbon, biochar and bone charcoal, graphene, and other materials. The comparison of fluoride adsorption properties of different carbon-based adsorbents under different conditions is shown in Table 3. Activated carbon is considered as an efficient adsorbent because of its high porosity, large specific surface area, and high catalytic activity. However, activated carbon has a relatively low adsorption capacity and low affinity for inorganic pollutants such as fluoride. To overcome these shortcomings, Choong et al. [39] also studied the palm shell activated carbon powder (PSAC) and the magnesium silicate ($\text{MgSiO}_3$) modified PSAC (MPSAC) for fluoride adsorption. The adsorption capacity of PSAC and MPSAC was 116 and 150 mg/g, respectively, showing excellent fluoride adsorption performance. In addition, the surface of activated carbon can also be modified to improve its adsorption performance, for example, by introducing functional groups (OH$^-$) with a solid affinity for fluoride ions [40].

Biochar is the product of biomass energy pyrolysis. On the one hand, biochar has the advantages of its huge specific surface area and abundant pore structure, rich surface functional groups, and good adsorption performance; on the other hand, biochar has a wide range of sources. At the same time, the waste can be recycled at a low cost, so it has an excellent fluoride ion adsorption performance. Sadhu et al. [46] studied the fluoride removal performance of watermelon rind (Citrus lanatus) biochar (WMRBC) and found that the maximum adsorption capacity of WMRBC for fluoride was 9.5 mg/g at pH 1. In addition, WMRBC retained about 60% of the adsorption capacity after three times reuse, indicating that WMRBC is an effective adsorbent for fluoride removal from drinking water and industrial wastewater. Bone charcoal, activated carbon obtained by heating, and degreasing animal bones, is mainly composed of hydroxyapatite. Bone charcoal adsorbs fluoride primarily because it contains hydroxyapatite, and the chemical formula is $\text{Ca}_10(\text{PO}_4)_6(\text{OH})_2$. It is not easy to be affected by various co-existing anions in wastewater. Carbon-based material is a common adsorbent, in which biochar can be obtained by calcining coconut shell, bark, peanut shell, and other biomass at high temperatures, and the surface of biomass carbon formed by incomplete combustion contains a large number of active groups, such as carboxyl group, phenolic hydroxyl group and so on. Hydrogen in these functional groups will form hydrogen bonds with

### Table 3
Comparison of adsorption properties of different carbon-based adsorbents for fluoride under different conditions

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg/g)</th>
<th>Concentration range (mg/L)</th>
<th>Contact time (min)</th>
<th>pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated alumina</td>
<td>–</td>
<td>2–20</td>
<td>24 h</td>
<td>6–8</td>
<td>[41]</td>
</tr>
<tr>
<td>La/Mg/Si-loaded palm shell-based activated carbon (LMSAC)</td>
<td>9.98</td>
<td>1–80</td>
<td>40 min</td>
<td>7 ± 0.2</td>
<td>[42]</td>
</tr>
<tr>
<td>Boron-doped biochar/$\text{Al}_2\text{O}_3$</td>
<td>196.1</td>
<td>20</td>
<td>–</td>
<td>3–8</td>
<td>[43]</td>
</tr>
<tr>
<td>Magnesium oxide impregnated biochar</td>
<td>83.05</td>
<td>50</td>
<td>400 min</td>
<td>8</td>
<td>[44]</td>
</tr>
<tr>
<td>Amorphous alumina-modified expanded graphite ($\text{Al}_2\text{O}_3$/EG)</td>
<td>1.18</td>
<td>5</td>
<td>120 min</td>
<td>3.0–7.0</td>
<td>[45]</td>
</tr>
</tbody>
</table>
electronegative atoms to enhance their adsorption properties. Biochar is easy to obtain, cheap, and environmentally friendly, so it has a good prospect in wastewater treatment.

3.3. Natural minerals

Natural minerals are natural single substances or compounds with a relatively fixed chemical composition formed by geological processes, and have obvious advantages in terms of scale, cost, and operation, and pollution control effect. They play a unique role in the field of environmental protection and environmental rehabilitation.[47]. Comparison of the adsorption properties of various minerals to fluoride under various conditions is shown in Table 4, including clay, zeolite, SiO2, and other minerals. Among them, clay is a crucial mineral material composed of many kinds of hydrated silicates and a certain amount of alumina, alkali metal oxides, and alkaline earth metal oxides, which have a large specific surface area and vital negative electricity. Due to its good physical adsorption and surface chemical activity, clay shows good adsorption and defluoridation performance.

As an adsorbent, zeolite is a water-containing alkali or alkaline earth metal aluminosilicate mineral with excellent ion exchange and adsorption properties. However, zeolites usually have a negative surface charge, resulting in a higher adsorption capacity for cations but a lower adsorption capacity for anions due to electrostatic repulsion. Therefore, many researchers use multivalent metal cations to modify the zeolite’s surface to improve the adsorption capacity of zeolites. Liu and Cao[53] synthesized a series of zeolites with different iron content by hydrothermal method. The results show that the adsorption capacity to fluoride decreases with the increasing iron content, confirming that the adsorption performance of iron-containing zeolites is disadvantageous. Compared to non-magnetic zeolites, the magnetization process has little impact on F- ion adsorption. Although the adsorption capacity of zeolite is lower than that of bone charcoal and activated alumina, the adsorption capacity of bone charcoal and activated alumina decreases obviously with the increase of regeneration times, while the adsorption capacity of zeolite increases with the increase of regeneration times. Natural minerals are rich in resources, cheap and easy to obtain, and have a large specific surface area and rich functional groups. They have not only strong chemical stability and can be recycled, but they also have good adsorption and ion exchange properties. They are kind of practical and effective adsorbents. However, they often need to be modified to enhance the adsorption capacity of natural minerals and improve adsorption efficiency.

3.4. Chitosan and chitosan modified materials

Chitosan is a derivative of chitin after deacetylation under alkaline conditions, which is a green and pollution-free adsorbent. Chitin and chitosan derivatives are not only cheap and widely sourced, but also contain a large number of –OH and –NH2 active functional groups in the molecules, which can be protonated, can adsorp, and remove a variety of pollutants from water, and have the advantages of non-toxicity and easy degradation[54]. However, due to the defects of low mechanical strength, easy loss and low adsorption capacity, unmodified chitosan is not suitable to be used directly as a defluoridation agent for wastewater. Chitosan can be modified by cross-linking, carboxymethyl-ation, chelation of transition metal elements, chelating rare earth elements, and mixing with inorganic materials, and it can introduce various functional groups to enhance the adsorption of fluoride ions (Table 5).

Regarding the mechanism of defluoridation, it is noted that the polymer chitosan as a matrix is rich in amino and carboxyl groups, which becomes a good adsorption site. Prabhu and Meenakshi[60] investigated a new approach to prepare polyamidoamine-grafted chitosan beads (PAAGCB) by loading different metal ions onto the protonated PAAGCB. The results showed that zirconium ion loading on PAAGCB had high selectivity and its maximum defluoridation capacity was 17.47 mg/g. Chitosan and chitosan-modified materials have a wide range of sources, low price, and large specific surface area, contain a large number of functional groups, and are a kind of environmentally friendly adsorbent with biodegradability. In order to improve the adsorption capacity and reduce the adsorbent cost, the chitosan surface is usually modified to improve the fluoride removal ability.

4. Electrochemical technology

4.1. Electrocoagulation

In electrocoagulation (EC), an electric field is applied between the electrodes of the electrolytic cell. The anode (iron or aluminum electrode) dissolves and oxidizes into a floculent, then agglomerates with suspended particles and pollutants and adsorbing the dissolved impurities and sediment to the bottom. At the same time, the cathode reacts

| Table 4 | Comparison of the adsorption properties of various minerals towards fluoride under different conditions |
|---|---|---|---|---|---|
| Adsorbent | Adsorption capacity (mg/g) | Concentration range (mg/L) | Contact time | pH | References |
| Tunisian raw clays | 16.05 | 2 | 30 min | 3-6 | [48] |
| Cationic surfactant/H2O2 modified organic matter-rich clay | 53.66 | 20-120 | 60 min | Acidic pH | [49] |
| MnO2 coated Na-bentonite | 2.4 | 5 | 30 min | 8 | [50] |
| Al/Fe oxide-modified diatomaceous earth | 7.63 | 10-100 | 50-60 min | 3-8 | [51] |
| Cerium modified mesoporous silica | 17.96 | – | 240 min | 3 | [52] |
with a reduction to produce hydrogen, and the insoluble flocs float to the solution's surface by air floatation, separating the surface sediments and flocs from solid to liquid. Finally, remove impurities from the water. The mechanism of fluoride removal is mainly the ion exchange of fluoride ion and hydroxide ion in hydroxyl precipitate. As shown in Fig. 3, the electrocoagulation process involves three stages: the formation of coagulant by anodic metal oxidation, the instability of pollutants and emulsion, and finally, the construction of flocs through the aggregation of pollutant particles or the adsorption of contaminants on the coagulant [61]. The simplest electrolytic cell consists of two electrodes; one is the anode, the metal is oxidized on the anode, and the other is the cathode, on which a series of electrolytic components are reduced. The kinds of ions formed in the electrode make the charge of the pollution particles in the water unstable. Halpegama et al. [62] optimized its operating parameters by electrocoagulation (EC) and found that the best fluoride removal efficiency reached 97%, and the chemicals in the solution matrix, especially $SO_4^{2-}$, significantly affected the hardness and fluoride removal efficiency.

As an efficient enhanced conventional treatment technology, electrocoagulation can effectively reduce fluoride content in the wastewater and improve the removal rate of pollutants such as organic matter, microorganisms, and colloidal particles and greatly enhance the flocculation performance. Compared with chemical precipitation and flocculation precipitation, the subsequent sludge quantity is less, which reduces the difficulty of treatment. The flocculation produced by EC activity is high, the dosage of aluminum salt added is lower than the traditional chemical flocculation precipitation. The precipitation effect is better, simple operation, simple equipment, widely used in seawater and brackish water fluoride removal. However, the electric flocculation process requires power consumption, the operating cost is slightly higher, the treatment efficiency is greatly affected by pH and coexisting ions, and the fluoride-containing groundwater is weakly alkaline, contains a large number of interfering ions, and needs to be pre-acidified, which limits its application in wastewater treatment.

### 4.2. Capacitive deionization technology

Capacitive deionization technology (CDI) is a new type of desalination technology that is attracting more and more attention due to its stable operation and energy saving, especially in the field of water desalination. CDI uses electrification to drive the charged material in water to the surface of the porous electrode for adsorption, and the saturated electrode desorption and discharge of the adsorbed material by applying a reverse voltage to achieve electrode regeneration. The typical operating system of electro adsorption is shown in Fig. 4. At present, there are relatively few studies on the application of fluoride removal. Jiang et al. [63] use the suitability and effectiveness of liquid flow electrode capacitive deionization to treat fluoride-containing brackish water. By comparing the operation modes of short circuit closed cycle (SCC), isolated closed cycle, and single cycle, it is found that the SCC mode is the most favorable.

Capacitive deionization technology has many advantages in water treatment [64]. Compared with ED, CDI technology also has a unique removal performance for other inorganic salt ions, colloids, and microorganisms in solution, and the adsorption capacity is much larger than that of traditional technology. Electroadsorption technology involves electrochemistry and adsorption, so the electrode materials need to be regenerated when the adsorption is
saturated. The selective removal rate of target pollutants can be improved by using suitable electrode materials [65]. The regeneration process only needs to connect the cathode and anode for a short time, which significantly improves the regeneration rate and can be used many times. Suppose electro absorption can be used extensively as an advanced drinking water treatment technology. In that case, effluent quality will be greatly improved, which can effectively reduce the impact of micro-pollution and even severe pollution.

5. Pressure-driven membrane technology

At present, membrane separation technology has attracted wide attention because of its good performance and stable operation in fluoride removal. Membrane separation technology is to apply a force on one side of the membrane to make use of the screening action of natural or synthetic membranes with a certain pore-size structure to separate fluoride from aqueous solution to achieve the purpose of wastewater purification. The study on the defluoridation performance of the membrane is helpful in guiding the wastewater treatment process. It is found that the defluoridation effect of the membrane depends on several factors (that is, the properties of the membrane, other ions, feed pH value, feed concentration, and pressure) [66]. Fig. 5 depicts the factors affecting the performance of the membrane. Ultrafiltration (UF) can effectively remove colloids, particles, bacteria, viruses, and other microorganisms in water, but it has poor ability to retain inorganic salt ions, mainly because the hydration radius of most inorganic salt ions is smaller than the micro pores of the ultrafiltration membrane. Hence inorganic ions enter into the produced water through the membrane during the filtration process.

5.1. Reverse osmosis (RO)/Nanofiltration (NF)

Currently, nanofiltration (NF) and reverse osmosis (RO) are the most commonly used membrane processes for fluoride removal (Table 6). In membrane filtration, water with high concentrations of pollutants is passed through a semi-permeable membrane, and pollutants are removed from the water and collected on the retention side. The principle of the reverse osmosis method is to apply a certain pressure to the solution on one side of the reverse osmosis membrane. When the pressure value exceeds the osmotic pressure, the solvent in the pressurized solution reverses the direction of natural osmosis and creates RO on the other side of the reverse osmosis membrane. Compared with electrodialysis, RO has the following advantages: Basically, no need to add many agents; RO system design and operation is simple and the construction cycle is short; RO purification is efficient and environmentally friendly. As a membrane separation technology, RO is designed to selectively scavenge fluoride ions in the solution under a pressure higher than the osmotic pressure of the solution. However, RO has high working pressure, low permeability flux and high energy demands, and the membrane is easy to be blocked, resulting in a short service life.

As a practical industrial wastewater treatment technology, nanofiltration stands out as being somewhere between reverse osmosis and ultrafiltration. The operating pressure of nanofiltration is relatively low, and the pore size is larger than that of RO membrane. Although similar to reverse osmosis, NF can generate the same permeation flux even under low pressure [67]. However, concentration polarization and membrane fouling are two important reasons for significant reduction in membrane permeability and selectivity. And since toxic wastewater is produced in the residue after fluoride ion concentration, some membranes are sensitive to pH, and the problems of clogging, scaling and fouling also deserve attention. Solving the membrane loss problem requires research and development of membrane materials with better performance, longer life and better selectivity. The selectivity of nanofiltration is a particular advantage over RO, which can provide research directions for the production and selection of targeted membranes.

As the most widely used desalination membrane treatment units, nanofiltration and RO have a broad application perspective in defluoridation, but the energy consumption and water production of nanofiltration and RO membrane have been the focus of attention. With the development of membrane materials and the maturity of membrane manufacturing technology, it is possible to manufacture and apply low-pressure nanofiltration/reverse osmosis
membrane, which can be started from the membrane material itself, and improve the water production and anti-pollution performance of the membranes. Both nanofiltration and reverse osmosis depend on the selective permeability of the membrane. Still, the negativity of the membrane enhances the electrostatic repulsion of negatively charged ions, and the pore of nanofiltration and reverse osmosis is lower than the hydration radius of ions. Fluoride ion is removed by sieving. The effect of fluoride removal by membrane technologies such as nanofiltration and reverse osmosis is less dependent on water quality conditions and operating parameters, but reliable pretreatment of influent is needed. Membrane fouling will reduce the stability of the long-term operation of the system, and the operating cost will be slightly higher. With the maturity of domestic membrane preparation technology, the membrane cost is gradually reduced, but the energy consumption of nanofiltration and reverse osmosis membranes, and at the same time improve materials and membrane modules to improve membrane fouling.

5.2. Electrodialysis

Electrodialysis is essentially a membrane separation technique powered by electric field forces. In electrodialysis (ED), the ED stack is used, in which anion- and cation-exchange membranes are constructed; under the action of a DC electric field, the cations move to the cathode, and the anions to the anode, and then a large number of terminal ions accumulate in the concentrated water channel. The purified freshwater flows out from the freshwater channel in the equipment. Electrodialysis has a unique advantage in the removal of ionic pollutants. Combined with a selective ion exchange membrane, electrodialysis can improve the selectivity of fluoride removal from saline solution. It is one of the superior fluoride removal technologies [71]. Its principle is shown in Fig. 6. Aliaskari and Schäfer [72] used intermittent electrodialysis (ED) system to find that the removal rate of fluoride increased at high potential (>15 V), and the increase of salinity delayed the removal of fluoride. The results show that the ionic characteristics of contaminants determine the removal efficiency of pollutants by ED.

Electrodialysis includes electrochemical and membrane separation processes, which can efficiently remove all kinds of salt ions in water, which can run for a long time and do not need to be added. Nevertheless, the application of this technology in drinking water treatment will result in excellent energy consumption. Most of the nanofiltration membranes are derived from RO membranes, but the NF operating energy requirement is lower than the RO energy requirement for treating low-salinity wastewater. Compared to RO, ED uses almost half the energy of RO in pilot plants and has a higher recovery rate for the same wastewater quality and

Table 5
Comparison of the adsorption properties of various chitosan-modified materials towards fluoride under different conditions

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg/g)</th>
<th>Concentration range (mg/L)</th>
<th>Contact pH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic iron oxide fabricated hydrotalcite/chitosan (Fe₃O₄HTCS)</td>
<td>5.03</td>
<td>10</td>
<td>20 min</td>
<td>5 [55]</td>
</tr>
<tr>
<td>Fe-impregnated chitosan (Fe-CTS)</td>
<td>1.97</td>
<td>10</td>
<td>6 h</td>
<td>- [56]</td>
</tr>
<tr>
<td>Zirconium immobilized cross-linked chitosan (Zr-CCS)</td>
<td>48.26</td>
<td>20–200</td>
<td>40 min</td>
<td>6 [57]</td>
</tr>
<tr>
<td>Hydrous zirconium oxide-impregnated chitosan beads</td>
<td>22.1</td>
<td>9.7–369.2</td>
<td>160 h</td>
<td>5 [58]</td>
</tr>
<tr>
<td>Magnetic iron oxide encrusted hydrocalumite-chitosan (Fe₃O₄@HCCS)</td>
<td>6.8</td>
<td>20</td>
<td>30 min</td>
<td>3 [59]</td>
</tr>
</tbody>
</table>
of key technologies to form complete sets of technologies, Improve the production, modularization, and equipment and reasonable, convenient treatment and stable operation. ride removal technology with high efficiency, economical-functional materials, and take coagulation sedimentation, process and mechanism of defluoridation, based on the of people in high-fluoride areas. Clearly understand the strategy of “changing water sources,” drink fluoride-free hydrologic and water quality surveys, give priority to the groups of fluoride exposure in drinking water. Strengthen the areas with high fluoride pollution and the high-risk ing of fluoride pollution in groundwater, and determine of fluoride pollution, strengthen the prediction and screen to have a deep understanding of the formation mechanism pollution in drinking water fundamentally, it is necessary sludge. In this case, in order to prevent and control fluoride reducing the amount of fluoride agent and the discharge of performance correlation guided cerium-based metal–organic frameworks: superior adsorbents for fluoride removal in water, Chemosphere, 312 (2023) 137335, doi: 10.1016/j.chemosphere.2022.137335.

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References

Table 6
Comparison of fluoride removal effects of different membrane separation technologies

<table>
<thead>
<tr>
<th>Membrane separation technique</th>
<th>Removal efficiency</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reverse osmosis/nanofiltration (RO/NF)</td>
<td>Rejections of fluoride with RO membranes were higher than 96% (real wastewater), and with NF membranes higher than 40%</td>
<td>[68]</td>
</tr>
<tr>
<td>A solar-powered nanofiltration/ reverse osmosis (NF/RO) system</td>
<td>Both NF and RO membranes were efficient for removal of fluoride from the brackish water, among which the NF90 membrane achieved the optimum balance between produced water quantity and quality</td>
<td>[69]</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>NF90 membrane was proved to be particularly better in retaining the fluoride with very high efficiency (above 75%)</td>
<td>[70]</td>
</tr>
</tbody>
</table>

volume [73]. However, the price of ion exchange membranes is high, and the water quality conditions and operating parameters also affect the treatment results. The performance of different anion and cation exchange membranes is different, so they are rarely used in drinking water treatment. And as a membrane ion exchange technology, electrodeionization has to overcome the dialysis of anions, especially sulfate ions, and unique membrane materials; otherwise, the defluoridation efficiency of the electrodeionization will be reduced.

6. Conclusion
This paper summarizes the sources of high-fluoride wastewater and several treatment methods for fluoride-containing wastewater. Considerable efforts have been made worldwide to remove fluoride from the water, but with limited success. It is clear that the removal of fluoride from water is still a problem to be solved in many countries around the world. When selecting the fluoride removal method, it is necessary to comprehensively consider the pH values of the fluoride-containing wastewater, the fluoride content in the solution, and other components and other factors, but also make a reasonable evaluation of the effect and economic benefit of fluoride removal, not only need to improve the removal rate of fluoride ions, but also consider reducing the amount of fluoride agent and the discharge of sludge. In this case, in order to prevent and control fluoride pollution in drinking water fundamentally, it is necessary to have a deep understanding of the formation mechanism of fluoride pollution, strengthen the prediction and screening of fluoride pollution in groundwater, and determine the areas with high fluoride pollution and the high-risk groups of fluoride exposure in drinking water. Strengthen hydrologic and water quality surveys, give priority to the strategy of “changing water sources,” drink fluoride-free or low-fluoride groundwater, and control the health risks of people in high-fluoride areas. Clearly understand the process and mechanism of defluoridation, based on the innovation of water purification agents and environmental functional materials, and take coagulation sedimentation, adsorption, and membrane separation as the critical technical directions, innovate and develop a new type of fluoride removal technology with high efficiency, economical and reasonable, convenient treatment and stable operation. Improve the production, modularization, and equipment of key technologies to form complete sets of technologies, facilities, or equipment that adapt to different water quality characteristics and scales. The scientific operation and supervision of defluoridation facilities should be strengthened to ensure the long-term and stable operation of defluoridation facilities and maximize technological benefits.


