Synergistic Fluoride Adsorption by Composite Adsorbents Synthesized From Different Types of Materials—A Review

Yifei Wei, Li Wang*, Hanbing Li, Wei Yan and Jiangtao Feng

Xi’an Key Laboratory of Solid Waste Recycling and Resource Recovery, Department of Environmental Science and Engineering, School of Energy and Power Engineering, Xi’an Jiaotong University, Xi’an, China

The reduction of fluoride concentrations in water is one of many concerns. Adsorption is the most widely used technology for fluoride removal and the center to development of adsorption technology is the improvement of adsorbents. This review classifies the typical fluoride removal adsorbents into four types: metal oxides/hydroxides, biopolymers, carbon-based, and other adsorbents. The exploitation of new materials and the synthesis of composite materials are two ways of developing new adsorbents. In comparison to the discovery of novel adsorbents for fluoride adsorption, research into the composite synthesis of different types of conventional adsorbents has proliferated in recent years. The traditional adsorbents used the earliest, metal oxides, can act as active centers in a wide range of applications for modifying and compounding with other types of adsorbents. This study emphasizes reviewing the research on fluoride removal by composite adsorbents synthesized from different types of metal-modified materials. Seven factors were compared in terms of material characterization, initial fluoride concentration, adsorbent dose, pH, temperature, reaction time, and maximum adsorption capacity. The modification of composite adsorbents is facile and the synergistic effect of the different types of adsorbents significantly improves fluoride adsorption capacity. Metal composite adsorbents are synthesized by facile coprecipitation, hydrothermal, or impregnation modification methods. The adsorption mechanisms involve electrostatic attraction, ion exchange, complexation, and hydrogen bonding. The fluoride adsorption capacity of composite adsorbents has generally improved, indicating that most modifications are successful and have application prospects. However, to achieve significant breakthroughs in practical applications, numerous issues such as cost, separation/regeneration performance, and safety still need to be considered.

Keywords: fluoride adsorption, metal oxides/hydroxides, carbon-based adsorbents, biopolymer, modification
1 INTRODUCTION

Fluoride ions in water have a strong affinity with positively charged elements such as calcium (Bhatnagar et al., 2011), which is a major component of human bone and tooth structure (Rehman et al., 2015). Low concentrations of fluoride in drinking water (0.5–1.5 mg/L) (Chen et al., 2017) can strengthen bones and prevent dental caries, while excessive concentrations of fluoride (4–10 mg/L) can cause diseases such as fluorosis, osteoporosis, brittle bones, brain damage, and several thyroid disorders (Kumar et al., 2020). Excessive fluoride concentrations in water have become a public health concern in developing countries. High concentration (>10 mg/L) fluorinated wastewater is easier to treat and can be removed or reduced by coagulation, precipitation, electrochemistry, and other methods. The treatment of low concentration (2–10 mg/L) fluorinated wastewater is relatively difficult and is also a current research hotspot. The treatment methods include adsorption (Lin et al., 2016), membrane separation, ion exchange (Xu et al., 2017), nanofiltration (Wang A. et al., 2018), reverse osmosis (Ye et al., 2019), and electrodialysis (Fan et al., 2019). Among them, the adsorption method has the advantages of low cost, high flexibility, simple operation, and high efficiency (Sarkar et al., 2019). It is the most widely used and the treatment effect is more satisfactory.

The treatment effectiveness of the adsorption method is influenced by a number of factors, including adsorbent properties, fluoride ion selectivity, compatibility, solution pH, temperature, co-existing ions, and contact time (Pigatto et al., 2020). It mainly depends on the adsorbent properties such as particle size, pore size structure, zero charge point ($pH_{ZPC}$), and specific surface area ($S_{BET}$) (Biswas et al., 2017). High specific surface area (developed pore structure) and ideal chemical surface (abundant functional groups) are two essentials for effective removal of fluoride by adsorbents. Although not systematically categorized, this review found that the main traditional sorbents frequently used for fluoride removal are metal oxides/hydroxides (Dhillon et al., 2017), low-cost carbon materials (Zhang X. et al., 2021), biomolecular materials (Jia et al., 2018), and others such as clay, hydroxyapatite, and graphite. This review classifies the more researched fluoride removal adsorbents into four categories: metal oxide/hydroxide adsorbents, biopolymer adsorbents, carbon-based adsorbents, and other adsorbents (industrial waste, minerals, etc.).

For the development of new adsorbents, the discovery of novel adsorbents that have never been used before and the composite material synthesis by combining traditional adsorbents are the two main approaches to improve adsorption capacity. In comparison to the discovery of novel adsorbents that have never been used before, research into the composite synthesis of different types of conventional adsorbents for fluoride adsorption has proliferated in recent years. The emphasis of this study is placed on the fluoride adsorption effect of this adsorbent compounded from different types of conventional adsorbents. The study of other types of metal-modified adsorbents accounts for a major part. A total of seven factors were compared in terms of material characterization, initial fluoride concentration, adsorbent dose, pH, temperature, reaction time, and maximum adsorption capacity.

2 CONVENTIONAL TYPES OF ADSORBENTS

2.1 Metal Oxide/Hydroxide Adsorbents

Metal oxide/hydroxide nanoparticles were reported to show an affinity for fluoride and high performance in fluoride removal. The high reactivity (Lanas et al., 2016), specificity, specific surface area (Rathore and Mondal, 2017), stability, and self-assembly potential have attracted attention in fluoride removal studies. Nanoscale dimensions with desirable physicochemical properties, such as high density of hydroxyl ions on the high specific surface area, will further enhance the fluoride adsorption capacity.

2.1.1 Aluminum Oxide/Hydroxide

Aluminum oxide/hydroxide was the earliest studied and used adsorbents for fluoride removal (Chinnakoti et al., 2016a). Typically, aluminum hydroxide is first prepared by electrolysis or pyrolysis and then partially converted to aluminum oxide by calcination. One of the advantages of aluminum oxide/hydroxide adsorbents is the large specific surface area as shown in Table 1, and in general, $S_{BET} > 200$ m$^2$/g. Generally, high $pH_{ZPC}$ allows its surface to appear positively charged in water (Dhawane et al., 2018). Several studies have reported that the mechanism of fluoride adsorption by alumina mainly consists of electrostatic attraction and ion exchange (Rathore and Mondal, 2017), as shown in Figure 1A; the monodentate complex Al-F is the major formation after adsorption (Kang et al., 2018; Lin et al., 2020). Kang et al. (2018) synthesized an amorphous alumina microsphere using solvothermal reaction and calcination, with $S_{BET} = 400$ m$^2$/g and a maximum adsorption capacity of 129.4 mg/g; they proposed that the adsorption mechanism involves chemical reaction and pore filling in addition to ion exchange and electrostatic attraction. However, aluminum is easily leached out in aqueous solutions, especially under acidic conditions (Lin et al., 2020), leading to high concentration of aluminum residues in drinking water, which is also a major threat to human health.

2.1.2 Rare Earth Metal Compounds

Compared to aluminum, the rare earth metals (cerium, titanium, lanthanum, etc.) have further affinity for fluoride due to the ability to stabilize in the +3 or +4 valence state with a few numbers of outermost electrons; therefore, sufficient empty orbitals are available for fluo ride ions (Zhang K. et al., 2016). The solubility of rare earth metals is relatively limited over a wide pH range (Dhillon et al., 2016), so rare earth oxides/hydroxides have been increasingly investigated as substitution for aluminum in recent years. Among these, CeO$_2$ readily forms oxygen vacancies and, therefore, has particularly high oxygen storage/release capacity with high adsorption capacity (Kullgren et al., 2014; Wu and Gong, 2016; Kang et al., 2017). Kang et al. (2017) compared the physicochemical characteristics and adsorption performance of different
| Adsorbents                        | Preparation method                             | Dimension | $S_{BET}$ (m$^2$/g) | Aperture (nm) | $pH_{PZC}$ | Adsorption mechanism                          | Ref                      |
|----------------------------------|-----------------------------------------------|-----------|----------------------|--------------|------------|-----------------------------------------------|--------------------------|
| Cactus-like amorphous            | Solvothermal method                            | 40 μm     | 419.6                | 5.3          | 6.6        | Chemical coordination, electrostatic attraction, and ion exchange | Kang et al. (2018)       |
| alumina oxide microspheres       | without templates                              |           |                      |              |            |                                               |                          |
| Nano γ-alumina                   | Surfactant-assisted combustion                 | —         | 221                  | —            | 6.5        | —                                             | Chinnakoti et al. (2016a) |
| Mesoporous micro alumina         | γ-AlOOH calcined at 873 K                     | 0.9 mm    | 254.1                | 12.96        | 9.0        | Electrostatic attraction                      | Lanas et al. (2016)      |
| Al$_2$O$_3$ nanoparticles        | Flame spray pyrolysis (FSP)                   | 9.8 nm    | 213                  | 93           | —         | Electrostatic attraction                      | Hafshejani et al. (2017) |
| Porous-layered Al$_2$O$_3$       | Roasting of AlFu MOFs                          | —         | 329.3                | 3.8          | —         | Ion exchange, complexation                    | Yang et al. (2020)       |
| Activated alumina                | Al$_2$O$_3$ cauterized at 673 K               | 1–3 mm    | 185.6                | 5.1          | 8.5        | Lewis acid and base                           | Dhawan et al. (2018)     |
| Meso$$^{**}$$ $$^{**}$$ micro$$^{**}$$ | Electrolysis, calcination at 973 K            | 1.5 mm    | 253.2                | 4.7          | 7.52       | Electrostatic attraction                      | Rathore and Mondal (2017) |
| alumina                         |                                               |           |                      |              |            |                                               |                          |
| Cubical ceria nano-adsorbent     | Coprecipitation, calcination at 473 K         | 4.5 nm    | 98                   | 2.62         | 6         | Ligand exchange, complexation                  | Dhillon et al. (2016)    |
| CeO$_2$ nanorods                 | Hydrothermal at 373 K                          | 20'200 nm | 111.4                | 8.65         | —         | Ce$^{3+}$-O defect, ion exchange, —            | —                       |
| Pore filling                     |                                               |           |                      |              |            |                                               |                          |
| CeO$_2$ octahedron               | Hydrothermal at 453 K                          | 14 nm     | 160.2                | 9.66         | —         | —                                             | —                       |
| CeO$_2$ nanocubes                | Hydrothermal at 473 K                          | 25 nm     | 55.8                 | 15.1         | —         | —                                             | —                       |
| CeCO$_3$OH nanosphere            | Hydrothermal                                   | 250 nm    | 10.6                 | 15.5         | —         | Electrostatic attraction, ion exchange        | Zhang et al. (2016b)     |
| Porous MgO nanoplates            | Solvothermal, calcination at 773 K             | —         | 47.4                 | 3.3          | —         | Ligand exchange                               | Jin et al. (2016)        |
| Hollow MgO spheres               | Hydrothermal, calcination at 773 K             | 2 μm      | —                    | —            | 10        | Ligand exchange                               | Zhang et al. (2011b)     |
| Microsphere-like MgO             | Hydrothermal, calcination at 773 K             | 46 μm     | 120.7                | 5.12         | —         | Ion exchange                                  | Lee et al. (2017)        |
| Pillar-like MgO                  | Hydrothermal, calcination at 773 K             | 2'20 μm   | 99.44                | 6.26         | —         | Ion exchange                                  | Lee et al. (2017)        |
| γ-Fe$_2$O$_3$ nanoparticles      | Precipitation                                  | 5–20 nm   | —                    | —            | 8.13      | Complexation                                  | Jayarathna et al. (2015) |
| Trititanate nanotubes            | Hydrothermal at 403 K, 1 h                     | 8–12 nm   | 282                   | —            | 2.5       | Ion exchange, electrostatic attraction        | Chinnakoti et al. (2016b) |
| TiO$_2$                          | Solvothermal method                            | 1 μm      | 31.9                 | —            | 6.5       | Complexation                                  | Zhou et al. (2019b)      |
| La$_3$O$_5$ is a low-            | La$_5$O$_5$ cross-linking, Glutaraldehyde      | 1 mm      | 2.618                 | 1.441        | —         | Ion exchange                                  | Huo et al. (2011)        |
| lanthanum alinate bead           | cross-linking, Glutaraldehyde                  |           |                      |              |            |                                               |                          |
| Biopolymerpectinmalginate        | Hydrothermal mixing                            | —         | —                    | —            | —         | —                                             | Raghav et al. (2019)     |
| Porous zirconium alinate         | CaCl$_2$ cross-linking SA, Zr(NO$_3$)$_4$      | 2 mm      | 3                     | —            | —         | Electrostatic attraction, ion exchange        | Quisheng et al. (2015)   |
| Hydrothermal                     | immersion                                     |           |                      |              |            |                                               |                          |
| Shell biochar                    | Calcination at 1073 K                          | 0.5 mm    | 4                     | 413          | 6         | Complexation                                  | Lee et al. (2021)        |
| Nanoscale rice husk biochar      | Calcination at 873 K, ball milled              | —         | —                    | —            | —         | Ion exchange                                  | Goswami and Kumar (2018) |
| Mustard ash biochar              | Carbonization at 873 K                         | —         | —                    | —            | —         | Ion exchange                                  | Jadhav and Jadhav (2021) |
| Peanut shell biochar             | Pyrolysis at 873 K, 1 h                        | —         | 98                   | 7.05         | —         | —                                             | Kumar et al. (2020)      |
| Rhodophyta biochar               | Calcinated in muffle for 2 h                   | 75 μm     | 320                  | 1.28         | 5.4       | Complexation                                  | Naga Babu et al. (2020)  |
| Rice husk biochar                | Pyrolysis at 688 K in tube furnace             | —         | 3                    | 13.29        | 5.9       | Ion exchange                                  | Yadav and Jagadevan (2020) |
| Activated sugarcane ash          | Burning at 773 K in muffle furnace             | 150 μm    | 64                   | —            | —         | Ion exchange                                  | Mondal et al. (2016)     |
| KOH-treated jamun seed           | KOH activation, pyrolysis at 1173 K            | —         | 748                  | 2.19         | 4.9       | Ligand exchange                               | Araga et al. (2017)      |
| KOH-treated activated carbon     | KOH activation, pyrolysis at 1173 K            | —         | 1,006                | 1.95         | 6.11      | Protonation, ion exchange                     | Bhomick et al. (2019)    |
| Activated carbon                 | Surface modification                            | —         | —                    | —            | 6.86      | Electrostatic attraction                      | Chen et al. (2019)       |
| Coconut-shell carbon             | Carbonization at 1173 K in tube furnace         | 500 nm    | 358                  | —            | —         | Electrostatic attraction                      | Araga et al. (2019)      |
| Chicken bone biochar             | Burning at 873 K in muffle furnace             | 159 μm    | 126                  | —            | —         | Ion exchange                                  | Herath et al. (2018)     |
| Bone char                        |                                               | 0.8 mm    | 104                  | 11.4         | 8.4       | Electrostatic attraction                      | Medellin-Castillo et al. (2014) |

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The morphologies of CeO$_2$ (nanorods, octahedrons, and nanocubes) prepared under different hydrothermal conditions. The different morphologies of CeO$_2$ were found to expose distinct crystalline surfaces and proportions of oxygen defects, leading to significant differences in fluoride adsorption capacity, with CeO$_2$ nanorods having the largest $Q_{\text{max}}$ (71.5 mg/g). However, rare earth metal oxides are costly, prone to agglomeration, and high leaching concentrations can be toxic to water (Yu et al., 2015).

2.1.3 Magnesium Oxide

MgO is less dissolved, nontoxic, abundant in reserves compared to other metals, and has an affinity for fluoride (Jin et al., 2016), giving it an opportunity to be used. It has been reported that MgO has a high isoelectric point and relies on electrostatic attraction to adsorb fluoride (Suzuki et al., 2013). Y. Zhang et al. tested the zeta potential of hollow MgO spheres of $pH_{\text{PZC}} = 10$, which is the highest value reported. In order to improve the morphology, Z. Jin et al. used a typical solvothermal method followed by calcination to form porous MgO nanoplates with an increased maximum adsorption capacity from 115.5 mg/g to 185.5 mg/g. They suggested that the mechanism of adsorption mainly consists of ligand exchange between fluoride and hydroxyl groups and carbonates on the surface of MgO (Figure 1B). Thus, the presence of carbonate in the solution can affect the fluoride adsorption capacity of MgO.

The most significant problem concerning metal oxide/hydroxide nanoparticles is low structural stability and the tendency to leach in water causing secondary contamination (Lin et al., 2020).

2.2 Biopolymer Adsorbents

Biopolymers are the natural macromolecular materials derived from cellular or extracellular substances with properties such as biodegradability, nontoxicity, low waste generation, low leaching, biocompatibility, and hydrophilicity. The most researched fluoride removal biopolymer adsorbents in recent years include sodium alginate (SA), pectin, chitosan (CS), and carboxymethyl cellulose (CMC) (Araga and Sharma 2019). Hydrogels formed by chemical or physical cross-linking of biopolymers have hydrophobic, three-dimensional network structures, which are easier to separate compared to the

### TABLE 1 | (Continued) Summary of the preparation methods, characteristics, and adsorption mechanisms of four traditional adsorbents.

| Adsorbents | Preparation method | Dimension | $S_{\text{BET}}$ (m$^2$/g) | Aperture (nm) | $pH_{\text{PZC}}$ | Adsorption mechanism | Ref |
|------------|--------------------|-----------|--------------------------|--------------|-----------------|----------------------|-----|
| Bovine bone biochar | Burning at 773 K in muffle furnace | — | 115 | 3.823 | 2.2 | Ion exchange | Zhou et al. (2019a) |
| Kaolinite | Alkal–hydrothermal | — | 18 | 4 | 5 | Ion exchange | Wang et al. (2017b) |
| Activated clay | Sulfuric acid activation | — | 167 | 4.9 | — | — | Guza et al. (2019) |
| Fly ash–paper mill lime mud | Mixing, calcination | 60 μm | 58.9 | — | — | Ligand exchange, complexation | Ye et al. (2019) |
| Natural clay | — | — | 8 | — | — | — | Nabbou et al. (2019) |
| Natural pumice | — | 200 μm | 9.5 | — | 3 | — | Dehghani et al. (2016) |
| Natural zeolite | NaOH activation | — | — | — | — | Ion exchange, H-bonding | Cheng et al. (2018) |
| Clay | HCl immersion for 24 h | — | 44.29 | — | 6 | — | Asadi et al. (2018) |
| Porous nanohydroxyapatite | Organic template coprecipitation | 25 nm | 41.3 | — | 6.8 | Lattice substitution, precipitation | Wimalasiri et al. (2021) |
| Hierarchical hydroxyapatite | Ca and phosphate hydrothermal at 393 K | 2 μm | 83.17 | 11.52 | 7.73 | Electrostatic attraction, ion exchange | Gao et al. (2019) |
| NaP-hydroxyapatite | Hydrothermal with zeolite gel at 373 K | 2 μm | 45 | 13.7 | — | Ion exchange | Zendehdel et al. (2017) |
| Hydroxyapatite | Aqueous double decomposition | — | — | — | — | Ion exchange | Mourabet et al. (2015) |

**FIGURE 1** | Mechanism of fluoride adsorption by activated alumina (A) (Lin et al., 2020) and MgO (B) (Zhang Y. et al., 2021).
powder state, making them an environment-friendly adsorbent.

2.2.1 Sodium Alginate

Sodium alginate (SA) and pectin are both natural polysaccharides in colloidal form. Sodium alginate contains large numbers of -OH and -COOH groups on the main chain. The -COOH in the M unit is more bound by the surrounding electron cloud, while the -COOH in the G unit is arranged in the corner of the peak consisting of two adjacent carbon atoms; thus, G unit is more reactive (Wu T. et al., 2017). In the ionic cross-linking process (Figure 2A), when the dissolved colloidal sodium alginate is dropped into the solution of high-valent metal cations (Ca$^{2+}$, Ce$^{3+}$, Fe$^{3+}$, Al$^{3+}$, La$^{3+}$, etc.), the high-valent cations in the solution will rapidly replace Na$^+$ (Wu T. et al., 2017). In the ionic cross-linking process, the embedded high-valent cations form ligand chelate crosslinks with the oxygen atoms in the carboxyl and hydroxyl groups of the G-units, which form irreversible hydrogel-like microbeads (Qiusheng et al., 2015). The thermal stability and acid resistance of sodium alginate are further improved after the formation of the gel, while some of the carboxyl functional groups are occupied by high-valent metal cations, so the active sites with an affinity for fluoride ions are increased. Huo et al. (2011) used ionic cross-linking to prepare lanthanum alginate with stable skeletal junctions. SEM showed cracks in the dense surface structure after adsorption, with $Q_{\text{max}} = 197.2$ mg/g.

2.2.2 Pectin

Pectin is also rich in -COOH and -COOCH$_3$ groups. The active sites of sodium alginate and pectin are essentially identical, the only difference being the presence of -COOCH$_3$ in pectin (Sharma et al., 2019), whereas sodium alginate contains only -COOH. The ester group chelates better with metals through its lone pair of electron contribution. The carboxyl group is present in a dimeric form due to the conjugation effect, with the lone pair participating in the conjugation. Therefore, the ester group has a nucleophilic reaction to $F^-$ (Figure 2B), providing more active sites, and the pectin should have a higher fluoride removal.
| Adsorbents                          | Initial \( C_{F}^{-} \) (mg/L) | Adsorbent dose (g/L) | Reaction pH | Temperature (K) | Equilibrium time (min) | Isotherm model | Regeneration performance | \( Q_{\text{max}} \) (mg/g) | Ref                               |
|-----------------------------------|-------------------------------|---------------------|-------------|----------------|------------------------|----------------|--------------------------|----------------|-------------------------|
| Cactus-like amorphous alumina oxide microspheres | 50                             | 1                   | 5–8         | 298            | 300                    | Langmuir       | 80% at 5th cycle          | 129.40         | Kang et al. (2018)       |
| Nano γ-alumina                    | 8                              | 1                   | 4           | 303            | 120                    | Freundlich     | 80% at 5th cycle          | 32.00          | Chinnakoti et al. (2016a) |
| Mesoporous micro alumina          | 80                             | 0.5                 | 5.5         | 298            | 60                     | Langmuir       | —                        | 26.00          | Lanas et al. (2016)      |
| \( \text{Al}_2\text{O}_3 \) nanoparticles | 10                             | 0.5                 | 4–6         | 298            | 60                     | Langmuir       | —                        | 13.70          | Hafshejani et al. (2017)  |
| Amorphous porous-layered \( \text{Al}_2\text{O}_3 \) Activated alumina | 120                            | 5                   | 2–5         | 313            | 150                    | Langmuir       | —                        | 12.05          | Yang et al. (2020)       |
| Aluminum oxide/ hydroxide         | 10                             | 2                   | 6–8         | 318            | 120                    | Freundlich     | —                        | 4.31           | Dhawane et al. (2018)     |
| Cubical ceria nano-adsorbent      | 20                             | 1                   | 7           | 298            | 120                    | Langmuir       | —                        | 80.64          | Rathore and Mondal (2017) |
| \( \text{CeO}_2 \) nanorods       | 50                             | 0.5                 | 3.5         | 298            | 1,500                  | Langmuir       | —                        | 71.50          | Dhillon et al. (2016)    |
| \( \text{CeO}_2 \) octahedron     | 10                             | 1                   | 3–10        | 293            | 400                    | Langmuir       | —                        | 40.13          | Yang et al. (2017)        |
| \( \text{CeO}_2 \) nanocubes      | 50                             | 0.5                 | 3.5         | 298            | 1,500                  | Langmuir       | —                        | 28.30          | Zhang et al. (2016b)      |
| \( \text{CeO}_2 \)OH nanosphere   | 50                             | 0.5                 | 3.5         | 298            | 1,500                  | Langmuir       | —                        | 7.00           | Kang et al. (2017)        |
| Porous \( \text{MgO} \) nanoplates | 20                             | 1                   | 2–11        | 298            | 180                    | Freundlich     | —                        | 185.50         | Jin et al. (2016)         |
| Hollow \( \text{MgO} \) spheres   | 10                             | 1                   | 3–11        | 298            | 250                    | Freundlich     | —                        | 182.40         | Zhang et al. (2021b)      |
| Microsphere-like \( \text{MgO} \) | 100                            | 1                   | 3–9         | 298            | 300                    | Langmuir       | 40% at second cycle       | 166.70         | Lee et al. (2017)         |
| Pillar-like \( \text{MgO} \)      | 100                            | 1                   | 3–9         | 298            | 300                    | Langmuir       | 40% at second cycle       | 151.50         | Lee et al. (2017)         |
| γ-\( \text{Fe}_2\text{O}_3 \) nanoparticles | 100                            | 10                  | 4.5         | 298            | 15                     | —              | —                        | 3.65           | Jayaratna et al. (2015)   |
| Trititanate nanotubes             | 10                             | 0.5                 | 2           | 298            | 10                     | Langmuir       | —                        | 58.60          | Chinnakoti et al. (2016b) |
| \( \text{TiO}_2 \)                | 5                               | 0.5                 | 7           | 298            | 30                     | Langmuir       | —                        | 5.00           | Zhou et al. (2018b)       |
| Lanthanum alginate bead           | 10                             | 1                   | 4           | 298            | 1,440                  | Langmuir       | —                        | 197.20         | Huo et al. (2011)         |
| Biopolymer pectin and alginate    | 60                             | 0.1                 | 7           | 298            | 35                     | Langmuir       | —                        | 50.00          | Raghav et al. (2019)      |
| Porous zirconium alginate         | 20                             | 1                   | 2           | 303            | 1,200                  | Langmuir       | —                        | 27.95          | Qiusheng et al. (2015)    |
| Shell biochar                     | 300                            | 3.33                | 7           | 298            | 1,440                  | Langmuir       | 60% at third cycle        | 82.93          | Lee et al. (2021)         |
| Nanoscale rice husk biochar       | 5                               | 1                   | 7           | 303            | 60                     | Freundlich     | —                        | 21.70          | Goswami and Kumar (2018)  |
| Mustard ash biochar               | 5                               | 2                   | 2           | 303            | 150                    | Langmuir       | 30% at third cycle        | 4.42           | Jadhav and Jadhav (2021)  |
| Peanut shell biochar              | 10                             | 8                   | 7           | 298            | 120                    | Langmuir       | —                        | 3.66           | Kumar et al. (2020)       |
| Rhodophyta biochar                | 15                             | 0.6                 | 6           | 303            | 90                     | Freundlich     | 80% at fifth cycle        | 2.10           | Naga Babu et al. (2020)   |
| Rice husk biochar                 | 4                               | 5                   | 6           | 303            | 360                    | Langmuir       | —                        | 1.86           | Yadav and Jagadevan (2020) |
| Activated sugarcane ash           | 5                               | 2                   | 2           | 303            | 100                    | Langmuir       | —                        | 10.99          | Mondal et al. (2016)      |
| KOH-treated jamun seed            | 10                             | 0.4                 | 2.5         | 298            | 120                    | D-R            | —                        | 3.65           | Araga et al. (2017)       |
| KOH-treated activated carbon      | 5                               | 3                   | 4           | 303            | 100                    | Langmuir       | —                        | 2.52           | Bhomick et al. (2019)     |
| Activated carbon                  | 380                            | 2                   | 3           | 298            | —                      | —              | 50% at fifth cycle        | 1.15           | Chen et al. (2019)        |
| Coconut-shell carbon              | 4.4                             | 10                  | 2           | 323            | 180                    | Langmuir       | —                        | 0.36           | Anag et al. (2019)        |
| Chicken bone biochar              | 10                             | —                   | —           | 298            | 1,440                  | Langmuir       | —                        | 11.20          | Herath et al. (2018)      |

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capacity in comparison (Raghav and Kumar 2019). SA and pectin hydrogels accomplish adsorption by exchanging hydroxyl groups in the structure with fluoride.

### 2.3 Carbon-Based Adsorbents

Carbon-based adsorbents have developed pore structures, large specific surface areas, stable chemical properties, easily adjustable surface properties, good regenerability, and widely available and general waste, which is of low cost with promising applications.

#### 2.3.1 Biochar

Biochar (BC) is made from waste biomass from a wide range of sources such as reed (Singh and Majumder 2018), rice husks (Yadav and Jagadevan 2020), straw (Angelin et al., 2021), teak peel, and algae. BC is a carbon-rich, fine-grained, porous, and highly aromatized material and well suited as an adsorbent for the resource utilization of waste. BC contains lignocellulosic components capable of effectively adsorbing fluoride (Yadav and Jagadevan 2020). The pyrolysis temperature is a key factor in controlling the number of functional groups on the surface of BC (Wang et al., 2021). Generally, biochar prepared by hydrothermal pyrolysis below 573 K is rich in oxygen-containing functional groups (-COOH, -OH, etc.) and has stronger ion exchange capacity (Naga Babu et al., 2020). As the pyrolysis temperature increases, the abundance of hydroxyl, amino, and carboxyl groups decrease and the degree of carbonation increases (Kumar et al., 2020). Biochar prepared at 673–973 K has developed porosity (Figure 3A) and thermal stability (Goswami and Kumar 2018). Brunson and Sabatini (2015) recorded a significant increase in specific surface area (from 0.9 m²/g to 327 m²/g) and surface zero charge point (from pHₚₑᵦ = 5.8 to pHₚₑᵦ = 9.4) when the pyrolysis temperature of charcoal was increased from 573 to 873 K. BC also contains minerals such as potassium, calcium, magnesium, and phosphorus, which can be complex with fluoride ions or precipitate. Lee et al. (2021) found that the biochar biochar could contain up to 56.9% CaCO₃, and when the pyrolysis temperature was raised to 1073 K, CaCO₃ was converted to Ca(OH)₂; the structure was more conducive to the adsorption of fluoride. The adsorption mechanism was outer-sphere complexation between Ca and F. Although shell biochar has low carbon content and alone has an average low adsorption effect but has the advantage of being easily modified (Wang et al., 2021).

#### 2.3.2 Activated Carbon

Activated carbon (AC) is usually made from coconut shells, hard cores, bamboo, coal, wood, and other raw materials (Collivignarelli et al., 2020), and the pyrolysis temperature is generally higher than 1173 K (Araga et al., 2019). After pyrolysis, further physical or chemical activation is required (Chen et al., 2019). Chemical activation has high activation yield but is highly corrosive to the equipment (Tomar et al., 2014). As shown in Figure 3B, AC has the advantage of high porosity and large
specific surface area. Araga et al. (2017) and Bhomick et al. (2019) used KOH to activate mustard seed activated carbon and commercially available activated carbon, respectively, and the modified specific surface area reached 747 m²/g and 1,005 m²/g, respectively. The -OH group on the AC surface is protonated with fluoride at pH < pH_{PZC} (acidic media). Numerous studies have demonstrated that fluoride adsorption on AC consists of the mechanism for the deprotonation of -OH functional groups on carbon surfaces (He et al., 2020).

2.3.3 Bone Char
Bone char is the charring product of animal bones and generally contains about 20% carbon and 80% hydroxyapatite (HAp) (Medellin-Castillo et al., 2014), with the content of each component varying slightly depending on the charring temperature. When the charring temperature is below 573 K, more organic matter remains in the bones, but the specific surface area and pore structure is not well developed (Zhou J. et al., 2019). The charring temperatures above 873 K may change the structure of the hydroxyapatite and also lead to reduction in fluoride adsorption capacity. The fluoride adsorption by bone char is reported to be mainly carried out by hydroxyapatite. Medellin-Castillo et al. (2014) found that fluoride in aqueous solutions was mainly adsorbed to HAp in bone char but not to other components. HAp in bone char contains most of the OH⁻ that can be replaced by F⁻; the adsorption mechanism includes ion exchange and chemical precipitation. The detailed mechanism of fluoride adsorption by HAp is described in the following section.

2.4 Other Types of Adsorbents
Other materials such as natural mineral clays (clay (Zhang S. et al., 2016), bentonite (Mudzielwana et al., 2017), etc), industrial solid waste (zeolite (Ghosal and Gupta 2018), etc), and hydroxyapatite are also used for fluoride adsorption. Natural clay (Figure 3C) contains the main compounds SiO₂ and Al₂O₃ and has the chemical potential to adsorb fluoride (Guiza et al., 2019). Zeolite is an aqueous skeletal structure composed of aluminosilicate minerals with the lattice of many pores and channels that have the structural potential to adsorb fluoride. However, these two types of materials usually show weak fluoride adsorption capacities (Table 2) and are generally modified by chemical activation or metal loading.

2.4.1 Hydroxyapatite
Hydroxyapatite [(Ca₁₀(PO₄)₆(OH)₂, HAp] is also a promising inorganic material for fluoride adsorption, with excellent biocompatibility, stability, and mechanical properties. Due to its unique crystal structure, HAp has a porous surface, large specific surface area, and high ion exchange capacity. The hydroxyl group in HAp is prone to rapid exchange with anion and has a strong binding capacity with fluoride (Raghav et al., 2018). F⁻ replaces OH⁻, fills in the lattice of HAp forming insoluble fluorapatite (FAp), and OH⁻ is released into solution. When high concentrations of fluoride ions are present in the solution, Ca²⁺ in HAp reacts with F⁻ forming CaF₂ precipitate, and phosphate is correspondingly released into the solution. Various forms of HAp have been reported for fluoride adsorption in water, such as nano-hydroxyapatite (Mourabet et al., 2015; Zendehdel et al., 2017), porous hydroxyapatite (Nijhawan et al., 2020), and layered hollow hydroxyapatite (Gao et al., 2019). The mechanism of fluoride adsorption by HAp mainly consists of the following: 1) electrostatic attraction by the surface of HAp to F⁻. 2) Anion exchange between OH⁻ or PO₄²⁻ and F⁻. 3) Complexation reaction of Ca²⁺ with F⁻ ligates and forms surface precipitation. 4) F⁻ can also form hydrogen bonds with OH⁻ in the HAp lattice.
| Adsorbents                  | Initial $C^-$ (mg/L) | Adsorbent dose (g/L) | Reaction pH | Temperature (K) | Equilibrium time (min) | Isotherm model | Regeneration performance | $Q_{max}$ (mg/g) | Ref                  |
|----------------------------|----------------------|----------------------|-------------|----------------|------------------------|----------------|--------------------------|-----------------|---------------------|
| Mn–Al binary metals        | 380                  | -                    | 7           | 298            | 720                    | Langmuir       | -                        | 94.83           | Wu et al. (2017a)   |
| Ce–Zn binary metals        | 10                   | 0.15                 | 3–7         | 298            | 45                     | Langmuir       | 68% at sixth cycle       | 64.66           | Dhillon et al. (2017) |
| Ce–Ti oxide                | 10                   | 1                    | 7           | 298            | -                      | Langmuir       | -                        | 44.37           | Abo Markeb et al. (2017) |
| Mg/Fe-LDHs                 | 30                   | 4                    | 7           | 298            | 150                    | Langmuir       | —                        | 28.65           | Wu et al. (2015)    |
| Fe-La                      | 10                   | 1                    | 6           | 298            | 60                     | Langmuir       | —                        | 27.42           | Wang et al. (2018c)  |
| La/MA                      | 10                   | 2                    | 6           | 298            | 360                    | Sips           | 70% at fifth cycle       | 26.45           | He et al. (2019)     |
| Fe–Ag magnetic oxide       | 10                   | 0.5                  | 3           | 298            | 20                     | Langmuir       | 85% at sixth cycle       | 20.57           | Azari et al. (2015)  |
| La-modifying               | 5                    | 10                   | 7.4         | 303            | 600                    | Langmuir       | —                        | 1.51            | García-Sánchez et al. (2016) |
| Fe$_2$O$_3$                 | 5                    | -                    | 6.6         | 303            | 600                    | Langmuir       | —                        | 1.42            | García-Sánchez et al. (2016) |
| Ce–Mg-Zr oxide             | 100                  | 0.5                  | 7           | 298            | 160                    | Freundlich     | 70% at fifth cycle       | 370.37          | Wang et al. (2022)  |
| Ce–Ti@Fe$_2$O$_3$          | 10                   | 1                    | 7           | 298            | 15                     | Langmuir       | 93% at fifth cycle       | 91.04           | Abo Markeb et al. (2017) |
| Fe$_2$O$_3$@La-Ce          | 10                   | 0.5                  | 4           | 303            | 60                     | Freundlich     | —                        | 56.80           | Han et al. (2019)   |
| Fe$_2$O$_3$@Fe-Ti          | 4                    | 1                    | 7           | 298            | 2                      | Freundlich     | 77% at ninth cycle       | 41.80           | Zhang et al. (2016a) |
| Fe-Mg-La                   | 10                   | 0.1                  | 7           | 298            | 300                    | Langmuir       | 90% at third cycle       | 185.90          | Yu et al. (2015)     |
| Al-Zr-La                   | 200                  | 0.5                  | 3           | 308            | 500                    | Langmuir       | —                        | 90.48           | Zhou et al. (2018)  |
| Mg/Fe-La                   | 5                    | 0.5                  | 7           | 308            | 100                    | Langmuir       | 57% at fifth cycle       | 59.34           | Wu et al. (2017b)   |
| Fe-Mg-La                   | 20                   | 1                    | 7           | 298            | 360                    | Langmuir       | —                        | 40.40           | Chen et al. (2018)  |
| Al-F-Fe LDH                | 2                    | 1.5                  | 6           | 298            | 600                    | Sips           | 70% at fifth cycle       | 20.00           | Hongtao et al. (2018) |
| Fe-Al-Ce-Ni                | 10                   | 0.4                  | 5           | 303            | 50                     | Freundlich     | 50% at sixth cycle       | 250.00          | Raghav and Kumar (2018) |
| SA-Cal@Fe/                 | 10                   | 30                   | 5           | 303            | 30                     | Freundlich     | 55% at fifth cycle       | 333.00          | Sapna et al. (2018) |
| La/Ni                      | 10                   | 0.4                  | 7           | 318            | 90                     | Freundlich     | 86% at fifth cycle       | 285.00          | Raghav and Kumar (2019) |
| Alginate-Fe/Al/            | 10                   | 0.4                  | 7           | 298            | 90                     | Langmuir       | 84% at fifth cycle       | 200.00          | Raghav and Kumar (2019) |
| SA/pectin-Fe/Al/           | 60                   | 0.1                  | 7           | 298            | 35                     | Halsey         | 65% at ninth cycle       | 142.90          | Raghav et al. (2019) |
| SA/CMC-Ca-Al               | 40                   | -                    | 2           | 298            | 600                    | Langmuir       | —                        | 101.40          | Wu et al. (2016b)   |
| SA-Mg/Fe oxide             | 10                   | 10                   | 7           | 298            | 600                    | Langmuir       | 80% at third cycle       | 32.31           | Wu et al. (2017c)   |
| SA-Mg/Al/2r                | 40                   | 2.5                  | 6           | 303            | 1800                   | Langmuir       | —                        | 31.72           | Wang et al. (2017a) |
| SA-Mg/Al/Fe                 | 40                   | 5                    | 6           | 303            | 3,600                  | Freundlich     | 65% at third cycle       | 26.12           | Wang et al. (2018a) |
| Pectin Fe bead             | 10                   | 2                    | 5           | 298            | 600                    | Freundlich     | —                        | 20.00           | Sharma et al. (2019) |
| CS-Ce                      | 30                   | 0.3                  | 3           | 293            | 400                    | Freundlich     | 80% at fourth cycle      | 153.00          | Zhu et al. (2017)   |
| Fe$_2$O$_3$/CS/Al(OH)$_3$  | 10                   | 0.1                  | 5           | 298            | 60                     | Langmuir       | —                        | 76.63           | Hu et al. (2018)    |
| Fe-Al-Mn@CS                | 6                    | 0.5                  | 7           | 298            | 160                    | Langmuir       | —                        | 40.50           | Chaudhary et al. (2021) |
| Rare earth CS bead         | 10                   | 2                    | 5           | 298            | 480                    | Freundlich     | 70% at seventh cycle     | 22.35           | Liang et al. (2018) |
| La–magnetic CS             | 10                   | 2                    | 5           | 298            | 480                    | Langmuir       | 40% at seventh cycle     | 20.53           | —                   |
| Zr–CS bead                 | 20                   | 1                    | 7           | 303            | 80                     | Freundlich     | —                        | 17.47           | Prabhu and Meenakshi (2015) |
| La–CS bead                 | 20                   | 1                    | 7           | 303            | 80                     | Freundlich     | —                        | 14.49           | —                   |
| Ce–CS bead                 | 20                   | 1                    | 7           | 303            | 60                     | Freundlich     | —                        | 11.50           | —                   |
| Al–CS bead                 | 20                   | 1                    | 7           | 303            | 60                     | Freundlich     | —                        | 7.45            | —                   |
| Fe$_2$O$_3$@TiO$_2$-CS     | 2                    | 0.4                  | 5           | 298            | 30                     | Langmuir       | 75% at sixth cycle       | 14.62           | Sadeghi et al. (2019) |
| Fe$_2$O$_3$-CS             | 5                    | 1                    | 7           | 293            | 60                     | Freundlich     | 88% at fifth cycle       | 9.26            | Mohseni-Bandpi et al. (2018) |

(Continued on following page)
synthesis of metal modifications to other types of adsorbents accounts for the majority.

### 3.1 Multi-Metal Oxide/Hydroxide Adsorbents

Different metal oxide adsorbents have their individual strengths and weaknesses for fluoride removal, so recently there have been research studies using multi-metal oxide/hydroxide adsorbents (Chen et al., 2018). Compared to conventional metal oxides, various valence cations are often present in one multi-metal oxide, providing more chemisorption sites (Raghav and Kumar, 2018). The tunability of the chemistry of each element ensures an abundance of active sites, and the components can be adjusted to each other, possessing different outstanding properties and therefore having unique quantum coupling effect and synergistic effects, resulting in more than doubling or tripling of the adsorption capacity. There are two common types of multi-metal oxide adsorbents. One is prepared by compounding each metal element in a certain ratio (Wu K. et al., 2017) such as layered double/triple hydroxides (Wu P. et al., 2017), and the other is to modify one metal oxide with others; the ones mostly reported are modified alumina (He et al., 2019) or magnetic iron oxides.

#### 3.1.1 Layered Double/Triple Hydroxides

A series of layered double/triple hydroxides (LDHs) have a high affinity for anions with high ion exchange capacity and high adsorption volume, which are often used as anion exchangers and trapping agents. LDHs are two-dimensional layered materials whose structural formula can be expressed as \([M_{1-x}M_x(OH)_2]^{3+}(A^{n-})_{\text{inter}} \cdot mH_2O\), where \(M^{2+}\) is the positive divalent metal ion (\(\text{Mg}^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}\), etc.), \(M^{3+}\) is the positive trivalent metal ion (\(\text{Fe}^{3+}, \text{Al}^{3+}, \text{La}^{3+}, \text{Ce}^{3+}\), etc.), and \(A\) is the interlayer anion (\(\text{Cl}^-, \text{CO}_3^{2-}, \text{NO}_3^-, \text{etc.}\). LDH consists of positively charged main lamellae and negatively charged interlayer ions. The lamellar structure of LDH is longitudinally stable (Wu et al., 2015). This lamellar structure facilitates adequate contact between the metal sites and the fluoride ions during adsorption and accelerates the charge transfer at the interface. The surface of the main layer is rich in hydroxyl functional groups, which bind to cations in different ways such as electrostatic gravitational forces and hydrogen bonding, providing a large anion exchange capacity with fluoride ions. The synthesis of triple hydroxide by doping of layered double hydroxide with high-valent metal cations has been shown to be effective in enhancing its adsorption activity. When the highly valent cation \(M^{3+}\) replaces \(M^{2+}\), the main lamellae are positively charged and therefore require the interlayer anions to be negatively charged to balance the overall charge (Hongtao et al., 2019).

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| Adsorbents                  | Adsorption condition | Isotherm model | Regeneration performance | \(Q_{\text{max}}\) (mg/g) | Ref            |
|-----------------------------|----------------------|----------------|--------------------------|-----------------------------|----------------|
| La-CS/β cyclodextrin        | 10                   | 2              | 7                        | 303                         | 30             | Freundlich     |
|                             |                      |                |                          | 56% at fifth cycle          | 8.14           | Preethi and Meenakshi (2018) |
| Ce-cellulose nanobead       | 2.5                  | 1              | 3                        | 303                         | 50             | Langmuir       |
| CMKGM-La-Al                 | 40                   | 2              | 2                        | 40                          | 120            | Langmuir       |

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**FIGURE 5** | Schematic principle (A) and fluoride adsorption mechanism (B) of multi-metal–modified sodium alginate and pectin (Raghav et al., 2019).
TABLE 4 | Summary of modification methods, characteristics, and adsorption mechanisms of multi-metal and metal-biopolymer composite adsorbents.

| Adsorbents                  | Modification method                        | Dimension | SBET (m²/G) | Aperture (nm) | pHpzc | Adsorption mechanism                      | Ref                        |
|-----------------------------|-------------------------------------------|-----------|-------------|---------------|-------|-------------------------------------------|---------------------------|
| Mn–Al binary metals         | Oxidation and coprecipitation             | —         | 43          | 0.33          | 8.7   | Surface complexation                      | Wu et al. (2017a)          |
| Ce–Zn binary metals         | Coprecipitation, calcination at 873 K     | 22.4 nm   | 499         | 15            | 6     | Ion exchange                              | Dhillon et al. (2017)     |
| Ce–Ti oxide                 | Coprecipitation                           | 1–2 nm    | —           | —             | —     | Ion exchange                              | Abo Markeb et al. (2017)  |
| Mg/Fe-LDHs                  | Coprecipitation, hydrothermal at 543 K    | 100 nm    | —           | —             | 10.42 | Ion exchange                              | Wu et al. (2015)           |
| Fe-La                       | Coprecipitation, hydrothermal at 423 K    | —         | 113         | 21.78         | 8.5   | Ion exchange                              | Wang et al. (2018c)       |
| La/MA                       | Impregnation, calcination at 673 K        | —         | 237         | 4.81          | 10.2  | Electrostatic attraction, chemisorption   | He et al. (2019)           |
| Fe–Ag magnetic oxide        | Coprecipitation                           | 5 nm      | 254         | 0.13          | 6.03  | Ion exchange                              | Azari et al. (2015)       |
| La-modifying Fe3O4          | Coprecipitation, calcination at 873 K     | 22.4 nm   | 499         | 15            | 6     | Ion exchange                              | Abo Markeb et al. (2017)  |
| Al-modifying Fe3O4          | Coprecipitation, calcination at 873 K     | 22.4 nm   | 499         | 15            | 6     | Ion exchange                              | Abo Markeb et al. (2017)  |
| Ca-Mg-Zr oxide              | Hydrothermal, calcination at 923 K        | —         | 119         | 14.03         | 11.5  | Electrostatic attraction, ion exchange    | Wang et al. (2022)        |
| Ce-Ti@Fe3O4                 | Coprecipitation                           | 15 nm     | —           | —             | —     | —                                         | —                         |
| Fe3O4@La-Ce                 | Coprecipitation                           | —         | 40          | 20.3          | 6     | Ligand exchange, electrostatic attraction | Han et al. (2019)         |
| Fe3O4@Fe-Ti                 | Precipitation of Fe3O4@Fe-Ti, granulation | 10 μm     | 99          | 15.3          | —     | Ion exchange                              | Zhang et al. (2016a)      |
| Fe-Mg-La                    | Coprecipitation                           | 40 μm     | —           | —             | 6.3   | Ion exchange                              | Yu et al. (2015)          |
| Al–Zr-La                    | Coprecipitation                           | —         | 36          | 8.4           |      | Electrostatic attraction, ion exchange    | Zhou et al. (2018)        |
| Mg/Fe/La                    | Hydrothermal, calcination at 873 K        | —         | 59          | 22.3          | —     | Electrostatic attraction, ion exchange    | Wu et al. (2017b)         |
| Fe-Mg-La                    | Coprecipitation                           | 65 nm     | 78          | 30            | 8.8   | Ligand exchange, electrostatic attraction | Chen et al. (2018)        |
| Mg-Al-Fe LDH                | Coprecipitation                           | —         | 130         | 24.47         |      | Electrostatic attraction, ion exchange    | Hongt ao et al. (2018)    |
| Fe-Al-Ce-Ni                 | Coprecipitation, calcination at 873 K     | —         | 184         | 51.43         | 6.2   | Electrostatic attraction, ion exchange    | Raghav and Kumar (2018)   |
| SA-Ca@Fe/La/Ni              | Fe-La-Ni oxides mixing SA, CaC2 cross-linking | 1–2 mm | 257         | 10.4          | 7     | Ion exchange, H-bonding                   | Sapna et al. (2018)       |
| Pectin-Fe/Ai/Ni             | Aerogel formation by coprecipitation, freezing | 886 nm | 275         | 0.15          |      | Isomorphic substitution                   | Raghav and Kumar (2019)   |
| Alginate-Fe/Ai/Ni           | Aerogel formation by coprecipitation, freezing | 914 nm | 96          | 0.13          |      | Isomorphic substitution                   | Raghav and Kumar (2019)   |
| SA/pectin-Fe/A/Al/Ce        | Fe-Al-Ce coprecipitation with pectin and alginate | —       | 275         | 7.17          |      | Isoharmic substitution, complexation       | Raghav et al. (2019)      |
| SA/CMC-Ca-Al               | SA/CMC mixing, Ca2+ cross-linking, Al3+ soaking | 2–2 mm | —           | —             |      | Coordination reaction                     | Wu et al. (2016b)         |
| SA-Mg/Fe oxide              | Mg/Fe oxide mixing SA, CaC2 cross-linking | 1 mm      | —           | —             | 10.52 | Ligand exchange, electrostatic attraction | Wu et al. (2017c)         |
| SA-Mg/Ai/Zr                 | Mg-Al-Zr oxide mixing SA, CaC2 cross-linking | 1 mm     | —           | —             |      | Ion exchange, electrostatic attraction    | Wang et al. (2017a)       |
| SA-Mg/Ai/Al/Ce              | Mg-Al oxide mixing SA, CaC2 cross-linking  | —         | —           | —             |      | Ion exchange                              | Wang et al. (2018a)       |
| Pectin Fe bead              | Grafting, FeCl3 impregnation              | 43 nm     | —           | —             | —     | Ligand exchange                           | Sharma et al. (2019)      |
| CS-Ce                       | Coprecipitation, glutaraldehyde cross-linking | 200 nm | 17          | 5.3           |      | Electrostatic attraction, ligand exchange | Zhu et al. (2017)         |
| Fe3O4/CS/AI(OH)3            | FeCl3 mixing, Fe3O4 NP adding             | 200 nm    | —           | —             | —     | Electrostatic attraction, ligand exchange | Hu et al. (2018)          |
| Fe-Al-Mn@CS                | Coprecipitation                           | —         | 42          | —             | —     | Electrostatic attraction, ligand exchange | Chaudhary et al. (2021)   |
| Rare earth CS bead          | Rare earth mixing, Fe3O4 adding, cross-linking | —       | 21          | 7.92          | 5     | Ligand exchange                           | Liang et al. (2018)       |
| La3+ magnetic CS           | La mixing, Fe3O4 adding, cross-linking     | —         | 17          | 8.15          | 5     | Ligand exchange                           | —                         |

(Continued on following page)
The addition of rare earth metals has been reported to further enhance the affinity for fluoride. Wu et al. (2017) introduced La into Mg/Fe LDH to form Mg/Fe/La hydrotalcite-like compounds with layered porous structure, which significantly enhanced the fluoride adsorption capacity of Mg/Fe LDH.

3.1.2 Metal-Modified Magnetic Iron Oxides
Al- and Fe-based oxides are mostly doped or load-modified by another metal. Metal-modified Al₂O₃ generally absorbs fluoride by complexation and ion exchange (Figure 4A). Iron oxides (Fe₂O₃ or γ-Fe₂O₃), in addition to adsorption advantages, provide strong magnetic properties and large magnetic response with easy separability and controllability; thus, there have been more reported recently. Magnetic iron oxide nanoparticles can be used directly for fluoride adsorption or as a nucleus material for core-shell particles. The magnetic core particles are generally combined with metal oxide nano-shells by methods such as surface coating to ensure stronger magnetic response, more functional groups, and better properties (Zhang C. et al., 2018). Recent research has mostly used rare earth metals to modify magnetite. Rare earth ions are greater in radius than other elements in the iron oxides; doping with the appropriate amount of rare earth elements can replace some of the other elements in the iron oxides with a smaller ion radius, disturb the lattice and can improve the physical activity. Most importantly, the hard Lewis acid nature of the rare earth metal ions (especially La) has a strong affinity for fluoride (Figure 4B) (Han et al., 2019). Ce can promote the dispersion of nanoparticles, giving the adsorbent a larger specific surface area, pore volume, and more active functional sites. Correspondingly, magnetic particles can attenuate the agglomeration effect of rare earth metal oxides, reducing the amount of precious metals used and improving the separation characteristics by magnetic assistance to reduce residues in water and avoid rare earth metal toxicity (Abo Markeb et al., 2017). Han et al. (2019) used VSM tests to show that Fe₃O₄ and Fe₃O₄@La-Ce were both superparamagnetic, and it was easy to separate the particles from the solution using the external magnetic field. The adsorption amount of Fe₃O₄@La-Ce was increased up to 20 times compared to Fe₃O₄.

3.2 Metal-Biopolymer Adsorbents
Large-scale applications for fluoride removal in aqueous systems require the development of composite hydrogel materials with good mechanical properties and stability. For hydrogels with poor adsorption properties, the cross-linking of composites by cementing other high performance adsorbent materials onto biopolymers can effectively reduce the degradation of properties. The preparation of biopolymer-based composites is divided into three types: 1) doping of metals/metal oxides (Sapna et al., 2018), 2) blending with inorganic materials (Wang et al., 2020), and 3) mixing between polymeric organic substances (Preethi and Meenakshi 2018). This section summarizes the doping by metal oxide modification studies.

3.2.1 Metal-Doped Alginate/Pectin
The biocompatibility and biodegradability of natural polymeric materials make sodium alginate and pectin effective substrates for the incorporation of multivalent metal ions. Studies have reported to dope SA with metals; co-mingling and cross-linking to form a stable gel structure can improve both the stability and mechanical properties of SA (Wu T. et al., 2017), while having an anchoring effect on metal oxides, reducing the agglomeration and leaching of metal oxides and maximizing the adsorption properties (He et al., 2020). Furthermore, the doping of metals can increase the metal active sites in the porous structure and combine the properties of organic and inorganic components to improve the adsorption capacity (Zhao et al., 2021). Mono and multi-metal doping options are available. Recent research has focused on the doping of sodium alginate and pectin with multi-metals. Compared to monometals, the multi-metals provide an enhanced abundance of active sites as mentioned earlier. In addition, the multi-metals used in the studies tend to be the composite of +2 valent and higher valent cations. The addition of +3 and +4 valent metal ions, especially rare earth metals, can improve the stability, recyclability, and adsorption capacity. Raghav and Kumar (2019) obtained a high adsorption capacity (Table 3) for all the composite hydrogels prepared by SA and pectin embedding Fe-Al-Ni (285 mg/g and 200 mg/g) and SA/pectin co-embedding Fe-Al-Ce (142.9 mg/g) (Raghav et al., 2019). Figure 5 shows the
reaction process of multi-metal–modified SA and pectin and the exchange sites for fluoride adsorption.

### 3.2.2 Metal-Doped Chitosan

Chitosan (CS) is an N-deacetylated derivative of the natural polysaccharide chitin and is rich in free amino acids. The -NH₂ group in chitosan is more reactive (Zhu et al., 2017), easy to be chemically modified (Chaudhary et al., 2021), and exhibits high adsorption potential. Despite the numerous advantages such as biodegradability, biocompatibility, flexibility, hydrophilicity, and versatility, CS tends to be readily soluble in acidic solutions and has a weak chemical resistance.

| Adsorbents | Modification method | Dimension | S_BET (m²/G) | Aperture (nm) | pH_Pzc | Adsorption mechanism | Ref |
|------------|---------------------|-----------|--------------|--------------|--------|----------------------|-----|
| Wood biochar-La | Impregnation, pyrolysis | 0.8 mm | 165 | 3.91 | 6.6 | Ion exchange | Habibi et al. (2019) |
| Al-modified corn biochar | Pyrolysis at 623 K, calcination | — | 1 | 410 | 2 | Ion exchange | Zhang et al. (2021a) |
| MgO shell biochar | Impregnation, one-step calcination | 0.5 μm | 182 | 2–10 | — | Electrostatic attraction, complexation | Wan et al. (2019) |
| Pomelo peel BC-La | Impregnation, calcination at 1073 K | — | 269 | — | 5.8 | Ion exchange | Wang et al. (2018b) |
| ZrO₂-seed shell biochar | One-step impregnation and calcination T | — | — | — | 4.45 | Ion exchange | Mei et al. (2020) |
| Magnetic biochar | Charring, impregnation-pyrolysis | 100 μm | 494 | 0.3 | 11 | Electrostatic attraction, H-bonding | Bombuwalu Dewage et al. (2018) |
| Mg-Mn-Zr AC | Ultrasound impregnation, coprecipitation | — | 834 | 2.43 | 11.9 | Electrostatic attraction, ion exchange | Mullick and Neogi (2019) |
| Zr-impregnated AC | Ultrasonic impregnation | 14 μm | 1,104 | 2.30 | 5.03 | Electrostatic attraction, ligand exchange, electrostatic attraction | Mullick and Neogi (2018) |
| La-functionalized AC | Impregnation, rotary evaporation, heat | 0.5 mm | 367 | 0.68 | 7.3 | Ion exchange, physical adsorption | Mohanta and Ahmaruzzaman (2018) |
| Activated carbon@SnO₂ | Ultrasound impregnation, precipitation | — | 126 | 3.54 | 3 | Ion exchange, physical adsorption | Zühiga-Muro et al. (2017) |
| Ce-containing bone biochar | Impregnation, heat treatment | 0.7 mm | — | — | — | Electrostatic attraction, ion exchange | Zhou et al. (2019a) |
| Magnetic bone biochar | Impregnated biomass, calcination | — | 42 | 17.45 | 2.4 | Ion exchange | Zheng et al. (2019b) |
| Graphene oxide with Ti | Hydrothermal at 453 K, calcination | — | 278 | 2.55 | 7 | Electrostatic attraction, ion exchange | Nehra et al. (2019) |
| Al-polyacrylic acid | Impregnation | — | 44 | 84.63 | 6 | Electrostatic attraction, ion exchange | Xu et al. (2017) |
| CeO₂@SiO₂ microsphere | Coprecipitation | 117 μm | 86 | 25–97 | 3.9 | Electrostatic attraction, ion exchange, chemisorption | Wang et al. (2019a) |
| Magnetic γ-Fe₂O₃–GO-La | Fe coprecipitation, La impregnation, calcination | — | — | — | 7.9 | Ion exchange, complexation | Wen et al. (2015) |
| Zn-modifying slag | Impregnation | 0.1 mm | 58 | — | 7.9 | Ion exchange, ligand exchange, electrostatic attraction | Sarkar et al. (2019) |
| ZrO₂-graphene oxide | One-step ultrasound hydrothermal impregnation | — | 632 | — | 7.3 | Ion exchange, physical adsorption | Mohan et al. (2016) |
| Hydrous Fe/Al GO | Coprecipitation, impregnation | 200 μm | — | — | 6 | Electrostatic attraction, ion exchange | Kanrar et al. (2016) |
| Fe-modifying pumice | Impregnation | 200 μm | 25 | — | 3 | — | Dehghani et al. (2016) |
| FeOOH–graphene oxide | In-situ hydrolysis | — | 203 | 7.1 | 1.8 | Ion exchange | Kuang et al. (2017) |
| Aluminum/olivine | Wet impregnation, calcination | — | — | — | — | Physical adsorption | Ghosal and Gupta (2018) |
| Polyhydroxy-iron | Impregnation | — | 100 | — | 8 | — | Muschin et al. (2021) |
| 3D Y-GO hydrogels | GO-mixing SA, YO₂ cross-linking | — | 147 | 15.26 | 6.74 | Ion exchange | He et al. (2018) |
| A2CO₃-chitosan biochar | HBO₂ cross-linking, calcination | — | — | — | 6 | Ion exchange | Jiang et al. (2018) |
| Graphene oxide/eggshell | Impregnation | — | — | — | — | — | Nor et al. (2020) |
| Ce-SA/BC beads | SA/BC mixing, CeO₂ cross-linking, calcination | 2 mm | 237 | 3.97 | 8.26 | Ion exchange, electrostatic attraction | Wei et al. (2022) |
| Ca-pectin-hydroxyapatite | Coprecipitation | — | 157 | 3.1 | 7 | Ion exchange, electrostatic attraction | Raghav et al. (2018) |
| Polypropylene onto BC | Mixing, FeCl₃ impregnation | — | — | — | 8.6 | Ion exchange | Wang et al. (2017c) |
Carbon-based adsorbents have the advantage of large specific surface area and rich pore structure (Shang et al., 2022), but they have low adsorption capacity for fluoride removal alone and require some modification. Research on carbon composites has focused on the doping of carbon with nanoparticles (Cai et al., 2022). More individual metal loadings are used, and multi-metal modifications are also available. More active sites enhance the adsorption performance, and the modified adsorbent surface is richer in specific types of adsorption sites, which may further increase the adsorption capacity.

### 3.3.1 Metal-Modified Biochar

The ability of biochar to remove pollutants is greatly influenced by the nature of the raw material, preparation technology, and pyrolysis conditions. Unsuitable pyrolysis conditions tend to under-carbonize or over-carbonize BC, so the adsorption performance of unmodified BC is limited. The raw biochar has a relatively poor adsorption effect on anions as the negative charge occupies the majority of the functional groups (Mei et al., 2020). Highly valent metal cations can provide sufficient positive charge to effectively alter surface physicochemical properties (Wang et al., 2019c). AlCl₃ has been reported to generally increase the anion exchange capacity in all BC. Brunson and Sabatini (2015) studied the changes in charcoal surface area and surface chemistry following aluminum nitrate impregnation and found that the aluminum modification reduced the zero charge point of the charcoal in water (from pHₚＺＣ = 9.6 to pHₚＺＣ = 5.7) but significantly increased the adsorption capacity. Rare earth metal ions such as Ce³⁺, Zr⁴⁺, and La³⁺ are more alkaline, have a relatively low ionic potential, and show strong tendency to dissociate hydroxyl groups into ions. The possibility of ionic exchange with F⁻ is higher and the affinity is stronger. Habibi et al. (2019) modified woody BC with LaCl₃ and showed that the maximum adsorption capacity of 164.23 mg/g and adsorption equilibrium could be reached within 30 min. They concluded that H⁺ in functional groups such as carboxyl and sulfate groups on the surface of BC may exchange with La³⁺ ions. The presence of La³⁺ increased the adsorption mechanism with Lewis acid-base interaction and ion exchange. The F⁻ adsorption rate of the adsorbent was still 80% at fifth recycling, indicating that the rare earth metals loaded on the BC are not easily leached. The modification of iron oxides can confer magnetic properties to BC, improving the separation and recovery performance. BC has good electrical conductivity, which is conducive to electron transfer and reduction of Fe³⁺. The stronger synergistic effect can further promote the fluoride adsorption performance (Wang et al., 2019c).

### 3.3.2 Metal-Modified Activated Carbon

Activated carbon has large specific surface area and pores, which can act as carriers and dispersants to avoid agglomeration of the metal nanoparticles (Cai et al., 2022). More individual metal loadings are used, and multi-metal modifications are also available. More active sites enhance the adsorption performance, and the modified adsorbent surface is richer in specific types of adsorption sites, which may further increase the adsorption capacity. Li et al. (2018) precipitated Ti(OH)₃ on the surface of AC, which further increased the specific surface area of Ti-AC to 1700 m²/g, providing more adsorption sites for fluoride ions. They confirmed that the adsorption capacity of Ti-AC was
produced by Ti(OH)$_4$ loaded on AC. The saturation adsorption capacity of Ti(OH)$_4$ in Ti-AC was 62.1 mg/g, which was much higher than that of Ti(OH)$_4$. It has also been reported that the loading of different metal oxides/hydroxides can form new functional groups on the AC surface with high affinity for fluoride adsorption, significantly improving the adsorption efficiency. A et al. used ultrasonically assisted polymetallic impregnation of AC (Mohanta and Ahmaruzzaman 2018; Mullick and Neogi 2018). The specific surface area decreased after modification, but the pH$_{pzc}$ increased to 11.9 and the adsorption capacity increased by four times compared to monometallic impregnation (Mullick and Neogi 2019).

3.3.3 Metal—Other Types of Adsorbents
Graphene oxide (GO) is a two-dimensional honeycomb carbon nanomaterial formed by the close packing of carbon atoms in a sp-hybridization pattern (Kanrar et al., 2016). GO carries various functional oxygen-containing groups (such as -OH, -COOH, C=O, and -CH(O)CH-) and provides active sites to connect to other substances (Jeyaseelan et al., 2021). GO generally adsorbs fluoride through electrostatic attraction, π-π stacking, and hydrogen bonding. It has been reported to have a huge theoretical specific surface area (up to 2,630 m$^2$/g) (Mohan et al., 2017) and can be an excellent host for metal nanoparticles. In turn, nanometallic particles provide structural rigidity by inhibiting the restacking of different layers of GO and provide a higher surface area and many active centers (Mohanty et al., 2017). Mohan et al. (2017) hydrothermally synthesized ZrO$_2$/GO with $S_{BET} = 632$ m$^2$/g. The fixed-bed continuous flow experiments showed that the desorption elution efficiency of the adsorption column regenerated with 10% NaOH solution was greater than 95% for $F^-$ within three cycles, indicating the role of the ion exchange mechanism in the adsorption of $F^-$. Nehra et al. (2019) hydrothermally synthesized TiO$_2$/GO with a maximum fluoride adsorption capacity of 342 mg/g, which is the highest reported capacity available. Ti$^{4+}$ forms strong bonds with the oxygen-containing functional groups of GO by electrostatic attraction and reacts with NaOH on the GO side to form basic titanium hydroxide on the GO layer. The adsorption mechanism for fluoride consists of a complexion reaction with Ti and F and an ion exchange between OH$^-$ and $F^-$. 

3.4 Multiple Types of Metal-Modified Composite Adsorbents
Studies have also reported on composite adsorbents synthesized from three or more types of materials, with combinations of metal-modified biopolymers and inorganic materials making up the bulk of the adsorbents (Table 5). The compound of metallic, inorganic, and biomaterials effectively combine the advantages of different types and can yield further synergistic effects. He et al. (2018) achieved a maximum adsorption capacity of 288.96 mg/g for yttrium-based GO/SA hydrogels prepared by sol–gel. Wei et al. (2022) mixed reed biomass powder with SA, cross-linked with CeCl$_3$ solution, and then calcined to obtain cerium alginate biochar beads. The composite adsorbent RBM-Ce has greatly

![FIGURE 7](Nehra et al., 2019.)

![FIGURE 8](Preparation of magnetic biochar by impregnation and subsequent calcination (Bombuwala Dewage et al., 2018).)
improved the maximum adsorption capacity, $S_{BET}$, pH$_{PZC}$, and stability compared to individual components.

### 3.5 Modified Synthesis Methods

In summary of the aforementioned composite adsorbent synthesis methods (Tables 4, 5), it can be seen that the general principle of metal-modifying adsorbents is to coat the opposing surface with metal salts. The main methods of modification are chemical coprecipitation, impregnation, and hydrothermal methods, which are described here.

#### 3.5.1 Chemical Coprecipitation

Chemical coprecipitation is a common method for the preparation of multi-metals (Table 4) and metal-modified inorganic adsorbents (Table 5). In the preparation of multi-metal nanoparticles, the chemical coprecipitation method first mixes each metal salt solution in proportion to the atoms of the target product to be prepared to form an aqueous solution of the metal ions. The metal ions are then simultaneously precipitated out of the solution by the addition of appropriate precipitants to form hydroxide precipitate (Wu et al., 2013). The precipitates are separated out and then dried or calcined to obtain powdered multi-metal hydroxide/oxide nanoparticle adsorbents (Zhou et al., 2018). When modifying inorganic adsorbents with metals, the inorganic material is first put into a metal salt solution via methods such as adjusting the pH of the solution; the metal ions in the solution are induced to produce nano-metal particles that precipitate and load onto the surface and pore paths of the inorganic material, which are then dried or calcined to form composite adsorbents (Zhou et al., 2018). When modifying inorganic adsorbents with metals, the inorganic material is first put into a metal salt solution via methods such as adjusting the pH of the solution; the metal ions in the solution are induced to produce nano-metal particles that precipitate and load onto the surface and pore paths of the inorganic material, which are then dried or calcined to form composite adsorbents (Zhou et al., 2018). When modifying inorganic adsorbents with metals, the inorganic material is first put into a metal salt solution via methods such as adjusting the pH of the solution; the metal ions in the solution are induced to produce nano-metal particles that precipitate and load onto the surface and pore paths of the inorganic material, which are then dried or calcined to form composite adsorbents (Zhou et al., 2018). When modifying inorganic adsorbents with metals, the inorganic material is first put into a metal salt solution via methods such as adjusting the pH of the solution; the metal ions in the solution are induced to produce nano-metal particles that precipitate and load onto the surface and pore paths of the inorganic material, which are then dried or calcined to form composite adsorbents (Zhou et al., 2018). When modifying inorganic adsorbents with metals, the inorganic material is first put into a metal salt solution via methods such as adjusting the pH of the solution; the metal ions in the solution are induced to produce nano-metal particles that precipitate and load onto the surface and pore paths of the inorganic material, which are then dried or calcined to form composite adsorbents (Zhou et al., 2018).

#### 3.5.2 Hydrothermal

The hydrothermal method is also commonly used for the preparation of multi-metals (Table 4), and some studies have also been used for the modification of other materials by metals. Similarly, the metal ions are first prepared in a mixed solution in a certain proportion and then placed in a hydrothermal reactor at 423–573 K for a specific time. The principle of the hydrothermal method is that in a closed reaction environment, the precursor undergoes high temperature and pressure to fully dissolve in the solvent (Nehra et al., 2019). Then hydrolysis and nucleation according to a certain crystallization mode to grow nano-microcrystalline particles, to obtain a uniform particle size and good dispersion of composite powder (Figure 7). The nanomaterials prepared by the hydrothermal method have homogeneous morphology and the products are well dispersed. However, high pressure and temperature-resistant instrumentation are required, with long reaction times and production cycles, which are not conducive to mass production. Thus, it is often used in the laboratory to prepare nanomaterials with special morphologies for research. By controlling the crystallization time, crystallization temperature, and other factors, nanopowders with different morphologies can be prepared.

#### 3.5.3 Impregnation

Impregnation is commonly used for metal-modified inorganic materials (carbon, clay, GO, etc. Table 5). The powdered inorganic material is first pre-treated by immersion in a metal salt solution (AlCl$_3$, CaCl$_2$, FeCl$_3$, LaCl$_3$, etc.). The metal ions in the solution can be loaded on an inorganic surface or internally via auxiliary heating and ultrasonic dispersion. The composite adsorbent is then dried or calcined (Figure 8). The impregnation preparation method is also facile but slightly more time-consuming, relying on the specific surface area of the inorganic material and bonding of the active sites on the surface to the metal.
Some preparations are calcined after coprecipitation, impregnation, or hydrothermal treatment (Figures 6–8). For example, metal-modified biochar is calcined to form metal oxide nanoparticles on the surface of BC, which further enhances the adsorption capacity (Table 5). LDH is also sometimes calcined (Table 4). During heating, LDH can be transformed into mixed metal oxides as the interlayer anions are eliminated by thermal decomposition. After the adsorbent is

| Adsorbents | Initial $C_F$ (mg/L) | Adsorbent dose (g/L) | Reaction pH | Temperature (K) | Equilibrium time (min) | Isotherm model | Regeneration performance | $Q_{\text{max}}$ (mg/g) | Ref |
|------------|----------------------|----------------------|-------------|-----------------|------------------------|----------------|-------------------------|---------------------------|-----|
| Wood biochar-La | 40 | 5 | 6 | 298 | 50 | Langmuir | 53% at sixth cycle | 164.20 | Habibi et al. (2019) |
| Al-modified corn biochar | 50 | 1 | 6.8 | 298 | 100 | Langmuir | 74.14 | Zhang et al. (2021a) |
| MgO shell biochar | 20 | 1 | 6–8 | 298 | 360 | Langmuir | — | 57 | Wan et al. (2019) |
| Pomelo peel BC-La | 10 | 2 | 6.5 | 298 | 1,200 | Langmuir | 19.86 | Wang et al. (2018b) |
| ZrO$_2$-seed shell biochar | 10 | 1.6 | 3–9 | 298 | 180 | Langmuir | 50% at third cycle | 9.63 | Mei et al. (2020) |
| Magnetic biochar | 10 | 2 | 2–9 | 308 | 5 | Langmuir | 9.04 | Bombuwala Dewage et al. (2018) |
| Mg-Mn-Zr AC | 10 | 1 | 2–10 | 303 | 180 | Langmuir | — | 26.27 | Mullick and Neogi (2019) |
| Zr-impregnated AC | 10 | 2 | 4 | 303 | 180 | Langmuir | 5.40 | Mullick and Neogi (2018) |
| La-functionalized AC | 200 | 1 | 7 | 303 | 180 | Sips | 10.51 | Merodio-Morales et al. (2019) |
| Activated carbon@SnO$_2$ | 10 | 0.3 | 6 | 303 | 180 | Langmuir | 80% at third cycle | 4.60 | Zúñiga-Muro et al. (2017) |
| Ce-containing bone char | 50 | 2 | 5 | 303 | 840 | Sips | — | 47.16 | Zhou et al. (2019a) |
| Magnetic bone biochar | 20 | 5 | 8 | 298 | 1,440 | Freundlich | 38% at fourth cycle | 5.23 | |
| Graphene oxide with Ti | 50 | 3.5 | 6 | 308 | 100 | Langmuir | 54% at sixth cycle | 342 | Nehra et al. (2019) |
| Al-polyacrylic acid | 10 | 1 | 2 | 298 | 200 | Freundlich | 283.48 | Wang et al. (2019a) |
| CeO$_2$/SiO$_2$ microsphere | 50 | 1.5 | 3 | 298 | 45 | Langmuir | 257.70 | Wang et al. (2019a) |
| Magnetic γ-Fe$_2$O$_3$-GO-La | 10 | 0.2 | 7 | 298 | 30 | Langmuir | 77.12 | Wen et al. (2015) |
| Zn-modifying slag | 50 | 0.5 | 5 | 298 | 30 | Freundlich | 60 | Sarkan et al. (2019) |
| ZrO$_2$-graphene oxide | 25 | 0.5 | 7 | 303 | 50 | Langmuir | 45.7 | Mohan et al. (2016) |
| Hydrous Fe/Al GO | 10 | 3 | 5 | 308 | 60 | Langmuir | 22.9 | Kannan et al. (2016) |
| Fe-modifying pumice | 3 | 0.7 | 3 | 298 | 50 | Freundlich | 21.74 | Dehghani et al. (2016) |
| FeO(OH)-graphene oxide | 25 | 2.5 | 2–10 | 298 | 120 | Langmuir | 17.62 | Kuang et al. (2017) |
| Aluminum/olivine | 10 | 2 | 6 | 303 | 60 | Langmuir | 12.94 | Ghosal and Gupta (2018) |
| Polyhydroxy-iron | 25 | 1 | 7 | 298 | 40 | Freundlich | 11.09 | Muschin et al. (2021) |
| 3D Y-based GO hydrogels | 20 | 0.2 | 4 | 293 | 1,440 | Langmuir | 72% at third cycle | 288.96 | He et al. (2018) |
| Al2O3-chitosan biochar | 20 | 1 | 3 | 298 | 1,440 | Langmuir | 196.1 | Jiang et al. (2018) |
| Graphene oxide/eggshell | 30 | 0.25 | 7 | 298 | 120 | Langmuir | 56.6 | Nor et al. (2020) |
| Ce-SA/BC beads | 10 | 1 | 3–9 | 293 | 20 | Langmuir | 34.86 | Wei et al. (2022) |
| Ca-pectin-hydroxyapatite | 10 | 1 | 7 | 298 | 30 | Langmuir | 28.47 | Raghav et al. (2018) |
| Polypyrrole onto BC | 10 | 1 | 6.5 | 298 | — | Langmuir | 53% at 4th cycle | 18.52 | Wang et al. (2017c) |
put into a fluoride solution, it will undergo a rehydration process. During rehydration, these oxides are in turn rebuilt into original layered structures by adsorbing various anions from the aqueous solution, known as the “memory effect” (Wu P. et al., 2017). The specific surface area and anion exchange capacity of LDH increases further after calcination. After coprecipitation or impregnation, the modification of biopolymers is generally achieved by the sol–gel method for the preparation of hydrogels (Wang A. et al., 2017).

3.6 Adsorption Mechanism

The adsorption mechanism can be divided into physical adsorption and chemisorption. Physical adsorption is generally considered to be caused by van der Waals forces, which are nonselective and reversible, and can be desorbed under certain conditions. Current research on the physical adsorption of fluoride ions is mainly based on electrostatic attraction and hydrogen bonding. Chemisorption is mainly the formation of chemical bonds between molecules and is described by the Langmuir model; the adsorption is selective and irreversible and desorption is more difficult. Physical adsorption depends mainly on the active pore volume and specific surface area (Wang H. et al., 2017), while chemisorption depends more on chemical or electro-affinity. The fluoride adsorption mechanism by various metal-modified adsorbents is summarized in Tables 4, 5. A total of four main adsorption mechanisms can be found: electrostatic attraction, ion exchange, hydrogen bonding, and complexation. The actual adsorption process is usually accompanied by several mechanisms (Figure 9).

When metal oxide enters the aqueous solution, the hydrogen ions are attracted to lone pair electrons of the oxygen element in metal oxide, forming a hydroxyl ligand (Zhang and Jia 2016). The fluoride removal by metal oxides and metal-modified composite adsorbents exploits the large number of hydroxyl groups on the surface (Figure 9A). When the solution pH is less than zero charge point ($pH_{ZPC}$) of the composite adsorbent, hydroxyl functional groups become protonated, forming $OH_2^+$ and are positively charged. The positive charge surface attracts negatively charged fluoride ions by electrostatic attraction (Figure 9B).

Fluoride is attracted to the surface of composite adsorbents for immobilization, but ion pairs (Figure 9C) are weakly interacting with each other and easily desorbed. Several studies have confirmed the involvement of hydroxyl groups in the adsorption reaction by FTIR and XPS characterization. F− has the same charge and similar radius composition as $OH^-$ and can replace $OH^-$ in the structure of composite adsorbents (Figure 9A). F− is bonded to a metal-occupying active site, $OH^-$ is released, and the solution pH rises after adsorption. Most studies have been based on the anion exchange mechanism. As pH rises above the $pH_{ZPC}$ of the adsorbent, there is no significant decrease in adsorption. indicating that adsorption is mainly controlled by ion exchange. Generally, when the solution pH > 10, the large amount of free $OH^-$ in the solution competes with F−, resulting in a significant decrease in adsorption capacity. Complexation between metals and fluoride has also been suggested (Suzuki et al., 2013). Metal-modified composite adsorbents often have polar functional groups containing hydrogen, such as -OH, -COOH, and -NH2 (Yang et al., 2017). The shared electron pairs of polar functional groups are strongly biased toward oxygen or nitrogen, leaving the hydrogen atom almost naked. The lone pair electrons of electronegative fluoride will interact with the hydrogen atom forming a hydrogen bond with a bond angle of 180° and immobilize (Figure 9C).

4 CONCLUSION AND FUTURE DIRECTION

Comparison of Table 2 with Tables 3, 6 reveals an overall increase in fluoride adsorption capacity of metal-modified composites. It indicates that most of the modifications are successful with application prospects. However, there are still many issues that need to be considered to achieve a big breakthrough in practical applications. The multi-metals enrich active sites for fluoride, but agglomeration and easy leaching are still problems, and individual preparation still requires some cost. Metal-modified biopolymers improve the stability of hydrogels, and metals can also be dispersed and immobilized in the macromolecular structure. However, it is reported that the dense surface of hydrogel makes it difficult for fluoride ions to enter the internal pores of beads, and beads sink easily so they have a limited contact area with fluoride. Metal-modified carbon, mineral clay, and other inorganic materials can also improve the dispersion and immobilization of metals to some extent, but there are still problems of dissolution, and loaded metals are easily dislodged and poorly recycled. Low-cost inorganic materials balance the price of rare earth metals and reduce the amount of metals, but at the same time, present the safety risk of waste use. The metal and inorganic materials are both in powder form, and the issue of separation and recycling has not been addressed. Studies combining metals, inorganic materials, and biopolymers appear to address the agglomeration and immobilization of metals, expanding the pore space and fluoride contact area of hydrogel beads, while improving the separation and recovery properties of inorganic materials. However, more than 90% of studies mentioned in this review avoided exploring metal dissolution concentrations and less than 10% of adsorbents were able to achieve more than 80% fluoride adsorption at the fifth cycle. Future studies will need to pay attention to the simplicity, efficiency, and cost of preparation procedure. Overall, the search for future defluoridation adsorbents is not limited to the requirement for increasing adsorption capacity. More important is the attention to cost levels, regeneration performance, separation and recovery, and safety issues for practical applications.

AUTHOR CONTRIBUTIONS

YW summarized and wrote the article under the guidance of LW. All authors contributed to conceptualizing, editing, commenting on, and reviewing the manuscript.
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