separations

MDPI

Review

Fluoride Removal from Water Sources by Adsorption on MOFs

Athanasia K. Tolkou and Anastasios I. Zouboulis *

Laboratory of Chemical and Environmental Technology, Department of Chemistry,
Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece; tolkatha@chem.auth.gr
* Correspondence: zoubouli@chem.auth.gr; Tel.: +30-2310-997794

Abstract: Fluoride is present in several groundwaters due to natural or anthropogenic origins. Although it is necessary for physiological human functions (in small amounts, i.e., 0.5–1.2 mg/L), it could be very harmful when it exceeds the maximum permissible concentration limit of 1.5 mg/L (according to WHO). Among the numerous technologies for removing fluoride from waters, metal–organic framework (MOF) materials are considered to be promising adsorbents due to their advantages of high porosity, high specific surface area, diverse functions and easy modification. In this study, the synthesis of MOFs and the progress of their application to the removal of fluoride from contaminated water, as published in the recent literature mainly over the past five years, are reviewed. The adsorption mechanism(s) and its main characteristics, such as effect of initial fluoride concentration, adsorbent dosage, solution pH, contact time, adsorption capacity, thermodynamic and regeneration studies, etc., for the removal of fluoride with the addition of different MOFs are compared. According to these comparisons, the hydrothermal/solvothermal synthesis method is most commonly used for the preparation of MOFs, whereas higher BET surface areas are shown by specific MOFs based on aluminum metal ions. The main fluoride adsorption mechanisms were found to be electrostatic attraction and/or complexation. The most common pH for conducting experiments was 7.0, but several examined materials were found to be effective over a wide pH range. Four to six regeneration cycles were successfully applied on average, regarding the MOFs under review, whereas in the majority of these cases, the sorption process was found to be endothermic.

Keywords: MOFs; fluoride ions removal; adsorption

check for updates

Citation: Tolkou, A.K.; Zouboulis, A.I. Fluoride Removal from Water Sources by Adsorption on MOFs. *Separations* **2023**, *10*, 467. https://doi.org/10.3390/separations10090467

Academic Editors: Eduardo Díez and Araceli Rodríguez

Received: 3 August 2023
Revised: 15 August 2023
Accepted: 21 August 2023
Published: 24 August 2023

1. Introduction

Common pollutants in wastewaters mainly consist of heavy metal ions (HMIs), radioactive constituents, pharmaceuticals, poly-aromatic hydrocarbons, pesticides and dyes [1] and can be characterized in some cases as high-strength industrial wastewaters [2]. Regarding their chemical composition, these pollutants can be generally categorized into organic and inorganic (IOCs), such as ammonia, nitrogen, phosphorus, sulfide and fluoride [1,2]. Particularly, fluoride is among the most common anions present in ground or surface waters, and several industries, such as metallurgies or even cement production, may release excessive amounts of wastewaters containing fluoride [3]. Depending on the concentration of fluoride in water sources, it may have either harmful or beneficial effects on human health; in lower concentrations, it is considered as a fundamental micro-nutrient for humans, preventing caries, but the excessive fluoride ion concentrations can cause bone inactivation, brain damage and infertility [4]. The World Health Organization (WHO) and the EU Directive 98/83/EC [5,6] have established the guideline/max permissible concentration value for fluoride in drinking water to be 1.5 mg/L.

Several treatment methods, such as precipitation [7–9], reverse osmosis [10], membrane separation [11–13], coagulation [14], etc., are commonly used to remove fluoride anions from water. However, the disadvantages of these technologies are that they have high costs and require expensive operational and labor costs and advanced technologies. On the other hand, adsorption [15–17] is the most widely used technique, not only because of its simplicity in design and operation but also because it is an economical and environmentally friendly method and provides high efficiency [18]. Consequently, this review is mostly focusing on the removal of excess fluoride anions from water sources by adsorption.

Diverse sorbent materials, such as activated carbons [15,19], hydroxide-based materials [20], biochar [21–23], graphene oxide [15,24,25], fly ash [26,27], zeolite [26], etc., have been used lately for examining the removal of fluoride. Nevertheless, these adsorbents still present certain limitations, such as rather small specific surface area, leading to lower adsorption capacity, poor selectivity, etc. [3]. To address this problem, especially during recent years, novel materials showing adaptable porosity, high BET (Brunauer–Emmett–Teller) surface area, diverse functionality and easy modification, known as metal–organic frameworks (MOFs), have proven to be efficient adsorbents for water treatment [2]. Furthermore, MOFs are therefore the most broadly developed porous materials due to their outstanding properties, besides the large surface area, such as their low density, high crystallinity and easily tunable surface chemistry [28–31]. Accordingly, in this review, the recent advances regarding fluoride removal over the past five years are briefly discussed and compared, considering also the synthesis and specific applications of MOFs. The purpose of this review is to keep MOF researchers abreast of the latest trends in the literature so that they can properly organize and structure their future innovation-oriented research.

2. Metal–Organic Frameworks (MOFs)

MOFs constitute a rather new category of porous polymers made by linking several inorganic metal ions or clusters with organic ligands as bridging elements [3,32,33]. Regarding the synthesis of MOFs, a variety of metal ions, organic ligands and the subsequent structures have produced several combinations, leading to a wide variety of MOFs [34]. Main metals generally used for the synthesis of MOFs may be (among others) Al^{3+}, Zr^{4+}, Fe^{3+}, Ca^{2+}, La^{3+}, Ce^{3+}, Cd^{2+} and Ti^{3+} [3,34].

In Figure 1, the several properties, applications and synthetical methods for MOFs are illustrated [32]. As can be seen, MOFs are expected to be promising materials for removing pollutants in water treatment, especially by sorption, because they present several relevant advantages, such as high porosity, specific surface area, high pore volume and abundant active sites, and in some cases, they are also highly stable in water matrices [3,32]. Furthermore, MOFs have found diverse applications, used, e.g., as carriers for drug delivery, for gas or energy storage, for the safe disposal of wastes, in the field of catalysis [35–37] and in environmental science, where they can be used for the adsorptive removal of pollutants from wastewaters [3]. The applications of MOFs in water treatment are mainly described in the respective literature as being for the elimination of dyes or other organic pollutants [38]. Recently, the UiO-66 MOFs (Universitet i Oslo family), which are highly stable in water, have been found to have several applications, e.g., for the removal of organic dyes, heavy metals, pharmaceuticals, phosphates, fluoride, etc., as represented in Figure 2 [39].

During recent years, some reviews have examined the use of MOFs as adsorbents for the removal of fluoride (Figure 3) by using alternative MOFs based on different central metal ions. These reviews summarize the recent trends, regarding MOFs and their defluorination capability, focusing initially on the detection and then on the aspects of removal of fluoride ions from aqueous solutions [28,32,39,40]. Table 1 describes the several categories of relevant MOFs and their various characteristics, focusing on fluoride removal. In another review, the specific use of zirconium, iron, aluminum, lanthanum and cesium-based MOFs is also summarized [4]. The developments and progress of MOFs for the removal of fluoride from water, especially during the last five years, are mainly reported in the current review.

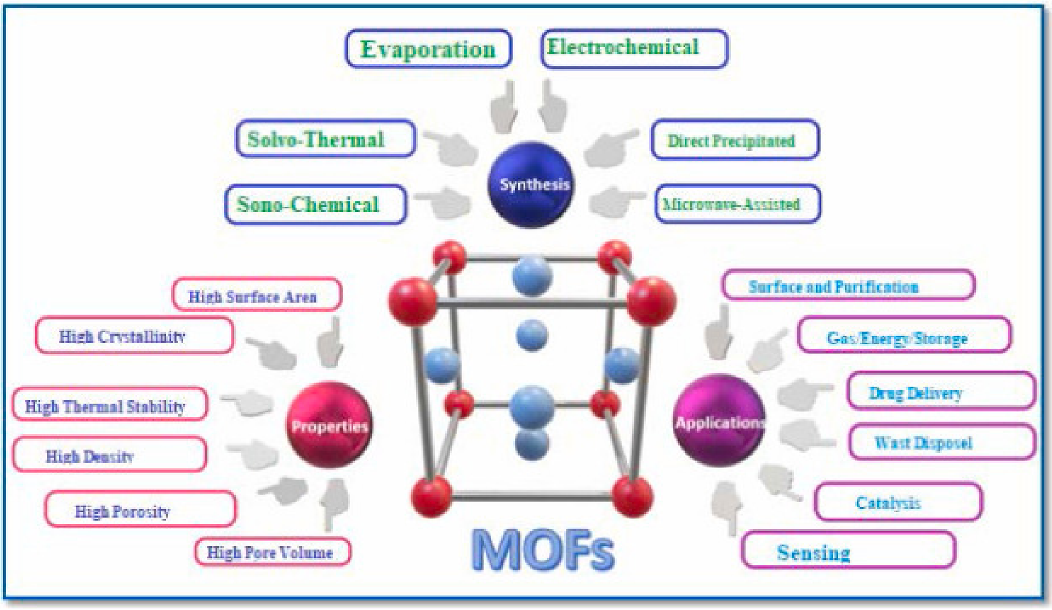


Figure 1. Properties, applications and main synthetical routes for MOFs; it is reprinted with permission from [32].

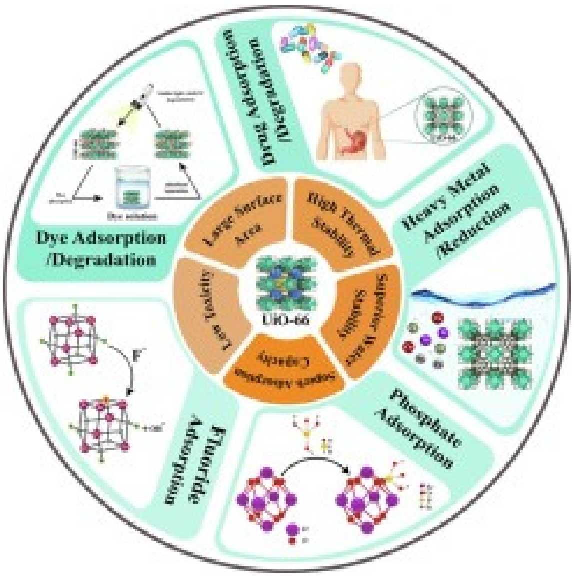


Figure 2. Applications of UiO-66 MOFs; it is reprinted with permission from [39].

Moreover, most of the MOFs studied in the literature are homometallic, i.e., composed of one type of metal. On the other hand, MOFs that contain more than one metal in their structure are called heterometallic, and their main advantages are their multifunctionality and that they combine the properties of the materials in a given application [41,42]. Heterometallic MOF chemistry provides potentials to modify the properties of already known homometallic MOFs and also enables the preparation of a new unique series of compounds with remarkable sorption properties [41]. Although heterometallic MOFs can offer significant advantages over their homometallic counterparts, offering excellent chemical stability and synergistic cooperation to modify adsorption properties, controlling the distribution of metals in them remains a challenge [43]. MOF-5 (divalent metal ions) and UiO-66 (tetravalent metal ions) are the two best known heterometallic MOF families. It is observed that bimetallicity is generally more favorable for cation pairs with adjacent sizes, due to a charge transfer mechanism within secondary building units. For particularly dissimilar size cation pairs, such as the UiO-66 family, metal mixing is globally less favorable due to the high cluster coordination number [44].

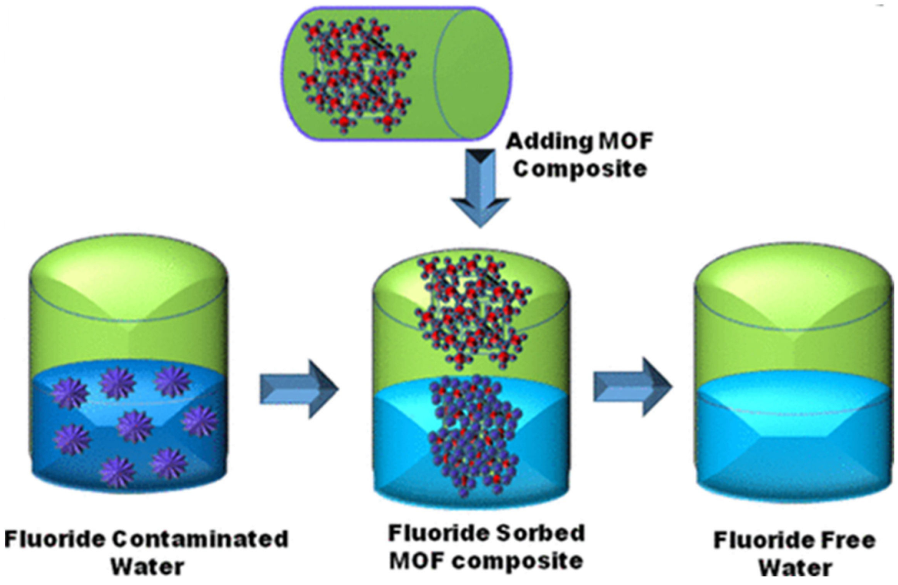


Figure 3. Removal of fluoride by the addition of MOFs. It is reprinted with the permission from [45].

Table 1. Main categories of MOFs and their different features, focusing on fluoride removal; it is reprinted with permission from [32].

Types of MOFs	Characteristics
The MILs Family (Materiaux de I′ Institut Lavoisier)	The MIL-53(Fe) and MIL-53(Cr) materials have shown lower adsorption capacity than the MIL-96 (Al).
The UiO-66 family (University of Oslo)	Have a basic framework of zirconium cluster that can attract the fluoride ions. They are best matched with the amine functional group for improving the adsorption of fluoride.
The MOF-801 family	They have a basic framework of an octahedral zirconium cluster that can attract fluoride ions together with the ion-exchange mechanism of the cluster's hydroxyl groups.
The Metal-ion seeded MOFs	Used metals can be, e.g., cerium, zirconium, hafnium, etc.; as zirconium and hafnium present a similar electronic structure, UiO-66(Zr) and UiO-66(Hf) show related removal mechanisms. Aluminum can be also inserted inside the MOF, as this metal ion will attract the fluoride ions via electrostatic interactions due to the high electronegativity of fluoride anions.
The ZIFs Family	The zeolite imidazolate frameworks-7,8,9 show good fluoride adsorption, while not presenting higher efficiency, than the other adsorbents.

The removal mechanisms of fluoride by MOFs can be mainly attributed to physio-sorption and chemi-sorption [32]. As shown in Figure 4, chemi-sorption mainly includes chemical bonding, acid-base interactions, π–π interactions and ion exchange, which are strongly electrostatic in nature. Physio-sorption includes Van der Waals interactions and diffusion [46]. Among the unique characteristics of MOF materials is that they can act as either electron donors or electron acceptors [28,39].

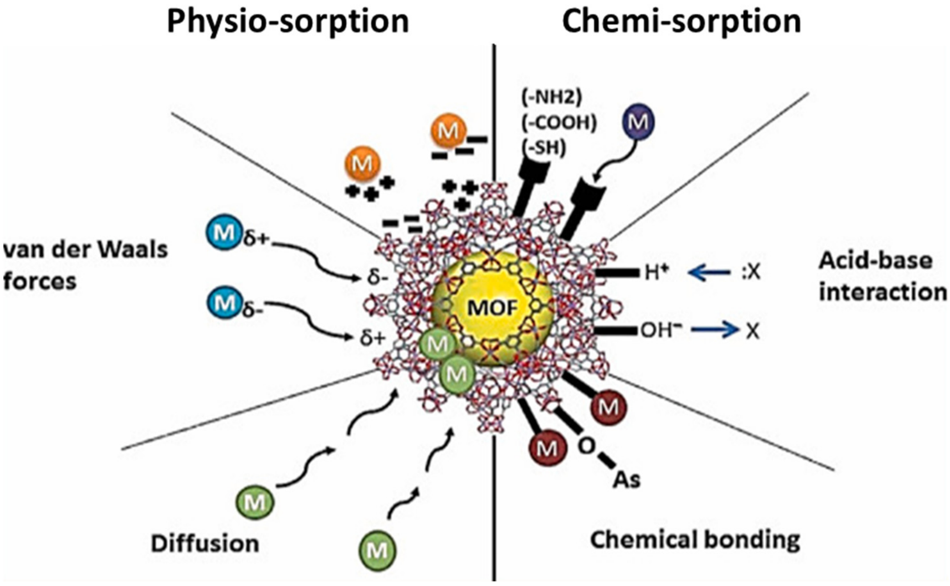


Figure 4. Schematic representation of various types of interactions when MOFs are used for the removal of fluoride [46].

3. Main Synthesis Methods for MOFs

3.1. Typical Synthesis Methods

There are different methods and conditions that are commonly used for the synthesis of MOFs, as detected in the relevant literature, which are shown in Figure 5 [47]. The overall synthesis method for MOFs is analogous to molecular sieve synthesis [48]. The reaction temperature is one of the main parameters influencing and directing the synthesis of MOFs. Thus, conventional synthesis is usually used in reactions carried out with conventional electric heating [49]. Regarding the adsorption of anions, the respective typical synthesis methods mainly include the hydrothermal/solvothermal method and additionally the microwave, the electrochemical, the mechanochemical and the sonochemical methods. The advantages and disadvantages of each method are varied; however, the most suitable one can be selected, according to the specific needs of synthesis conditions and the properties of produced material and considering the most efficient adsorption/removal of fluoride ions [41,42]. During the synthesis of MOFs, the main goal is the formation of defined inorganic building blocks preventing the decomposition of the organic linker. A facile synthesis of MOFs is important, as it contributes to cost reduction and also to achieving fundamental knowledge and practical applications [48]. Moreover, according to the literature [50,51], the synthesis method affects the physicochemical properties of MOFs. In addition, agitation of the reaction mixture during the synthesis (stirring or sonication) enhances the formation of more developed surfaces leading to the development of smaller crystals than those formed when the synthesis is carried out without stirring under static conditions [52].

The conventional method most commonly used for MOF synthesis involves the mixing of organic ligand, of metal (possibly in the form of metal salt solution), and of the proper solvent in an appropriate liquid phase, followed by the reaction, the subsequent filtration of the obtained product and finally drying (usually by evaporation) to obtain the purified MOF material [40,41]. Table 2 summarizes the main synthetic methods used and the respective physical properties of obtained MOFs, as analyzed in this review; it can be observed that the method mostly applied for the synthesis of MOFs is the hydrothermal/solvothermal method, which is usually achieved under conventional electrical heating at a controlled temperature.

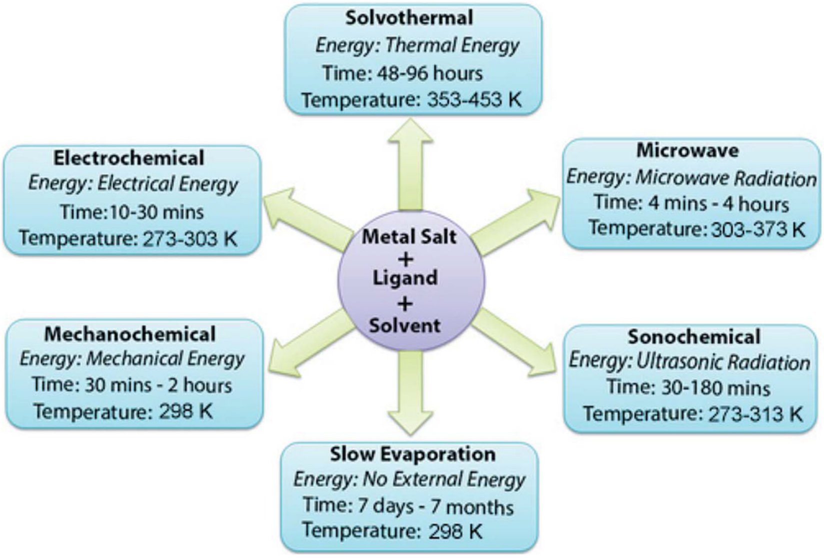


Figure 5. Synthetical methods and conditions commonly used for the preparation of MOFs; it is reprinted with permission from [47].

Table 2. Summarizing the synthetic methods and the main physical properties of MOF materials used as adsorbents, as discussed in this review.

MOFs	Synthetic Method	BET Surface Area, S_{BET} (m^2/g)	Average Pore Size (nm)	Total Pore Volume, V_T (cm^3/g)	Ref.
AlFu	Hydrothermal	1156.0	1.7	NR [1]	[38]
b-CD@AlFuMoF	Hydrothermal	779.2	5.6	0.36	[53]
Al-MOF-5	Hydrothermal	1264.0	3.1	NR [1]	[54]
Zr@Fu	Hydrothermal	NR [1]	NR [1]	NR [1]	[45]
La@Fu	Hydrothermal	NR [1]	NR [1]	NR [1]	
Fe@Fu	Hydrothermal	NR [1]	NR [1]	NR [1]	
$[Ce(L1)_{0.5}(NO_3)(H_2O)_2]\cdot 2DMF$	NR [1]	NR [1]	NR [1]	NR [1]	[29]
$[Eu_3(L2)_2(OH)(DMF)_{0.22}(H_2O)_{5.78}]\cdot$guest	NR [1]	NR [1]	NR [1]	NR [1]	
MOF1 ($\{[Zn_3L_3(BPE)_{1.5}]\cdot 4.5DMF\}n$)	Solvothermal	270.3	NR [1]	0.15	[55]
MOF1	NR [1]	NR [1]	10–20	NR [1]	[56]
Sn(II)-TMA	Solvothermal	360.8	4.0	0.46	[57]
Fe@BDC	Hydrothermal	53.7	9.0	0.14	[58]
Fe@ABDC	Hydrothermal	68.8	4.2	0.42	
Ce@BDC	Hydrothermal	NR [1]	NR [1]	NR [1]	[59]
Ce@ABDC	Hydrothermal	NR [1]	NR [1]	NR [1]	
La@BTC	Hydrothermal	NR [1]	NR [1]	NR [1]	[60]
La-BTC	Solvothermal	2.4	18.1	0.01	[61]
Fe-Al BDC	Solvothermal	120.3	1.4	NR [1]	[62]
Al-TDC	Hydrothermal	1251.7	1.3	0.87	[63]
Ce-TDC	Hydrothermal	859.7	1.7	0.36	
Zr-TDC	Hydrothermal	923.3	1.4	0.37	
ZrFu MOF	NR [1]	537.5	1.8	0.23	[64]
Zn- MOF-801	Hydrothermal	725.0	0.1	0.40	[65]
Zn- MOF-801	Solvothermal	522.0	0.3	1.51	[66]
Uio-66	NR [1]	NR [1]	NR [1]	NR [1]	[67]
UiO-66-NH_2	Hydrothermal	945.0	2.0	NR [1]	[68]
La-UiO-66-$(COOH)_2$	Solvothermal	80.3	1.3–2.2	0.15	[69]
MIL-96(RM)	Hydrothermal	NR [1]	NR [1]	NR [1]	[70]
MIL-53 (Fe)	NR [1]	51.3	NR [1]	NR [1]	[71]

[1] Not referred.

3.2. Reviewing Synthesis of MOFs Materials Applied for the Removal of Fluoride in Recent Literature

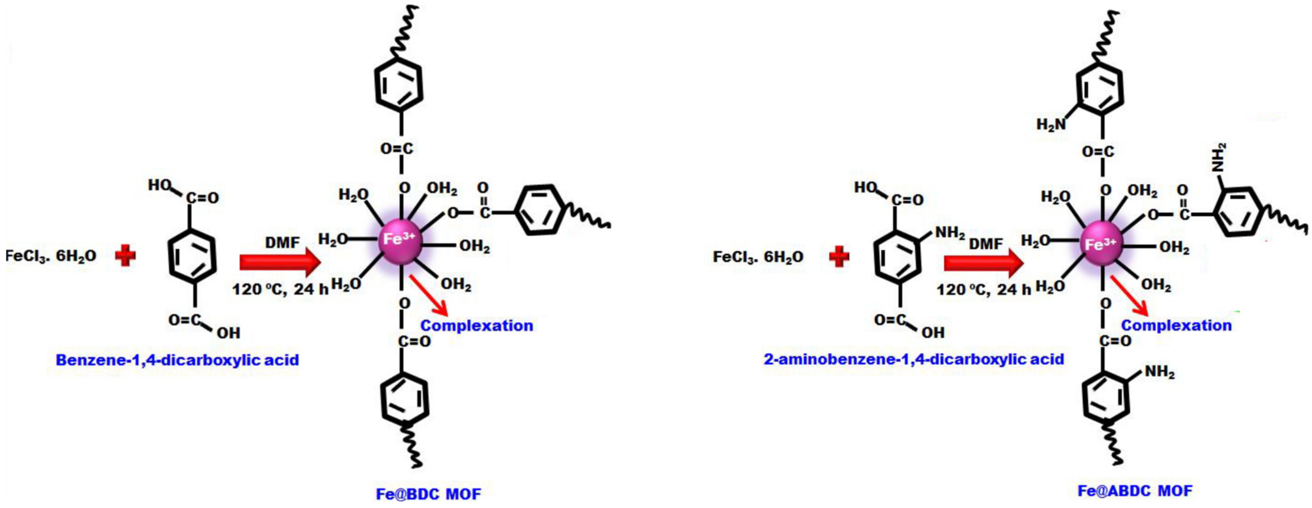
Several types of MOFs have been synthesized for the removal of fluoride, as presented in Table 1. The main trends in the relevant literature, especially over the past five years, are discussed in the following section.

Particularly, Karmakar et al. [33] synthesized by the hydrothermal method a laboratory-prepared aluminum-fumarate metal organic framework (MOF), namely AlFu MOF, for fluoride removal. AlFu MOF was found to present a micro-porous structure, exhibiting a relatively large surface area (1156 m^2/g) and an average pore size of 1.7 nm. Moreover, the modified AlFu MoF obtained by the hydrothermal method when using the b-cyclodextrin impregnation treatment in order to produce b-CD@AlFu MoF also presented with a large specific surface area (779.2 m^2/g) and a porous structure with an average pore diameter of 5.6 nm and a pore volume of 0.36 cm^3/g [53]. Wang et al. [54] synthesized a novel aluminum-based MOF, i.e., Al-MOF-5, for the potential fluoride removal from water by using the hydrothermal method. This Al-MOF-5 material presented the highest specific surface area (1264 m^2/g) of all MOFs described in Table 2. It has a mesoporous structure with microporous characteristics, providing an average pore size of 3.12 nm. Recently, fumaric acid-based MOFs have been hydrothermally produced by using several metal ions, such as Zr^{4+}, La^{3+} and Fe^{3+}, thus obtaining Zr@Fu, La@Fu and Fe@Fu composite MOFs, respectively, which have been applied for defluoridation studies [45].

Additionally, more complexes have been synthesized for the efficient removal of fluoride ions. In particular, Ma et al. [29] composed two new lanthanide-based MOFs, i.e., $[Ce(L1)_{0.5}(NO_3)(H_2O)_2]\cdot 2DMF$ and $[Eu_3(L2)_2(OH)(DMF)_{0.22}(H_2O)_{5.78}]$, although without presenting sufficient details about the applied synthesis method or their specific surface characteristics. Furthermore, in the study of Aliakbari et al. [55], a zwitterion metal–organic framework, MOF1/($\{[Zn_3L_3(BPE)_{1.5}]\cdot 4.5DMF\}n$), was synthesized by the solvothermal method in acidic media, where the components were initially mixed, and then drops of N,N-dimethylformamide (DMF) were added. The BET surface area and pore volume of this MOF1 material were determined as 270.3 m^2/g and 0.12 cm^3/g, respectively. In addition, another zirconium-based relevant-to-MOF1 material, which is simply synthesized by the mixing of zirconium tetrachloride and tetrafluoroterephthalic acid, was investigated for defluoridation studies with pore sizes around 10–20 nm, as derived from the N_2 isotherms [56].

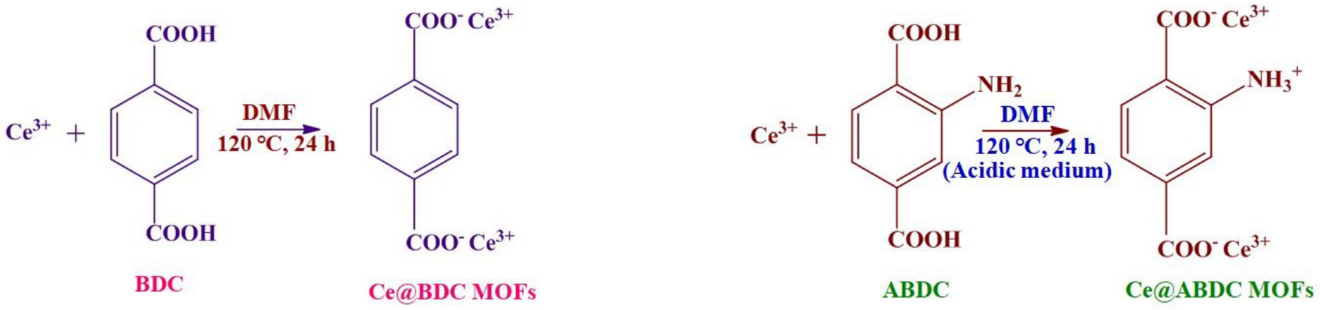
In the study of Ghosh et al. [57], another core metal was used, i.e., Sn^{2+}, mixing with benzene-1,3,5-tricarboxylic acid (TMA) as the organic linker, to synthesize via the solvothermal method the respective Sn(II)-TMA MOF. The examination by the BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) methods showed that this type of MOF had a mesoporous structure with an average pore size of 4 nm, a specific surface area of 360.8 m^2/g and a pore volume of 0.46 cm^3/g.

Moreover, Fe@BDC and Fe@ABDC MOFs were synthesized with the application of hydrothermal synthesis by using Fe^{3+} and benzene-1,4-dicarboxylic acid (BDC) in the first derivative and 2-aminobenzene-1,4-dicarboxylic acid (ABDC) for the second one, as shown in Figure 6 [58]. The relative BET surface area of Fe@ABDC MOF was higher than that of Fe@BDC without any noticed enhancement from the presence of amine, i.e., 68.8 and 53.7 m^2/g, respectively. Furthermore, Jeyaseelan et al. [50] also used cerium (Ce^{3+}) in addition to the use of Fe^{3+} (Figure 7) as the core metal, producing, namely, Ce@BDC and Ce@ABDC MOFs, aiming to produce rare earth metal-based (REM) MOFs by applying the hydrothermal synthesis method. In addition, by replacing BDC with benzene-1,3,5-tricarboxylic acid (BTC) and using lanthanum (La^{3+}) as a rare earth metal, they also produced La@BTC MOFs [60] (Figure 8) in parallel with the Ce@BTC MOF. Moreover, Yin et al. [61], in their study, synthesized several lanthanum-based MOFs (La-MOFs) by the solvothermal method, varying only the organic ligands. Among the produced adsorbents, the La-BTC presented a rather small BET surface area (2.4 m^2/g), a pore size of 18.1 nm and 0.01 cm^3/g pore volume.



(**a**) (**b**)

Figure 6. Synthesis conditions of (**a**) Fe@BDC and (**b**) Fe@ABDC MOF materials; it is reprinted with permission from [58].



(**a**) (**b**)

Figure 7. Synthesis conditions of (**a**) Ce@BDC, and (**b**) Ce@ABDC MOFs [59].

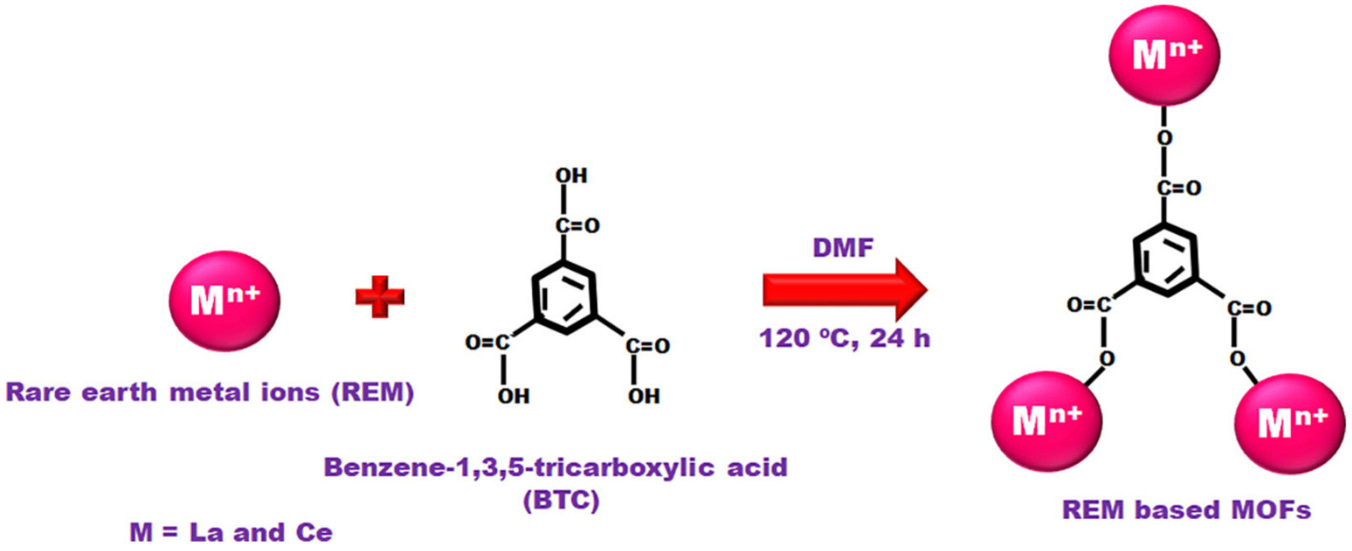
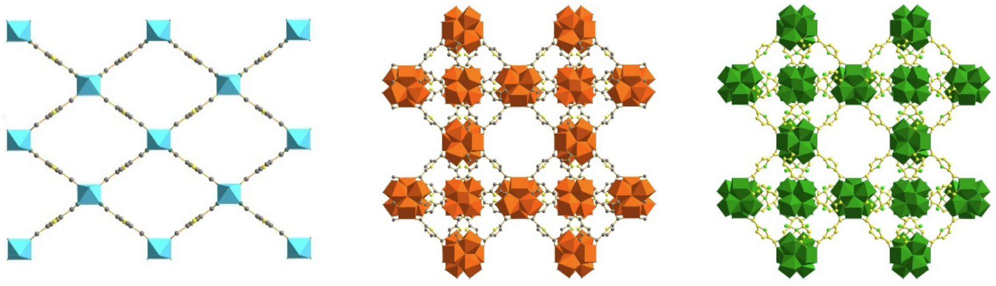


Figure 8. Synthesis conditions of La@BTC and Ce@BTC MOFs; it is reprinted with permission from [60].

The solvothermal method was also used in the study of Mukherjee et al. [62] for the synthesis of 3D rod-like bimetallic MOF (with Fe^{3+} and Al^{3+} as metals) by using BDC as the organic linker in dimeethylfromamide (DMF) medium. This Fe-Al BDC MOF material presented a surface area of 120.3 m^2/g.

Another organic ligand, 2,5-thiophenedicarboxylate (H2TDC), was used to synthesize TDC-MOFs (2,5-thiophenedicarboxylic acid MOFs) via the hydrothermal method and by adding Al^{3+}, Ce^{4+} or Zr^{4+} as the central metal ions, forming Al-TDC, Ce-TDC and Zr-TDC, respectively [63], whose structure is illustrated in Figure 9. As shown in Table 2, the BET surface area of Al-TDC, Ce-TDC and Zr-TDC measured 1251.7, 859.7 and 923.3 m^2/g, respectively. Regarding the pore volumes and pore sizes, the relative values were found to be 0.87 cm^3/g and 1.3 nm for the Al-TDC; 0.36 cm^3/g and 1.7 nm for the Ce-TDC; and 0.36 cm^3/g and 1.4 nm for the Zr-TDC. These values lead to the recommendation that all three of these TDC-MOFs can exhibit potential adsorption efficiency for fluoride removal.



(**a**) (**b**) (**c**)

Figure 9. Crystal structures of (**a**) Al-TDC, (**b**) Ce-TDC and (**c**) Zr-TDC MOFs; reprinted with permission from [63].

In addition, a zirconium fumarate (ZrFu) MOF has also been prepared as an efficient adsorbent for fluoride removal from industrial wastewaters, providing a surface area of 537.5 m^2/g, according to BET analysis, a pore volume of 0.23 cm^3/g and a pore size of 1.8 nm [64].

Several studies synthesized members of the MOF-801 family. According to Zhu et al. [65], a produced zirconium fumarate MOF-801 exhibited a surface area of 725 m^2/g, a pore diameter of 0.1 nm and a pore volume of 0.40 cm^3/g. Tan et al. [66] also synthesized Zr-MOF-801 by using the solvothermal method (Figure 10), Zr^{4+} as the central metal and several organic linkers. The corresponding BET surface area and the calculated pore volume were found to be smaller than those of Zhu et al. [65], i.e., 522 m^2/g and 0.26 cm^3/g, respectively; however, they presented larger average pore diameters (1.51 nm). The BJH method also indicated the presence of micropores, which may enhance the fluoride adsorption [66].

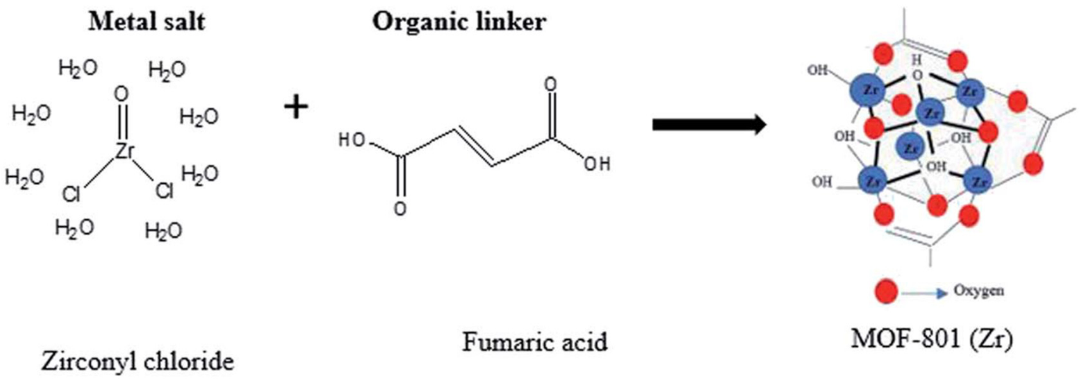


Figure 10. Zr-MOF-801 synthesis and formation mechanism [66].

The UiO-66 family MOFs have also been referred to in recent literature for the effective removal of fluoride from contaminated waters [72]. Several studies were reviewed, and among them is the study of Lacalamita et al. [68], according to which the highly porous MOF UiO-66-NH_2 was synthesized by the hydrothermal method. The BET analysis provided a high surface area (about 945 m^2/g) with a pore size below 2 nm. On the other hand, Zhao et al. [69] prepared a novel adsorbent containing a Zr-based metal–organic framework (i.e., UiO-66-$(COOH)_2$) and La^{3+} as the metal. This dual-metal sites MOF, abbreviated as La-UiO-66-$(COOH)_2$, took the advantages of properties from each material separately, i.e., the non-toxicity and the ability of La^{3+} to link with the oxygen-containing ligands and the availability of UiO-66-$(COOH)_2$) in carboxyl groups that present affinity with the rare earth cations, combining them into a unique adsorbent material. However, it was observed in this study that with the addition of La, there was a reduction of the specific surface area (from 317.4 down to 80.3 m^2/g), as well as of pore volume (from 0.44 down to 0.15 cm^3/g), maybe due to the blocking of UiO-66-$(COOH)_2$ pores by the presence of La. Nevertheless, this addition significantly increases the active centers of this material for the efficient adsorption of fluoride ions [69].

Last but not least, the Matériaux Institut Lavoisier (Materials Institute Lavoisier) prepared an alternative metal–organic framework, also referred to in this review. Particularly, the MIL-96(RM) was produced via the hydrothermal synthesis method by using metal ions present in red mud (RM) and was applied for defluoridation studies [70]. In addition, an iron-based MOF, e.g., MIL-53 (Fe), was also synthesized [73], but it did not show a large surface area when compared to other MOFs, i.e., only 51.3 m^2/g; however, its fundamental structure makes it a potentially effective adsorbent for fluoride removal.

Based on the values reported in Table 2 and what was aforementioned, it seems that the hydrothermal/solvothermal synthesis method is the most frequently used for MOF preparation. Furthermore, regarding the properties and characteristics of these materials, the higher BET surface area is presented by the MOFs that are based on aluminum metal ions, i.e., AlFu (1156.0 m^2/g), Al-MOF-5 (1264.0 m^2/g) and Al-TDC (1251.7 m^2/g), followed by those that have zirconium metal in their structure. Regarding the average pore size (nm), MOFs that include the lanthanum metal in their structure presented the highest values, such as La-BTC (18.1 nm), whereas the Zn-MOF-801 presented the lowest (0.1 nm). The total pore volume was relatively similar for all materials, with Al-TDC presenting the largest value (0.87 cm^3/g). The high surface area and the microporous morphology of these materials are most likely to benefit the adsorption efficiency [66]. The aforementioned results suggest that all these adsorbents showed strong adsorption potential for the removal of fluoride from contaminated waters.

4. Application of MOFs for the Removal of Fluoride Anions

The potential for using MOF materials to remove fluoride from waters was evaluated with detail; the relevant materials were synthesized mainly during the last 5 years, described in Table 2 and compared systematically regarding their effectiveness. The main examined parameters include the effect of initial fluoride concentration, the adsorbent dosage, the solution pH, the contact time, the adsorption capacity and the thermodynamic and regeneration studies; they were properly correlated and analyzed. The respective values are listed in Table 3. The adsorption mechanisms of several MOFs for fluoride removal are also discussed.

According to the study of Karmakar et al. [38], the AlFu MOF was found to be an excellent adsorbent regarding the fluoride removal from groundwaters, and its adsorption capacity was very high (600 mg/g) by adding 0.75 g/L at pH 7.0. The values of ΔG^0 (-13.94 kJ/mol at 293 K) and ΔH^0 (-32.06 kJ/mol) indicated that this adsorption was spontaneous and exothermic, i.e., favored by the increase of temperature. In addition, the AlFu MOF can be regenerated in medium alkaline conditions. However, when modified with b-cyclodextrin AlFu MOF, i.e., b-CD@AlFu MoF [53], it exhibited substantially lower maximum fluoride adsorption capacity (39.95 mg/g) and was regenerated with an organic solution for seven cycles. In this case, the ideal conditions for the treatment of 30 mg/L initial fluoride concentration were found for pH 2.0 by adding a dosage of 0.75 g/L of this material. The thermodynamical analysis showed that the adsorption of fluoride onto b-CD@AlFu MoF is spontaneous and mostly driven by chemical adsorption, while the negative value of ΔH^0 (−140.84 kJ/mol) provided an indication that in this case the defluoridation process was exothermic in nature.

Moreover, the results of using another Al-based MOF, i.e., Al-MOF-5 [54], showed that this material presented an adsorption capacity of 46.08 mg/g. The study of kinetics showed that equilibrium was reached within 120 min by applying a 1.0 g/L dose at natural pH conditions. In addition, considering the higher specific surface area of this Al-MOF-5, as listed in Table 2, it could be assumed that this material can be an efficient selection for the adsorption of fluoride. However, in this case, the positive enthalpy change (ΔH^0), indicates that the adsorption process was endothermic. Nevertheless, this MOF type, despite the fact that it is effective for fluoride removal, has the disadvantages of higher production cost and lower durability/stability. For the regeneration of Al-MOF-5, several solutions were used, such as NaOH, HCl and ethanol, at different concentrations. However, the NaOH solution at 10 mg/L was found to be the most appropriate, as more than 50% of the fluoride was removed after five recycling cycles.

Table 3. Comparison of adsorption capacities between the main MOF adsorbents (literature data) for fluoride removal, as presented in this review.

MOFs	$[F]_o$ (mg/L)	Dosage (g/L)	pH_{init}	Contact Time (min)	Adsorption Capacity (mg/g)	[1] ΔH^0 (kJ/mol)	Recycling Cycles	Ref.
AlFu	30.0	0.75	7.0	60	600	−32.06	NR [2]	[38]
b-CD@AlFuMoF	30.0	0.75	2.0	120	39.95	−140.84	7	[53]
Al-MOF-5	10.0	1.0	7.0	120	46.08	21.30	5	[54]
Zr@Fu	10.0	0.1	7.0	30	4.92	0.37	6	[45]
La@Fu	10.0	0.1	7.0	30	4.93	0.45	6	
Fe@Fu	10.0	0.1	7.0	30	4.85	0.31	6	
$[Ce(L1)_{0.5}(NO_3)(H_2O)_2]\cdot 2DMF$	12.5	2.0	3.0–7.0	120	103.95	18.52	NR [2]	[29]
$[Eu_3(L2)_2(OH)(DMF)_{0.22}(H_2O)_{5.78}]\cdot guest$	12.5	2.0	3.0–7.0	120	57.01	25.32	NR [2]	
MOF1 ($\{[Zn_3L_3(BPE)_{1.5}]\cdot 4.5DMF\}n$)	NR [2]	NR [2]	7.0	20	NR [2]	NR [2]	5	[55]
MOF1	10.0	0.2	3.0–11.0	30	240	NR [2]	7	[56]
Sn(II)-TMA	12.0	1.0	3.0–10.0	150	30.86	10.1	NR [2]	[57]
Fe@BDC	10.0	0.1	7.0	30	4.90	0.56	6	[58]
Fe@ABDC	10.0	0.1	7.0	30	4.92	1.24	6	
Ce@BDC	10.0	0.1	7.0	30	4.88	0.38	6	[59]
Ce@ABDC	10.0	0.1	7.0	30	4.91	0.45	6	
La@BTC	10.0	0.1	7.85	30	4.98	0.58	6	[60]
Al-TDC	5.0	0.2	10.0–11.0	300	107.5	−25.37	4	[63]
Ce-TDC	5.0	0.3	3.0–4.0	300	94.9	−20.53	4	
Zr-TDC	5.0	0.3	3.0–4.0	300	97.0	−21.18	4	
Fe-Al BDC	10.0	1.0	7.0	45	NR [1]	NR [1]	NR [1]	[62]
La-BTC	20.0	0.5	5.0	180	105.2	19.68	4	[61]
La-BPDC	20.0	0.25	5.0	180	125.9	35.94	4	
La-BHTA	20.0	0.15	5.0	180	145.5	25.66	4	
La-PMA	20.0	0.25	5.0	180	158.9	36.47	4	
La-BDC	20.0	0.15	5.0	180	171.7	30.22	4	
ZrFu	10.0	3.0	6.0	60	49.66	NR [1]	6	[64]
Zn-MOF-801	10.0	0.7	no pH adjusting	40	40.0	NR [2]	NR [2]	[65]
Zn-MOF-801	10.0	1.0	NR [2]	120	17.33	NR [2]	4	[66]
Uio-66	14.6	0.4	7.0	41.5	31.09	NR [2]	5	[67]
$UiO\text{-}66\text{-}NH_2$	20.0	2.0	6.1	60	49.7	NR [2]	NR [2]	[68]
$La\text{-}UiO\text{-}66\text{-}(COOH)_2$	100.0	1.0	3.0	30	57.23	32.92	4	[69]
MIL-96(RM)	20.0	0.5	7.0	120	82.65	9.05	7	[70]
MIL-53(Fe)	10.0	0.25	4.0	60	4.34	NR [2]	NR [2]	[71]

[1] Values of $\Delta H^0 < 0$ (negative) indicate that defluorination is an exothermic process, whereas for $\Delta H^0 > 0$, it is endothermic. [2] Not referred.

In the study of Jeyaseelan et al. [45], several M@Fu-based MOFs were evaluated in terms of fluoride removal. Particularly, the Zr@Fu, La@Fu and Fe@Fu MOF composites, when applying the same conditions, i.e., initial fluoride concentration 10 mg/L, pH 7.0 and adsorbent dosage 1.0 g/L, indicated maximum capacities of 4.92, 4.93 and 4.85 mg/g, respectively; therefore, they are quite lower than those found in previous studies. However, for all these composite materials, the kinetic equilibrium can be reached after only 30 min. Among the advantages demonstrated by these MOFs is that they can be applied effectively for different initial pH conditions, as after the treatment, the solution pH remains around neutral values. In addition, the La@Fu MOF was found to present higher defluorination capacity than Zr@Fu and Fe@Fu MOFs over the entire pH range examined. The thermodynamic studies proved the endothermic nature of the process, as the determined values of ΔH^0 were positive. The regeneration and reusability studies (up to 6 treatment cycles by using the NaOH solution) proposed that the Zr@Fu, La@Fu and Fe@Fu MOF composites can be used adequately. Regarding the fluoride removal mechanism by using M@Fu-based MOF composites, as shown in Figure 11, it is possible that electrostatic adsorption and complexation are mainly taking place. This happens because the positively charged ions present in the prepared M@Fu-based MOF, i.e., Zr^{4+}, La^{3+} and Fe^{3+} for Zr@Fu, La@Fu and Fe@Fu MOF, respectively, can attract the negatively charged fluoride anions.

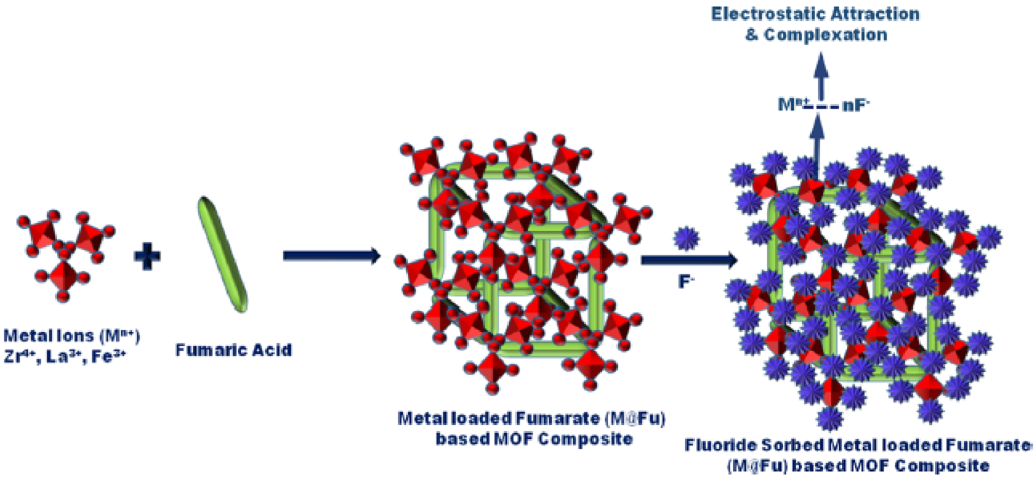


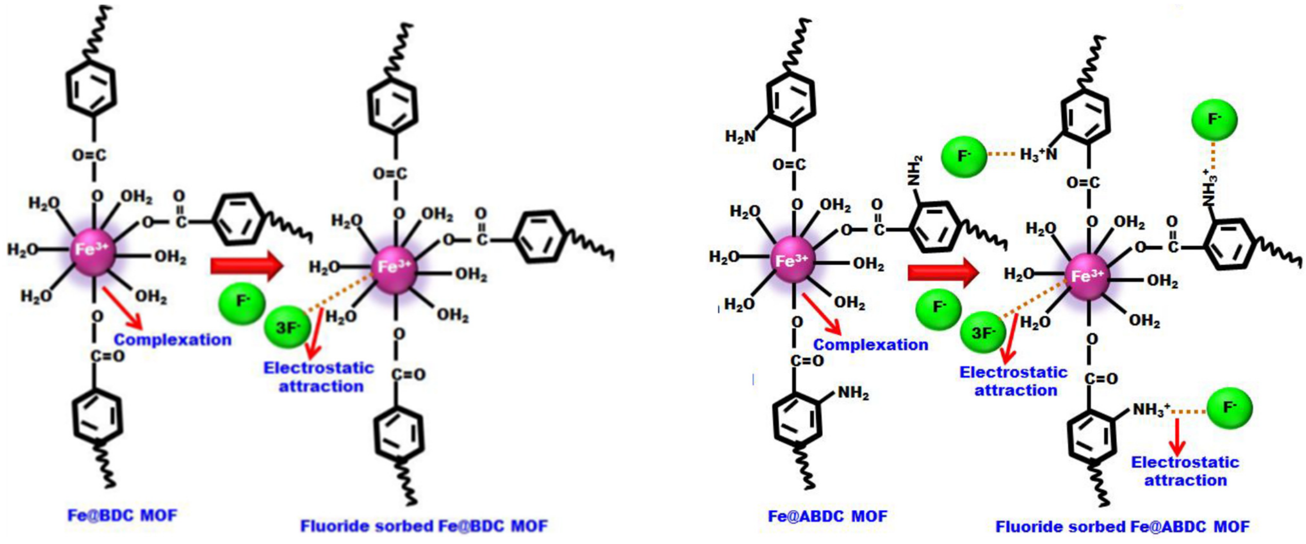
Figure 11. Fluoride adsorption mechanism of M@Fu-based MOF composites; reprinted with permission from [45].

The two lanthanide-based MOFs proposed in the study of Ma et al. [29], i.e., $[[Ce(L1)_{0.5}(NO_3)(H_2O)_2]\cdot 2DMF$ and $[Eu_3(L2)_2(OH)(DMF)_{0.22}(H_2O)_{5.78}]$,·have shown very good performance for the removal of fluoride. It was found that the $[[Ce(L1)_{0.5}(NO_3)(H_2O)_2]\cdot 2DMF$ material exhibits much higher adsorption capacity (103.95 mg/g) than the second one (57.01 mg/L), maybe due to the stronger interaction between fluoride and Ce. At lower (acidic) pH values, i.e., pH 3.0–7.0, the removal is higher, as the La-based MOFs are positively charged and the nucleophilic substitution of OH^- by F^- is favored. On the other hand, after the pH value reaches 8.0, the removal ability drops drastically due to the potential competition between F^- and OH^- anions. Furthermore, the ΔH^0 values for both adsorbents are positive (18.52 and 25.32 kJ/mol, respectively).

Another adsorbent, MOF1 ($\{[Zn_3L_3(BPE)_{1.5}]\cdot 4.5DMF\}n$) [55], showed high adsorption efficiency under both acidic and neutral pH conditions. The optimal pH range for the uptake of fluoride by MOF1 is between 4 and 10, and the rest of the experiments were conducted at the natural pH of drinking water. MOF1 was washed with methanol and reused after activation for five operational cycles, with only 10% reduction in efficiency. In addition, another zirconium based-MOF1, synthesized by Zhu et al. [56], showed that the adsorption efficiency reaches 92% within 30 min by applying a small dose of 0.2 g/L to efficiently treat the initial fluoride ion concentration of 10 mg/Lover a wide range of pH values (3.0–11.0). The calculated maximum adsorption capacity was found to be 240 mg/g, i.e., much higher than the aforementioned materials; seven cycles of adsorption-desorption experiments took place, and the results show that even after several times of reuse, the adsorbent is still sufficiently effective for the removal of fluoride.

When the Sn(II)-TMA MOF material [57] was used to treat the initial fluoride concentration of 12 mg/L, 84% removal efficiency was achieved over the pH range 3–10, leaving a residual concentration of fluoride anions close to the WHO limit of 1.5 mg/L. The maximum fluoride adsorption capacity was measured at 30.86 mg/g over the broad examined pH range (3.0–10.0) and by applying the optimum dose of 1.0 g/L. Kinetic experiments revealed that the fluoride adsorption onto the Sn(II)-TMA MOF is a combination of physisorption and chemisorption mechanisms. Looking for the most likely mechanism, the results showed that electrostatic interactions are primarily determining the adsorption of fluoride from waters in this case.

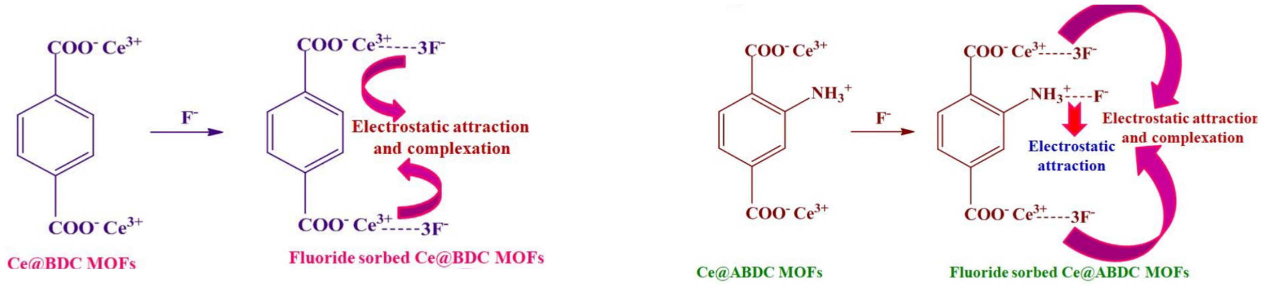
Jeyaseelan et al. [58] developed the Fe@BDC and Fe@ABDC MOF composites and examined them for the removal of fluoride. The highest fluoride adsorption was noticed at pH 7.0 for the fixed initial fluoride concentration (10 mg/L) by adding 0.1 g/L of Fe-based MOF and providing 4.90 or 4.92 mg/g adsorption capacities, respectively. Moreover, both enthalpy changes (ΔH^0) were positive, i.e., 0.56 and 1.24 kJ/mol for Fe@BDC and Fe@ABDC MOF composites, respectively, indicating that the process is endothermic in nature. The fluoride adsorption mechanisms of these MOF materials are controlled mainly by electrostatic attraction and complexation, as shown in Figure 12. The regeneration and recycling of Fe@BDC and Fe@ABDC MOF composites were performed for six operational cycles, using 0.1 M NaOH.



(**a**) (**b**)

Figure 12. Mechanisms of fluoride removal by using the following as sorbents: (**a**) Fe@BDC and (**b**) Fe@ABDC MOFs; reprinted with permission from [58].

Furthermore, regarding the cerium-based MOFs, Jeyaseelan et al. [59] also synthesized the Ce@BDC and Ce@ABDC MOF materials. The higher values of adsorption capacity (4.88 and 4.91 mg/g, respectively) were obtained for the solution pH values 6–7. As shown in Figure 13, positive Lewis acids, such as the Ce^{3+} ions, can significantly interact with the negatively charged Lewis base, such as the F^- ions, mainly by the electrostatic attraction mechanism. Additionally, in the case of Ce@ABDC MOFs, there are positively charged amine groups (NH_3^+) that can also attract fluoride anions via electrostatic forces. Moreover, both ΔH^0 values were found to be positive, i.e., 0.38 kJ/mol (for Ce@BDC) and 0.45 kJ/mol (for Ce@ABDC), indicating in this case the endothermic nature of the fluoride removal reaction. Finally, the recyclability of Ce@BDC and Ce@ABDC MOFs was high even after six cycles of adsorption–desorption studies in alkaline conditions (NaOH).



(**a**) (**b**)

Figure 13. Fluoride removal mechanisms when using (**a**) Ce@BDC and (**b**) Ce@ABDC MOF materials [59].

In the case of synthesized La@BTC MOF [60], which is one of the materials based on rare earth metals as central metals, the removal capacity was found to be 4.98 mg/g at the neutral pH. This gives the REM-based MOFs the advantage of being effective at various pH values. The thermodynamic analysis confirmed the spontaneous and endothermic (ΔH^0 0.58 kJ/mol) nature of fluoride adsorption in this case. The relevant fluoride adsorption mechanisms are depicted in Figure 14 and seem to also be complexation and electrostatic attraction. The La@BTC MOF regenerated up to six operational cycles, and NaOH was used as the eluent.

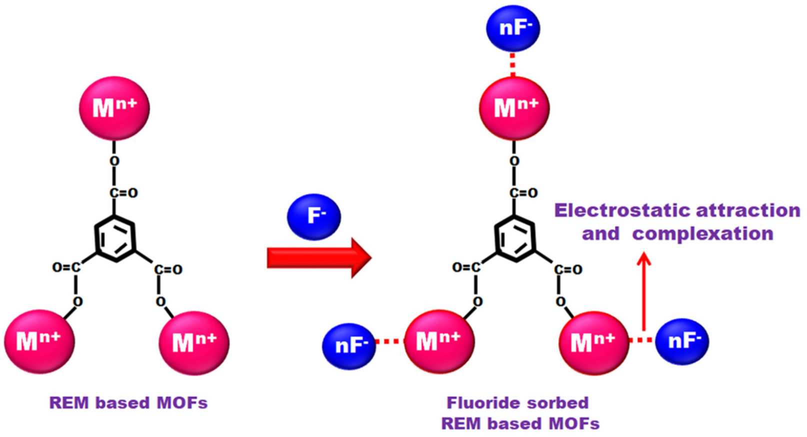


Figure 14. The probable fluoride adsorption mechanisms of rare earth metals (REM-based) MOFs; reprinted with permission from [60].

Yin et al. [61] also studied the lanthanum-based MOFs, such as La-BTC, La-BPDC, La-BHTA, La-PMA and La-BDC, having different organic (bridging) ligands, for the efficient removal of fluoride; 105.2, 125.9, 145.5, 158.9 and 171.7 mg/g, were the exhibited adsorption capacities, respectively, which were actually found to be higher than those of most of the other MOF materials, as comparatively analyzed in Table 3. The thermodynamics showed that the ΔH^0 values were in all these cases positive (19.68, 35.94, 25.66, 36.47 and 30.22 kJ/mole, respectively), demonstrating that the adsorption of fluoride was endothermic, and therefore enhanced by the increase of temperature. Moreover, the La-BTC, La-BPDC, La-BHTA, La-PMA and La-BDC MOFs are efficient over a wide pH range (4.0–9.0). Meanwhile, the main mechanisms taking place are electrostatic attraction and ligand exchange (Figure 15). It is worth noting that only a small addition of 0.15 g/L from La-BDC or La-BHTA MOF materials can decrease the fluoride concentration (from the relatively high initial concentration of 20 mg/L) to the WHO recommended drinking water limit.

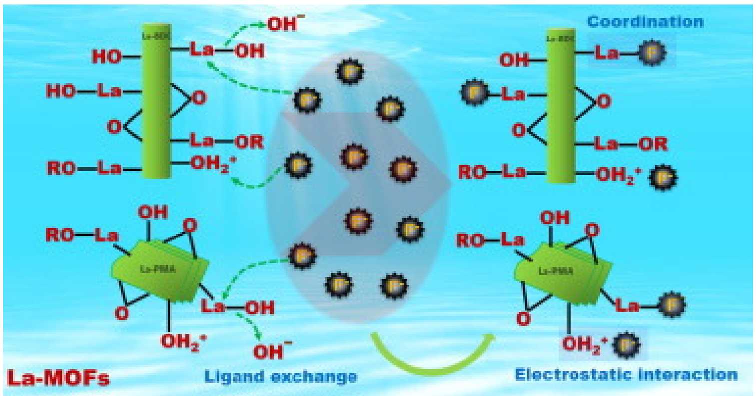


Figure 15. Schematic diagram of the main mechanisms for the case of La-based MOF materials regarding fluoride removal; reprinted with permission from [61].

The 3D rod-like bimetallic MOF, i.e., Fe-Al BDC [62], used for the removal of fluoride by the chemisorption mechanism, exhibited high removal efficiency by using 1.0 g/L and contact time 45 min at pH 7.0. The thermodynamic parameters exhibited that the adsorption in this case was spontaneous, and the ΔH^0 value was found to be −94.66 kJ/mol. As shown in Figure 16, the removal of F^- by using Fe-Al BDC MOF in an aqueous medium followed the surface-boundary-layer mechanism, which is based on electrostatic interactions.

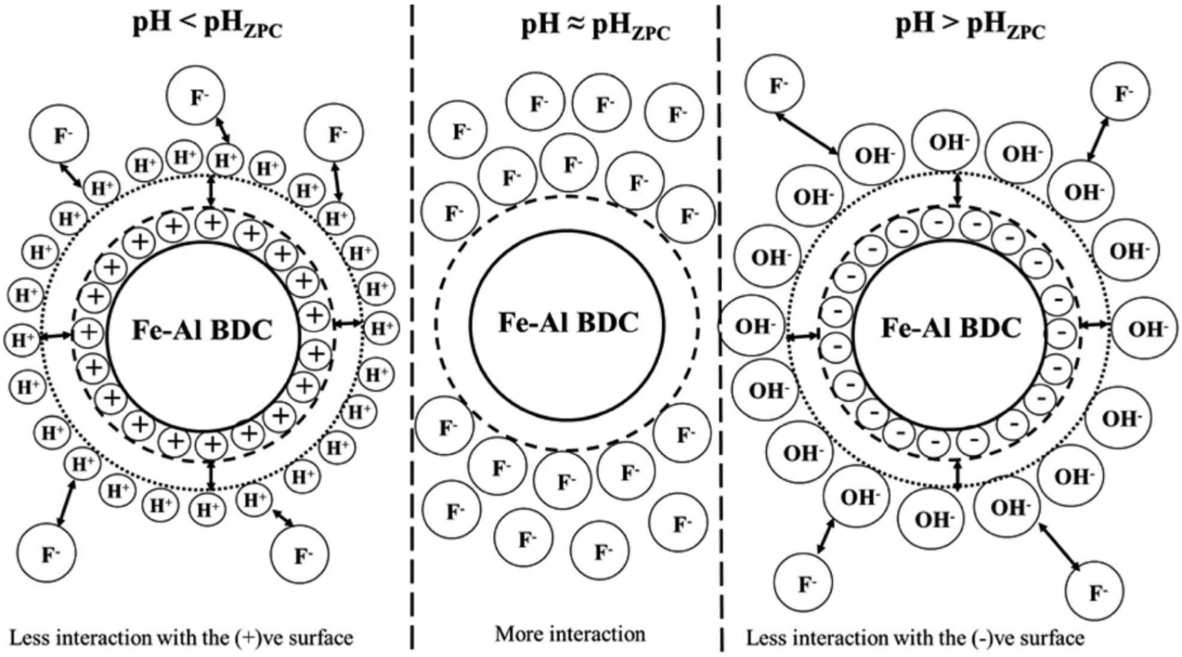


Figure 16. Schematic mechanism of F^- adsorption onto Fe-Al BDC MOF material by using the electrical double-layer model [62].

The three TDC-MOFs synthesized by Huang et al. [63], i.e., Al-TDC, Ce-TDC and Zr-TDC, displayed high chemical stability in a wide pH range (4–10) when used for the treatment of constant 5 mg/L initial fluoride concentration. The maximum adsorption capacities of Al-TDC, Ce-TDC and Zr-TDC MOFs for fluoride reached 107.5 mg/g, 94.9 mg/g and 97.0 m/g, respectively, which are among the highest values presented in Table 3. According to the XPS and FTIR characterization techniques conducted in this study, it is assumed that the leading mechanisms responsible for the adsorption of fluoride by the TDC-MOF materials were the ligand exchange and the electrostatic attraction (Figure 17). In addition, the literature showed that various characterization techniques supported fluoride adsorption through electrostatic, ion-exchange and hydrogen-bonding mechanisms [74–76]. The effect of pH showed that the adsorption capacity of Al-TDC increased significantly between the pH values 10.0 and 11.0, whereas for the cases of Zr-TDC and Ce-TDC MOFs, the adsorption was more favorable at pH values 3.0–4.0. The thermodynamics results showed that for all three TDC-MOFs, the ΔH^0 values were all negative, indicating an exothermic process. Furthermore, after four operational cycles using NaOH as the eluent, the adsorption/removal rates of Zr-TDC for fluoride were found to be still higher than 93% [63].

Moreover, the ZrFu MOF [64], i.e., a zirconium fumarate metal–organic framework, was found to be effective for fluoride removal under the optimum selected conditions (i.e., dose of 1.0 g/L, initial fluoride concentration of 10 mg/L, pH 6.0), removing fluoride almost completely and presenting an adsorption capacity 49.66 mg/g.

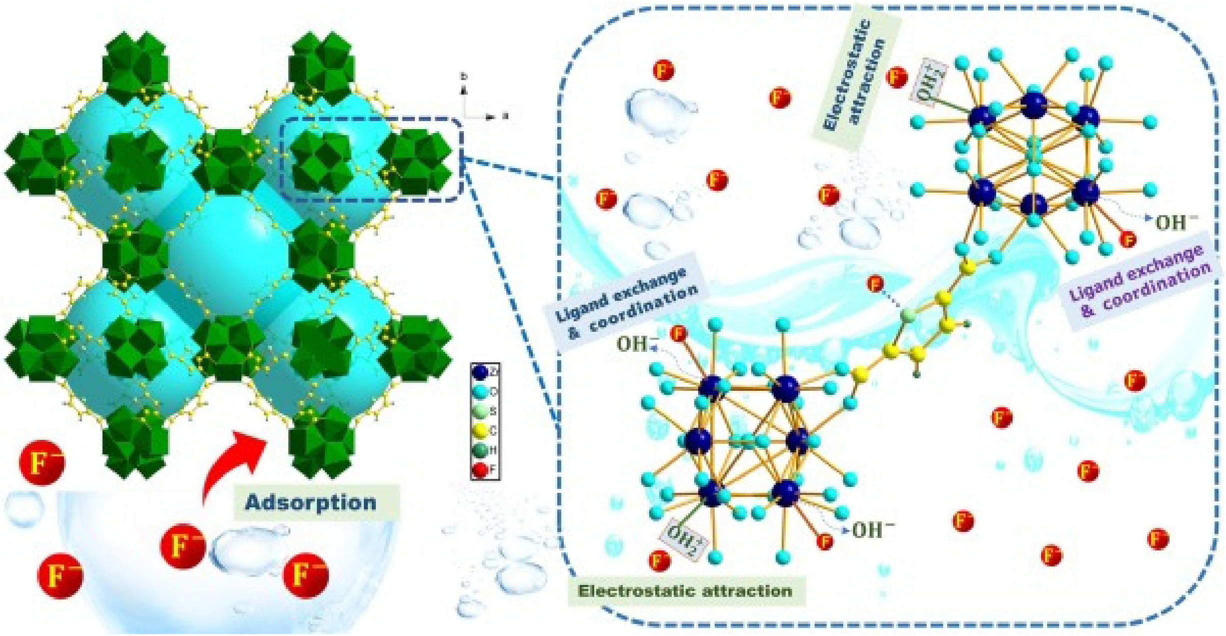


Figure 17. Probable mechanism model for the capture of fluoride by the TDC-MOF material; reprinted with permission from [63].

Regarding the studies of the zirconium fumarate metal–organic framework-801 (MOF-801), Zhu et al. [65] determined the respective fluoride adsorption capacity of this material (40 mg/g) through batch experiments; 0.7 g/L of this MOF found to be the optimum dosage to successfully remove 10 mg/L initial concentration of fluoride solution. The displayed results showed that it was not necessary to adjust the pH during the experiments, and, in fact, the major mechanism for the effective defluoridation treatment was the ion exchange between the fluoride ions and the hydroxyl groups of MOF-801. Regarding the mechanism of fluoride removal by MOF-801, Tan et al. [66] reached the same conclusion. As shown in Figure 18, the hydroxyl groups attached to Zr within the structure of MOF-801, upon the application of fluoride solution, are replaced by the fluoride ions through this anion exchange mechanism. Moreover, the electrostatic interaction between Zr^{4+} and F^- is described in the following Equation (1):

$$\mathrm{Zr-OH} + \mathrm{F}^- \rightarrow \mathrm{Zr-F} + \mathrm{OH}^- \quad (1)$$

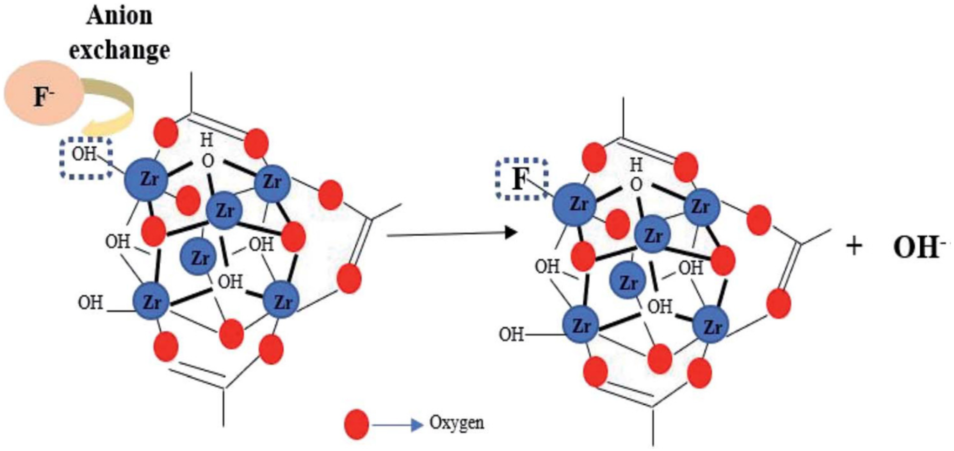


Figure 18. Proposed mechanism of MOF-801 material for fluoride adsorption [66].

In this study, the maximum adsorption capacity was found to be 19.42 mg/g, and the MOF-801 used up to four treatment cycles for the removal of fluoride, still reaching a 79% removal rate and hence suggesting that this is a material with very good reusability. NaOH was found to enhance the replacement of OH^- by F^- and was used to regenerate MOF-801.

Furthermore, several studies were conducted by using the novel University of Oslo (UiO-66) types of MOF materials. Particularly, Massoudinejad et al. [72] studied the use of Uio-66 for the removal of fluoride. The maximum capacity was found to be 31.09 mg/g by applying the optimum determined conditions, i.e., pH 7.0, initial fluoride concentration 14.6 mg/L, dosage 0.4 g/L and contact time 41.5 min, leading to the residual concentration of 1 mg fluoride/L (i.e., achieving 80.2% removal); therefore, it was a very good result regarding fluoride treatment in contaminated waters. Recently, Lacalamita et al. [68] modified the UiO-66 MOF material with amino groups, thus forming the UiO-66-NH_2 composite. The presence of amino groups provided several hydrogen bonds, which enhanced the adsorption of fluoride through the improvement of electrostatic attractions. The results showed that 70–80% of fluoride can be removed within 60 min by adding 2.0 g/L of UiO-66-NH_2 without changing the initial pH value. Another modification for the UiO-66 MOF can be found in the study of Zhao et al. [69], where the La anchored Zr-based hybrid MOF (La-UiO-66-$(COOH)_2$) adsorbent was produced; this adsorbent exhibited adequate adsorption capacity (57.23 mg/g) over a wide pH range (3.0–9.0), removing 87% of fluoride anions within just 5 min. The point of zero charge (pzc) for the La-UiO-66-$(COOH)_2$ was determined at the pH value 3.35. Thus, regarding the mechanism that occurs, when pH < 3.35, the electrostatic attractions between the positively charged La-UiO-66-$(COOH)_2$ and the negative fluoride ions prevails, whereas at pH values > 3.35, mainly the ion exchange mechanism occurs. According to thermodynamics, this adsorption process was spontaneous and endothermic. Four adsorption–desorption cycles were conducted, and at the end of the fourth cycle, the fluoride removal rate still remained at 79.7% [69].

Finally, the Materials Institute Lavoisier family MOFs are considered as promising materials for the removal of fluoride. MIL-96(RM) MOF [70] was effective over a wide pH range; the adsorption process was found to be spontaneous and endothermic, and the main mechanism in this case was the exchange between the F^- and OH^- ions. The maximum adsorption capacity was determined to be 82.65 mg/g, and the MIL-96(RM) material was reused after regeneration treatment with NaOH solution up to seven cycles. In addition, another material from the MIL family, MIL-53 (Fe) [73], demonstrated high removal rate for F^- (95.6%); however, it showed lower capacity (4.34 mg/g) under the optimal experimental conditions (i.e., pH 4.0, dose 0.25 g/L of MIL-53 (Fe), treating 10 mg/L initial fluoride concentration within 60 min contact time).

To conclude, several MOF materials have been used for the efficient adsorption of fluoride, proving to be a promising method for the removal of fluoride ions from contaminated waters.

5. Future Perspectives

As can be seen from the literature, there are many factors that can affect the effectiveness of MOFs, both in general and in the case of fluoride ion removal [28,32]. The ultimate goal in the research field of MOFs is to make them functional and suitable for real-world applications using real water or wastewater to develop a more comprehensive and accurate approach to future actions. Increasing the active sites by adding functional groups that attract fluoride ions is the main regulatory factor for adsorption. When selecting the appropriate MOF for defluorination, its adsorption capacity and stability should be considered over a wide pH range. Furthermore, the effect of co-ions should be minimal on MOFs, as they hinder fluoride adsorption, mainly from ion-abundant groundwaters. The formation of MOFs with specific metals such as Ca, Mg, Ce, Fe, etc., which have a high affinity to interact with fluoride ions [14,19,77], thus enhancing their adsorption capacity, should be considered. Therefore, an important point to consider when designing a high-stability MOF is the bond strength between the metal and linker.

In conclusion, the environmentally friendly, cost-effective design and fabrication of MOFs composites that can function at different pH conditions, even at high temperatures, are the main research goals. Due to their high cost, there is still a long research road to be able to use MOFs for large-scale fluoride removal facilities. Therefore, future research efforts are expected to address functional and practical problems in their use, as well as issues related to the commercialization of MOFs.

6. Conclusions

In recent years, the potential of using metal–organic framework (MOF) materials to remove fluoride anions from polluted waters has been increasingly researched, as they are very competitive in the field of adsorption for the removal of dissolved anions. This review focuses on the synthesis and relevant applications of MOFs and their derivatives, as found in the respective literature, emphasizing the research performed during the last five years.

The conventional method most commonly used for the preparation of respective MOFs is the hydrothermal/solvothermal method. Several types of MOFs have been synthesized and applied for the removal of fluoride. Furthermore, regarding the properties and the characteristics of these materials, the highest BET surface area was shown by MOFs based on aluminum metal ions, i.e., AlFu (1156.0 m^2/g), Al-MOF-5 (1264.0 m^2/g) and Al-TDC (1251.73 m^2/g), followed by those that have the zirconium metal in their structure. Regarding the average pore size (nm), the Zn-MOF-801 material presented the lowest value (0.06 nm). The total pore volume was relatively similar for all materials. The high surface area and the microporous morphology are likely to benefit the adsorption performance. The main parameters affecting adsorption, i.e., the effect of initial fluoride concentration, adsorbent dosage, solution pH, contact time, adsorption capacity and thermodynamic and regeneration studies, were correlated and analyzed.

Various MOFs have been used for effective fluoride adsorption, and according to the presented results, in most cases, the initial fluoride concentration was 10 mg/L. Only in the case of La-UiO-66-$(COOH)_2$ was a very high initial concentration (100 mg/L) examined. Regarding the dosage/concentration of MOFs applied, the highest used was 3 g/L (ZrFu) and the lowest was 0.1 g/L. The most common pH for conducting experiments was 7.0, but several materials were effective over a wide pH range. A total of 4–6 regeneration cycles were applied successfully on average, regarding the reviewed MOFs, without substantial decrease of efficiency, by using, in most cases, an NaOH solution as the regeneration agent. In the majority of them, the process was found to be endothermic in nature, except for a few cases where it was exothermic, according to thermodynamics. However, what is worth noting is the very high adsorption capacity shown by the homometallic AlFu material, i.e., 600 mg/g, as compared to all the other materials, which also exhibited the highest BET surface area, a fact that possibly explains this high capacity.

Author Contributions: Data curation, A.K.T.; investigation, A.K.T.; methodology, A.K.T.; writing—original draft, A.K.T.; validation, A.I.Z.; visualization, A.K.T. and A.I.Z.; writing—review and editing, A.K.T. and A.I.Z.; supervision, A.I.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Yan, C.; Jin, J.; Wang, J.; Zhang, F.; Tian, Y.; Liu, C.; Zhang, F.; Cao, L.; Zhou, Y.; Han, Q. Metal–organic frameworks (MOFs) for the efficient removal of contaminants from water: Underlying mechanisms, recent advances, challenges, and future prospects. *Coord. Chem. Rev.* **2022**, *468*, 214595. [CrossRef]
2. Gao, Q.; Xu, J.; Bu, X.H. Recent advances about metal–organic frameworks in the removal of pollutants from wastewater. *Coord. Chem. Rev.* **2019**, *378*, 17–31. [CrossRef]
3. Tang, X.; Zhou, C.; Xia, W.; Liang, Y.; Zeng, Y.; Zhao, X.; Xiong, W.; Cheng, M.; Wang, Z. Recent advances in metal–organic framework-based materials for removal of fluoride in water: Performance, mechanism, and potential practical application. *Chem. Eng. J.* **2022**, *446*, 137299. [CrossRef]
4. Vishwas, H.; Chatterjee, R.; Majumder, C. Removal of fluoride from contaminated water by metal organic framework adsorbent—Review. *J. Indian Chem. Soc.* **2020**, *97*, 2854–2858.
5. WHO. World Health Organization European Standards for Drinking-Water. *Am. J. Med. Sci.* **1970**, *242*, 56.
6. Herschy, R.W. Water quality for drinking: WHO guidelines. *Encycl. Earth Sci. Ser.* **2012**, *242*, 876–883. [CrossRef]
7. Singh, J.; Singh, P.; Singh, A. Fluoride ions vs. removal technologies: A study. *Arab. J. Chem.* **2016**, *9*, 815–824. [CrossRef]
8. Ye, Y.; Yang, J.; Jiang, W.; Kang, J.; Hu, Y.; Ngo, H.H.; Guo, W.; Liu, Y. Fluoride removal from water using a magnesia-pullulan composite in a continuous fixed-bed column. *J. Environ. Manag.* **2018**, *206*, 929–937. [CrossRef]
9. Wang, L.; Zhang, Y.; Sun, N.; Sun, W.; Hu, Y.; Tang, H. Precipitation methods using calcium-containing ores for fluoride removal in wastewater. *Minerals* **2019**, *9*, 511. [CrossRef]
10. Bhattacharya, P.; Roy, A.; Sarkar, S.; Ghosh, S.; Majumdar, S.; Chakraborty, S.; Mandal, S.; Mukhopadhyay, A.; Bandyopadhyay, S. Combination technology of ceramic microfiltration and reverse osmosis for tannery wastewater recovery. *Water Resour. Ind.* **2013**, *3*, 48–62. [CrossRef]
11. Mohamed, A.; Valadez Sanchez, E.P.; Bogdanova, E.; Bergfeldt, B.; Mahmood, A.; Ostvald, R.V.; Hashem, T. Efficient fluoride removal from aqueous solution using zirconium-based composite nanofiber membranes. *Membranes* **2021**, *11*, 147. [CrossRef] [PubMed]
12. Plattner, J.; Naidu, G.; Wintgens, T.; Vigneswaran, S.; Kazner, C. Fluoride removal from groundwater using direct contact membrane distillation (DCMD) and vacuum enhanced DCMD (VEDCMD). *Sep. Purif. Technol.* **2017**, *180*, 125–132. [CrossRef]
13. Tolkou, A.K.; Meez, E.; Kyzas, G.Z.; Torretta, V.; Collivignarelli, M.C.; Caccamo, F.M.; Deliyanni, E.A.; Katsoyiannis, I.A. A Mini Review of Recent Findings in Cellulose-, Polymer- and Graphene-Based Membranes for Fluoride Removal from Drinking Water. *C* **2021**, *7*, 74. [CrossRef]
14. Tolkou, A.K.; Mitrakas, M.; Katsoyiannis, I.A.; Ernst, M.; Zouboulis, A.I. Fluoride removal from water by composite Al/Fe/Si/Mg pre-polymerized coagulants: Characterization and application. *Chemosphere* **2019**, *231*, 528–537. [CrossRef] [PubMed]
15. Tolkou, A.K.; Manousi, N.; Zachariadis, G.A.; Katsoyiannis, I.A.; Deliyanni, E.A. Recently developed adsorbing materials for fluoride removal from water and fluoride analytical determination techniques: A review. *Sustainability* **2021**, *13*, 7061. [CrossRef]
16. Tolkou, A.K.; Trikkaliotis, D.G.; Kyzas, G.Z.; Katsoyiannis, I.A.; Deliyanni, E.A. Simultaneous Removal of As(III) and Fluoride Ions from Water Using Manganese Oxide Supported on Graphene Nanostructures (GO-MnO2). *Sustainability* **2023**, *15*, 1179. [CrossRef]
17. Kyzas, G.Z.; Tolkou, A.K.; Al Musawi, T.J.; Mengelizadeh, N.; Mohebi, S.; Balarak, D. Fluoride Removal from Water by Using Green Magnetic Activated Carbon Derived from Canola Stalks. *Water Air Soil Pollut.* **2022**, *233*, 424. [CrossRef]
18. Tolkou, A.K.; Zouboulis, A.I. Application of composite pre-polymerized coagulants for the treatment of high-strength industrial wastewaters. *Water* **2020**, *12*, 1258. [CrossRef]
19. Tolkou, A.K.; Trikalioti, S.; Makrogianni, O.; Trikkaliotis, D.G.; Deliyanni, E.A.; Kyzas, G.Z.; Katsoyiannis, I.A. Magnesium modified activated carbons derived from coconut shells for the removal of fluoride from water. *Sustain. Chem. Pharm.* **2023**, *31*, 100898. [CrossRef]
20. Damte, E.M. Removal of Fluoride From Water Using Granular Aluminium Hydroxide: Adsorption in a Fixed-Bed Column Removal of Fluoride From Water Using Granular Aluminium Hydroxide: Adsorption in a Fixed-Bed Column. Ph.D. Thesis, Addis Ababa University, Addis Ababa, Ethiopia, 2006.
21. Wan, S.; Lin, J.; Tao, W.; Yang, Y.; Li, Y.; He, F. Enhanced Fluoride Removal from Water by Nanoporous Biochar-Supported Magnesium Oxide. *Ind. Eng. Chem. Res.* **2019**, *58*, 9988–9996. [CrossRef]

22. Zhou, N.; Guo, X.; Ye, C.; Yan, L.; Gu, W.; Wu, X.; Zhou, Q.; Yang, Y.; Wang, X.; Cheng, Q. Enhanced fluoride removal from drinking water in wide pH range using La/Fe/Al oxides loaded rice straw biochar. *Water Supply* **2022**, *22*, 779–794. [CrossRef]
23. Xuebin, L.; Chunhui, L.; Jin, T.; Puli, Z.; Bin, Z.; Duo, B. Simultaneous removal of fluoride and arsenic in geothermal water in Tibet using modified yak dung biochar as an adsorbent. *R. Soc. Open Sci.* **2018**, *5*, 181266. [CrossRef]
24. Xu, N.; Li, S.; Li, W.; Liu, Z. Removal of Fluoride by Graphene Oxide/Alumina Nanocomposite: Adsorbent Preparation, Characterization, Adsorption Performance and Mechanisms. *ChemistrySelect* **2020**, *5*, 1818–1828. [CrossRef]
25. Singh, N.; Kumari, S.; Goyal, N.; Khan, S. Al2O3/GO cellulose based 3D-hydrogel for efficient fluoride removal from water. *Environ. Nanotechnol. Monit. Manag.* **2021**, *15*, 100444. [CrossRef]
26. Chen, J.; Yang, R.; Zhang, Z.; Wu, D. Removal of fluoride from water using aluminum hydroxide-loaded zeolite synthesized from coal fly ash. *J. Hazard. Mater.* **2022**, *421*, 126817. [CrossRef] [PubMed]
27. Geethamani, C.K.; Ramesh, S.T.; Gandhimathi, R.; Nidheesh, P.V. Alkali-treated fly ash for the removal of fluoride from aqueous solutions. *Desalin. Water Treat.* **2014**, *52*, 3466–3476. [CrossRef]
28. Ahmadijokani, F.; Molavi, H.; Rezakazemi, M.; Aminabhavi, T.M.; Arjmand, M. Simultaneous detection and removal of fluoride from water using smart metal-organic framework-based adsorbents. *Coord. Chem. Rev.* **2021**, *445*, 214037. [CrossRef]
29. Ma, A.; Ke, F.; Jiang, J.; Yuan, Q.; Luo, Z.; Liu, J.; Kumar, A. Two lanthanide-based metal-organic frameworks for highly efficient adsorption and removal of fluoride ions from water. *CrystEngComm* **2017**, *19*, 2172–2177. [CrossRef]
30. Ma, D.; Ma, D.; Li, Z.; Zhu, J.; Zhou, Y.; Chen, L.; Mai, X.; Liufu, M.; Wu, Y.; Li, Y. Inverse and highly selective separation of CO2/C2H2on a thulium-organic framework. *J. Mater. Chem. A* **2020**, *8*, 11933–11937. [CrossRef]
31. Liu, S.; Li, F.; Li, T.; Cao, W. High-performance ZnIn2S4/Ni(dmgH)2 for photocatalytic hydrogen evolution: Ion exchange construction, photocorrosion mitigation, and efficiency enhancement by photochromic effect. *J. Colloid Interface Sci.* **2023**, *642*, 100–111. [CrossRef]
32. Singh, N.; Dhillon, A.; Kumar, D. Metal-organic frameworks for adsorption of fluoride for groundwater treatment. *Groundw. Sustain. Dev.* **2023**, *23*, 100967. [CrossRef]
33. Karmakar, S.; Bhattacharjee, S.; De, S. Experimental and modeling of fluoride removal using aluminum fumarate (AlFu) metal organic framework incorporated cellulose acetate phthalate mixed matrix membrane. *J. Environ. Chem. Eng.* **2017**, *5*, 6087–6097. [CrossRef]
34. Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O.M. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* **1999**, *402*, 276–279. [CrossRef]
35. Liu, Y.; Cheng, M.; Liu, Z.; Zeng, G.; Zhong, H.; Chen, M.; Zhou, C.; Xiong, W.; Shao, B.; Song, B. Heterogeneous Fenton-like catalyst for treatment of rhamnolipid-solubilized hexadecane wastewater. *Chemosphere* **2019**, *236*, 124387. [CrossRef] [PubMed]
36. Rego, R.M.; Kuriya, G.; Kurkuri, M.D.; Kigga, M. MOF based engineered materials in water remediation: Recent trends. *J. Hazard. Mater.* **2021**, *403*, 123605. [CrossRef]
37. Liu, Y.; Huang, D.; Cheng, M.; Liu, Z.; Lai, C.; Zhang, C.; Zhou, C.; Xiong, W.; Qin, L.; Shao, B.; et al. Metal sulfide/MOF-based composites as visible-light-driven photocatalysts for enhanced hydrogen production from water splitting. *Coord. Chem. Rev.* **2020**, *409*, 213220. [CrossRef]
38. Karmakar, S.; Dechnik, J.; Janiak, C.; De, S. Aluminium fumarate metal-organic framework: A super adsorbent for fluoride from water. *J. Hazard. Mater.* **2016**, *303*, 10–20. [CrossRef]
39. Ahmadijokani, F.; Molavi, H.; Rezakazemi, M.; Tajahmadi, S.; Bahi, A.; Ko, F.; Aminabhavi, T.M.; Li, J.R.; Arjmand, M. UiO-66 metal–organic frameworks in water treatment: A critical review. *Prog. Mater. Sci.* **2022**, *125*, 100904. [CrossRef]
40. He, J.; Cai, X.; Chen, K.; Li, Y.; Zhang, K.; Jin, Z.; Meng, F.; Liu, N.; Wang, X.; Kong, L.; et al. Performance of a novelly-defined zirconium metal-organic frameworks adsorption membrane in fluoride removal. *J. Colloid Interface Sci.* **2016**, *484*, 162–172. [CrossRef]
41. Sapianik, A.A.; Fedin, V.P. Main Approaches to the Synthesis of Heterometallic Metal-Organic Frameworks. *Russ. J. Coord. Chem. Khimiya* **2020**, *46*, 443–457. [CrossRef]
42. Masoomi, M.Y.; Morsali, A.; Dhakshinamoorthy, A.; Garcia, H. Mixed-Metal MOFs: Unique Opportunities in Metal–Organic Framework (MOF) Functionality and Design. *Angew. Chemie-Int. Ed.* **2019**, *58*, 15188–15205. [CrossRef]
43. Castells-Gil, J.; Padial, N.M.; Almora-Barrios, N.; Gil-San-Millán, R.; Romero-Ángel, M.; Torres, V.; da Silva, I.; Vieira, B.C.J.; Waerenborgh, J.C.; Jagiello, J.; et al. Heterometallic Titanium-Organic Frameworks as Dual-Metal Catalysts for Synergistic Non-buffered Hydrolysis of Nerve Agent Simulants. *Chem* **2020**, *6*, 3118–3131. [CrossRef]
44. Trousselet, F.; Archereau, A.; Boutin, A.; Coudert, F.X. Heterometallic metal-organic frameworks of MOF-5 and UiO-66 families: Insight from computational chemistry. *J. Phys. Chem. C* **2016**, *120*, 24885–24894. [CrossRef]
45. Jeyaseelan, A.; Naushad, M.; Viswanathan, N. Development of Multivalent Metal-Ion-Fabricated Fumaric Acid-Based Metal-Organic Frameworks for Defluoridation of Water. *J. Chem. Eng. Data* **2020**, *65*, 2990–3001. [CrossRef]
46. Ramanayaka, S.; Vithanage, M.; Sarmah, A.; An, T.; Kim, K.H.; Ok, Y.S. Performance of metal-organic frameworks for the adsorptive removal of potentially toxic elements in a water system: A critical review. *RSC Adv.* **2019**, *9*, 34359–34376. [CrossRef]
47. Dey, C.; Kundu, T.; Biswal, B.P.; Mallick, A.; Banerjee, R. Crystalline metal-Organic frameworks (MOFs): Synthesis, structure and function. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* **2014**, *70*, 3–10. [CrossRef] [PubMed]
48. Das, A.K.; Vemuri, R.S.; Kutnyakov, I.; McGrail, B.P.; Motkuri, R.K. An Efficient Synthesis Strategy for Metal-Organic Frameworks: Dry-Gel Synthesis of MOF-74 Framework with High Yield and Improved Performance. *Sci. Rep.* **2016**, *6*, 28050. [CrossRef]

49. Khan, M.S.; Shahid, M. Synthesis of metal-organic frameworks (MOFs): Routes to various MOF topologies, morphologies, and composites. In *Electrochemical Applications of Metal-Organic Frameworks*; Elsevier: Amsterdam, The Netherlands, 2022; pp. 17–35. [CrossRef]
50. Bedia, J.; Muelas-Ramos, V.; Peñas-Garzón, M.; Gómez-Avilés, A.; Rodríguez, J.J.; Belver, C. A review on the synthesis and characterization of metal organic frameworks for photocatalytic water purification. *Catalysts* **2019**, *9*, 52. [CrossRef]
51. Huang, X.; Huang, L.; Babu Arulmani, S.R.; Yan, J.; Li, Q.; Tang, J.; Wan, K.; Zhang, H.; Xiao, T.; Shao, M. Research progress of metal organic frameworks and their derivatives for adsorption of anions in water: A review. *Environ. Res.* **2022**, *204*, 112381. [CrossRef]
52. Klimakow, M.; Klobes, P.; Thünemann, A.F.; Rademann, K.; Emmerling, F. Mechanochemical synthesis of metal-organic frameworks: A fast and facile approach toward quantitative yields and high specific surface areas. *Chem. Mater.* **2010**, *22*, 5216–5221. [CrossRef]
53. Ren, Y.; Wu, F.; Qu, G.; Ren, N.; Ning, P.; Chen, X.; He, M.; Yang, Y.; Wang, Z.; Hu, Y. Extraction and preparation of metal organic frameworks from secondary aluminum ash for removal mechanism study of fluoride in wastewater. *J. Mater. Res. Technol.* **2023**, *23*, 3023–3034. [CrossRef]
54. Wang, X.; Liu, K.; Zhu, H.; Sun, T.; Han, T.; Li, J.; Dai, H. An effective and selective stable metal-organic framework adsorben(Al-mof-5) for the removal of fluoride from water. *Desalin. Water Treat.* **2021**, *216*, 220–231. [CrossRef]
55. Aliakbari, M.; Gholami, R.M.; Borghei, S.M. A zwitterion metal-organic framework for the removal of fluoride from an aqueous solution. *J. Chem. Sci.* **2022**, *134*, 74. [CrossRef]
56. Zhu, L.; Zhang, C.; Wang, L.; Zhang, J. The simple synthesis of metal organic frameworks with high fluoride adsorption performance from water. *J. Solid State Chem.* **2022**, *307*, 122866. [CrossRef]
57. Ghosh, A.; Das, G. Green synthesis of a novel water-stable Sn(ii)-TMA metal-organic framework (MOF): An efficient adsorbent for fluoride in aqueous medium in a wide pH range. *New J. Chem.* **2020**, *44*, 1354–1361. [CrossRef]
58. Jeyaseelan, A.; Naushad, M.; Ahamad, T.; Viswanathan, N. Design and development of amine functionalized iron based metal organic frameworks for selective fluoride removal from water environment. *J. Environ. Chem. Eng.* **2021**, *9*, 104563. [CrossRef]
59. Jeyaseelan, A.; Naushad, M.; Ahamad, T.; Viswanathan, N. Fabrication of amino functionalized benzene-1,4-dicarboxylic acid facilitated cerium based metal organic frameworks for efficient removal of fluoride from water environment. *Environ. Sci. Water Res. Technol.* **2021**, *7*, 384–395. [CrossRef]
60. Jeyaseelan, A.; Viswanathan, N. Facile synthesis of tunable rare earth based metal organic frameworks for enhanced fluoride retention. *J. Mol. Liq.* **2021**, *326*, 115163. [CrossRef]
61. Yin, C.; Huang, Q.; Zhu, G.; Liu, L.; Li, S.; Yang, X.; Wang, S. High-performance lanthanum-based metal–organic framework with ligand tuning of the microstructures for removal of fluoride from water. *J. Colloid Interface Sci.* **2022**, *607*, 1762–1775. [CrossRef]
62. Mukherjee, A.; Dhak, P.; Dhak, D. The solvothermal synthesis of a 3D rod-like Fe–Al bimetallic metal–organic-framework for efficient fluoride adsorption and photodegradation of water-soluble carcinogenic dyes. *Environ. Sci. Adv.* **2022**, *1*, 121–137. [CrossRef]
63. Huang, Q.; Zhao, L.; Zhu, G.; Chen, D.; Ma, X.; Yang, X.; Wang, S. Outstanding performance of thiophene-based metal-organic frameworks for fluoride capture from wastewater. *Sep. Purif. Technol.* **2022**, *298*, 121567. [CrossRef]
64. Kumari, R.; Kumar, A.; Sarkar, S.; Ghosh, T.K.; Basu, S. Zirconium fumarate metal-organic framework: A selective adsorbent for fluoride from industrial wastewater. *Water Pract. Technol.* **2023**, *18*, 1074–1085. [CrossRef]
65. Zhu, X.H.; Yang, C.X.; Yan, X.P. Metal-organic framework-801 for efficient removal of fluoride from water. *Microporous Mesoporous Mater.* **2018**, *259*, 163–170. [CrossRef]
66. Tan, T.L.; Krusnamurthy, P.A.; Nakajima, H.; Rashid, S.A. Adsorptive, kinetics and regeneration studies of fluoride removal from water using zirconium-based metal organic frameworks. *RSC Adv.* **2020**, *10*, 18740–18752. [CrossRef] [PubMed]
67. Massoudinejad, M.; Shahsavani, A.; Kamarehie, B.; Jafari, A.; Ghaderpoori, M.; Amini, M.M.; Ghaderpoury, A. Highly efficient adsorption of fluoride from aqueous solutions by metal organic frameworks: Modeling, isotherms, and kinetics. *Fluoride* **2018**, *51*, 355–365.
68. Lacalamita, D.; Hoyez, G.; Mongioví, C.; Ponchel, A.; Morin-Crini, N.; Rousseau, C.; Loup, C.; Rousseau, J.; Raschetti, M.; Monflier, E.; et al. Efficient removal of fluoride ions present in industrial effluents using metal-organic frameworks of UiO-66-NH_2. *J. Water Process Eng.* **2023**, *53*, 103791. [CrossRef]
69. Zhao, X.; Zhang, J.; Dai, Z.; Lei, Y.; Liu, X.; Liu, G. Simple preparation and efficient fluoride removal of la anchored Zr-based metal-organic framework adsorbent. *J. Environ. Chem. Eng.* **2022**, *10*, 108807. [CrossRef]
70. Wang, X.; Zhu, H.; Sun, T.; Dai, H. Synthesis of a Matériaux Institut Lavoisier metal-organic framework 96 (MIL-96(RM)) using red mud and its application to defluorination of water. *Mater. Today Commun.* **2020**, *25*, 101401. [CrossRef]
71. Mohammadi, A.A.; Niazi, Z.; Heidari, K.; Afarinandeh, A.; Samadi Kazemi, M.; Haghighat, G.A.; Vasseghian, Y.; Rezania, S.; Barghi, A. Nickel and iron-based metal-organic frameworks for removal of organic and inorganic model contaminants. *Environ. Res.* **2022**, *212*, 113164. [CrossRef]
72. Massoudinejad, M.; Ghaderpoori, M.; Shahsavani, A.; Amini, M.M. Adsorption of fluoride over a metal organic framework Uio-66 functionalized with amine groups and optimization with response surface methodology. *J. Mol. Liq.* **2016**, *221*, 279–286. [CrossRef]

73. Hossien Saghi, M.; Chabot, B.; Rezania, S.; Sillanpää, M.; Akbar Mohammadi, A.; Shams, M.; Alahabadi, A. Water-stable zirconium and iron-based metal-organic frameworks (MOFs) as fluoride scavengers in aqueous medium. *Sep. Purif. Technol.* **2021**, *270*, 118645. [CrossRef]
74. Barathi, M.; Kumar, A.S.K.; Kodali, J.; Mittal, S.; Samhith, G.D.; Rajesh, N. Probing the Interaction between Fluoride and the Polysaccharides in Al(III)- and Zr (IV)-Modified Tea Waste by Using Diverse Analytical Characterization Techniques. *ChemistrySelect* **2017**, *2*, 10123–10135. [CrossRef]
75. Barathi, M.; Kumar, A.S.K.; Rajesh, N. Aluminium hydroxide impregnated macroreticular aromatic polymeric resin as a sustainable option for defluoridation. *J. Environ. Chem. Eng.* **2015**, *3*, 630–641. [CrossRef]
76. Barathi, M.; Krishna Kumar, A.S.; Kumar, C.U.; Rajesh, N. Graphene oxide-aluminium oxyhydroxide interaction and its application for the effective adsorption of fluoride. *RSC Adv.* **2014**, *4*, 53711–53721. [CrossRef]
77. Wu, T.; Mao, L.; Wang, H. Adsorption of fluoride from aqueous solution by using hybrid adsorbent fabricated with Mg/Fe composite oxide and alginate via a facile method. *J. Fluor. Chem.* **2017**, *200*, 8–17. [CrossRef]