Metal−Organic Framework-Based Materials for Adsorption and Detection of Uranium(VI) from Aqueous Solution

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ABSTRACT: The steady supply of uranium resources and the reduction or elimination of the ecological and human health hazards of wastewater containing uranium make the recovery and detection of uranium in water greatly important. Thus, the development of effective adsorbents and sensors has received growing attention. Metal−organic frameworks (MOFs) possessing fascinating characteristics such as high surface area, high porosity, adjustable pore size, and luminescence have been widely used for either uranium adsorption or sensing. Now pertinent research has transited slowly into simultaneous uranium adsorption and detection. In this review, the progress on the research of MOF-based materials used for both adsorption and detection of uranium in water is first summarized. The adsorption mechanisms between uranium species in aqueous solution and MOF-based materials are elaborated by macroscopic batch experiments combined with microscopic spectral technology. Moreover, the application of MOF-based materials as uranium sensors is focused on their typical structures, sensing mechanisms, and the representative examples. Furthermore, the bifunctional MOF-based materials used for simultaneous detection and adsorption of U(VI) from aqueous solution are introduced. Finally, we also discuss the challenges and perspectives of MOF-based materials for uranium adsorption and detection to provide a useful inspiration and significant reference for further developing better adsorbents and sensors for uranium containment and detection.

1. INTRODUCTION
The rapid growth of population and the world economy has made energy shortages a key consideration for every country. The gradual depletion of nonrenewable fossil energy sources such as oil, coal, and natural gas has made the development of efficient and clean new energy sources an urgent need, and the large-scale development of nuclear energy has become an inevitable choice.1−5 At the same time, radionuclide applications in military, industry, agriculture, medicine, and other scientific research fields are becoming more and more widespread. The amount of radioactive waste gas, wastewater, and solid wastes resulting from these applications is also increasing, especially the amount of radioactive wastewater, and the total amount of radioactivity it contains is very large.6,7 In radioactive wastewater, UO$_2^{2+}$ ion with a high water solubility and a half-life of up to 4.5 × 10$^9$ years can enter into the human body through groundwater and surface water and be deposited in our livers, kidneys, and bones, causing uranium poisoning.8−10 In addition, at the current rate of depletion, the entire land mass of uranium reserves will last less than a century,11 and the development of marine uranium resources (about 4.5 billion tons) which is nearly 1000 times the entire uranium reserves is of considerable significance for the sustainable and rapid development of the nuclear industry, as it can improve the overall utilization of available uranium resources.12−14 Based on the above-mentioned circumstances, detection, separation, and recovery of uranium are significant for both maintaining the ecology and rationally using uranium resources.

Many methods have been reported for the extraction of uranium in aqueous solutions, including chemical precipitation, biological treatment, evaporation concentration recovery, membrane filtration, ion exchange, and adsorption.15−21 However, most of these methods have some deficiencies. For instance, chemical precipitation and biological treatment, although low cost, cannot sufficiently reduce the concentration of uranium ions below the legally limited level while producing a large amount of sludge requiring secondary treatment. In
contrast, adsorption is a more promising technology because it has many advantages such as high efficiency, low cost, and ease of operation. Also, there are various methods to detect uranium in aqueous solutions, including X-ray fluorescence (XRF) spectroscopy, inductively coupled plasma mass spectrometry (ICP-MS), and laser-induced fluorescence (LIF), which have high sensitivity and accuracy. However, the disadvantages, such as the expensive operation and maintenance of the instruments and the requirement of complicated pretreatment procedures, limit their use for on-site and real-time detection of uranium, especially during the adsorption processes. Moreover, the adsorbent materials for uranium species accompanying the capability to simultaneously detect them are obviously more useful in uranium monitoring and remediation applications. Therefore, the development of convenient, effective, and on-site uranyl adsorbents, sensors, and adsorptive sensors have received more and more attention. Along with several other groups, we have recently focused our research on the adsorption, immobilization, and detection of uranium simultaneously.

Among various adsorbents and/or sensors of uranium, actinides, and heavy metals, in general, metal–organic frameworks (MOFs) have been widely explored due to their fascinating characteristics, such as high surface area, high porosity, tunable pore size, and luminescence features. MOFs are a class of compounds with one-, two-, or three-dimensional structures composed of metal ions or metal clusters ligated with organic ligands. MOFs are a subclass of coordination polymers and usually have porous properties. In some cases, the pores are usually used to eliminate guest molecules and can be refilled with other compounds. Therefore, MOFs are of interest for gas storage and separation, catalysis, water
purification and remediation, or sensing small molecules for environment pollutants, etc.\textsuperscript{38−41}

Currently, MOF-based materials are widely used for uranium adsorption and/or sensing. The developmental milestones of MOFs and MOF-based materials for adsorption and/or detection of U(VI) is illustrated in Figure 1. A safe special examples, the application of MOFs as novel adsorbents for the extraction of actinides, including uranium, from aqueous media was first reported by Carboni et al.\textsuperscript{42} Zhang et al.\textsuperscript{43} prepared coumarin-modified Zn-MOF-74 materials, reporting high adsorption capacity for U(VI) ions from water with maximum adsorption capacity of 360 mg/g, indicating it is a great potential adsorbent for the removal of uranium. For the uranium detection application of MOFs, [Cd_{3}(L)_{2}(bipy)-(H_{2}O)_{2}]·H_{2}O was synthesized as a luminescent sensor with a uranium detection limit of 0.9 μg/L.\textsuperscript{44} DUT-101 was constructed as the first reported dual-channel luminescence sensor for UO_{2}^{2+} with excellent sensitivity and selectivity.\textsuperscript{45}

There is also a class of bifunctional MOF materials that can simultaneously adsorb and detect uranium, such as the magnetic Fe_{2}O_{3}-CMC@ZIF-8@CD composite and MOF-76, which were reported by Guo et al.\textsuperscript{46} and Yang et al.,\textsuperscript{47} respectively. The current development of MOF-based materials with bifunctional capabilities of adsorption and detection is a promising and valuable research direction.

Several review papers have highlighted the potential application of MOF-based materials for simultaneous adsorption and detection of uranium, proving that they display great potential as uranium extraction adsorbents and detection sensors, not to mention on its bifunctional applications in simultaneous adsorption and detection of uranium.\textsuperscript{65−69} In order to fill this gap, we have thus reviewed the recent advances of different MOF-based materials used for both adsorption and sensing of uranium in water.

### Table 1. Adsorption Capacities and Main Parameters of Uranium Adsorption by MOF-Based Nanomaterials\textsuperscript{a}

| adsorbents                  | pH  | T (K) | Q_{max} (mg g^{-1}) | isotherm model | thermodynamics                | refs |
|-----------------------------|-----|-------|---------------------|----------------|-----------------------------|------|
| MIL-101-AO                  | 7   | 298   | 613.5               | Langmuir isotherm | endothermic/spontaneous     | 105  |
| Fe_{2}O_{3}@AMCA-MIL53(Al)  | 5.5 | 318   | 227.3               | Langmuir isotherm | endothermic/spontaneous     | 87   |
| MIL-101-Ship                | 4   | 298   | 27.99               | Langmuir model   | na                          | 91   |
| MIL-101-DETA                | 5.5 | 298   | 350                 | Langmuir model   | na                          | 52   |
| MIL-101-ED                  | 5.5 | 298   | 200                 | Langmuir model   | na                          | 52   |
| MOF-3                       | 7   | 298   | 314                 | Langmuir isotherm | na                          | 85   |
| MOF-5                       | 5   | 298   | 237                 | Langmuir model   | endothermic/spontaneous     | 75   |
| Y-MOF                       | 3   | 298   | 538                 | Langmuir isotherm | na                          | 90   |
| Sm-MOF                      | 3   | 298   | 265                 | Langmuir isotherm | na                          | 90   |
| Eu-MOF                      | 3   | 298   | 274                 | Langmuir isotherm | na                          | 90   |
| Gd-MOF                      | 3   | 298   | 371                 | Langmuir isotherm | na                          | 90   |
| Tb-MOF                      | 3   | 298   | 467                 | Langmuir isotherm | na                          | 90   |
| Dy-MOF                      | 3   | 298   | 478                 | Langmuir isotherm | na                          | 90   |
| Er-MOF                      | 3   | 298   | 515                 | Langmuir isotherm | na                          | 90   |
| Zn-MOF-74 w/coumarin (11.7 wt %) | 4.0 | 298 | 360 | na | na | 43 |
| Azo-MOFs                    | 6   | 298   | 3337.84             | Langmuir model   | endothermic/spontaneous     | 92   |
| ZIF-67                      | 4   | RT    | 1638.8              | Langmuir model   | na                          | 76   |
| PPy/ZIF-8                   | 3.5 | 318   | 534                 | Langmuir model   | endothermic/spontaneous     | 93   |
| Fe_{2}O_{3}@ZIF-8           | 3   | RT    | 523.5               | Langmuir model   | na                          | 109  |
| Fe@ZIF-8                    | 4.5 | 298   | 277.77              | Freundlich isotherm | na | 94 |
| rGO/ZIF-67 aerogel          | 4.01| 298   | 1888.55             | Langmuir model   | endothermic/spontaneous     | 2    |
| nZVI/Uio-66                 | 6   | 313   | 404.86              | Freundlich isotherm | endothermic/spontaneous     | 31   |
| UiO-8-F(O)(OEt)_{2}         | 2.5 | RT    | 217                 | Langmuir model   | na                          | 42   |
| UiO-66-NH_{2}               | 5.5 | 287   | 114.9               | Langmuir model   | na                          | 95   |
| UiO-66-NH_{2}/urea-POP      | 8   | RT    | 278                 | Langmuir model   | na                          | 96   |
| UiO-66-NH_{2}@CS-PDA        | 7   | 298   | 744.6               | Langmuir model   | endothermic/spontaneous     | 97   |
| PCN-222/GO-COOH            | 4   | 298   | 426                 | Langmuir model   | endothermic/spontaneous     | 72   |
| PCN-222-PA                  | 4.5 | 298   | 401.6               | Langmuir model   | na                          | 89   |
| PCN-222                     | 4.5 | 298   | 87                  | Langmuir model   | na                          | 89   |
| HKUST-1                     | 6   | 318   | 840.3               | Langmuir model   | endothermic/spontaneous     | 73   |
| MSONs-5                     | 4.0 | 298   | 526.6               | Langmuir isotherm | endothermic/spontaneous     | 98   |
| porous Cu-BTC              | 7   | 298   | 423.7               | Langmuir isotherm | endothermic/spontaneous     | 99   |
| La-PDA                      | 4   | 298   | 247.6               | Freundlich isotherm | endothermic/spontaneous     | 100  |
| DSHM-DAMN                   | 8   | 298   | 601                 | Langmuir model   | endothermic/spontaneous     | 101  |
| Zn(HTC)(L)_{2}(H_{2}O)_{2}  | 2   | 298   | 125.9               | Langmuir model   | endothermic/spontaneous     | 91   |
| HKUST-1H_{3}PW_{12}O_{40}   | 6   | 298   | 14.58               | Langmuir model   | endothermic/spontaneous     | 102  |
| SZ-3                        | 4.5 | RT    | 58.18               | Langmuir model   | na                          | 53   |
| ECUT-100                    | 5   | 298   | 381                 | Langmuir model   | na                          | 103  |

\textsuperscript{a}RT, room temperature; na, not available. $Q_{max}$ (mg g^{-1}) is the maximum adsorption capacity of U(VI) with the Langmuir model.
In this review, the elaboration of the uranium adsorption properties and mechanisms on MOF-based materials will be demonstrated using techniques such as macroscopic batch experiment, microscopic spectroscopy analysis, and theoretical calculations. The applications of MOF-based materials as uranium sensors will be firstly focused on their typical structures, sensing mechanisms, and some representative examples. The bifunctional MOF-based materials used as both adsorbents and sensors to simultaneously detect and adsorb U(VI) from aqueous solution will be then introduced. Current challenges and future perspectives of MOF-based materials for uranium adsorption and detection applications will also be discussed. We believe this review will bring about useful inspiration and significant reference to drive future research on MOF-based materials for uranium removal and sensing applications together.

2. MOF-BASED MATERIALS FOR URANIUM ADSORPTION

2.1. Classification and Adsorption Capacities of MOF-Based Materials. MOFs can be mainly classified into the following six categories:70−72 (1) Zeolitic imidazolate frameworks (ZIF) are MOFs with the zeolite structure synthesized by Zn(II) or Co(II) and imidazole ligand. (2) UiO (University of Oslo) materials are a zirconium-containing regular octahedral \([\text{Zr}_6\text{O}_4(\text{OH})_4]\) cluster directly connected with 12 organic ligands of terephthalic acid, forming a three-dimensional microporous structure containing an octahedral central pore cage and eight tetrahedral angle cages. (3) Materials of Institute Lavoisier (MIL) frameworks are formed by the coordination of metal ions such as Al\(^3\), Cr\(^3\), and Fe\(^3\) with dicarboxylic acid ligands. (4) Coordination pillared layer (CPL) materials are formed by the combination of hexagonal microporous structure containing an octahedral central pore cage and eight tetrahedral angle cages. (5) Materials of Institute Lavoisier (MIL) frameworks are formed by the coordination of metal ions such as Al\(^3\), Cr\(^3\), and Fe\(^3\) with dicarboxylic acid ligands. (4) Coordination pillared layer (CPL) materials are formed by the combination of hexagonal microporous structure containing an octahedral central pore cage and eight tetrahedral angle cages. (3) Materials of Institute Lavoisier (MIL) frameworks are formed by the coordination of metal ions such as Al\(^3\), Cr\(^3\), and Fe\(^3\) with dicarboxylic acid ligands. (4) Coordination pillared layer (CPL) materials are formed by the combination of hexagonal microporous structure containing an octahedral central pore cage and eight tetrahedral angle cages. (3) Materials of Institute Lavoisier (MIL) frameworks are formed by the coordination of metal ions such as Al\(^3\), Cr\(^3\), and Fe\(^3\) with dicarboxylic acid ligands. (4) Coordination pillared layer (CPL) materials are formed by the combination of hexagonal microporous structure containing an octahedral central pore cage and eight tetrahedral angle cages. (3) Materials of Institute Lavoisier (MIL) frameworks are formed by the coordination of metal ions such as Al\(^3\), Cr\(^3\), and Fe\(^3\) with dicarboxylic acid ligands. (4) Coordination pillared layer (CPL) materials are formed by the combination of hexagonal microporous structure containing an octahedral central pore cage and eight tetrahedral angle cages. (3) Materials of Institute Lavoisier (MIL) frameworks are formed by the coordination of metal ions such as Al\(^3\), Cr\(^3\), and Fe\(^3\) with dicarboxylic acid ligands. (4) Coordination pillared layer (CPL) materials are formed by the combination of hexagonal microporous structure containing an octahedral central pore cage and eight tetrahedral angle cages. (3) Materials of Institute Lavoisier (MIL) frameworks are formed by the coordination of metal ions such as Al\(^3\), Cr\(^3\), and Fe\(^3\) with dicarboxylic acid ligands. (4) Coordination pillared layer (CPL) materials are formed by the combination of hexagonal microporous structure containing an octahedral central pore cage and eight tetrahedral angle cages.
prone to structural collapse under high temperature, high pressure, or acid/alkaline environments, which severely limit their applications in water purification. Among the above-mentioned six MOFs, three representative water-stable MOFs series; that is, the ZIF, MIL, and UiO (ZIF-67, MIL-100(Al), UiO-66, etc.) have been widely used in uranium adsorption from aqueous solution as we can see from Table 1. For example, Su et al. found that ZIF-67 had a quite high U(VI) adsorption capacity ($Q_{\text{max}} = 1683.8 \text{ mg} \cdot \text{g}^{-1}$) and very high U(VI) removal efficiency at both ppm and ppb levels (>99%).

 Due to their promising properties of large specific surface area, tunable porosity, and abundant uncoordinated binding site, MOFs (especially the ZIF, MIL, and UiO series) have shown excellent adsorption capacity for U(VI) adsorption. In order to further improve their adsorption capacity, selectivity, stability, and reusability, more and more studies have been conducted on the modification of the original MOF materials for uranium removal. There are several adsorption mechanisms adsorbents analysis techniques refs

| Coordination Mechanism                      | Adsorbents                  | Analysis Techniques                                      | Refs |
|--------------------------------------------|------------------------------|----------------------------------------------------------|------|
| Coordination                               | Zn(HBTC)(L)-($\text{H}_2\text{O}$)$_2$ | SEM, EDS, and FTIR analyses                              | 86   |
| Coordination                               | DSHM-DAMN                    | XPS analysis                                              | 101  |
| Coordination                               | MIL-101-AO                   | XPS analysis                                              | 105  |
| Coordination                               | MOFs                         | FTIR and XRD analyses                                     | 98   |
| Coordination                               | ZIF-67                       | FTIR and XRD analyses                                     | 98   |
| Coordination                               | MIL-100(Al)                  | FTIR and XRD analyses                                     | 98   |
| Coordination                               | UiO-66                       | FTIR and XRD analyses                                     | 98   |
| Coordination                               | A-3:28.2 wt %Zn-MOF-74 w/coumarin (28.2 wt. %) | SEM, EDS, TG, XRD, and FTIR analyses | 43   |
| Coordination                               | PPy/ZIF-8                    | FTIR and XPS analyses                                     | 93   |
| Coordination                               | MOFs                         | SEM, EDS, and FTIR analyses                               | 122  |
| Coordination                               | La-PDA                       | XPS analysis                                              | 100  |
| Coordination                               | azo-MOFs                     | FTIR and TG analyses                                     | 92   |
| Coordination                               | Zn-MOF-74 w/coumarin (11.7 wt %) | SEM, EDS, TG, XRD, and FTIR analyses | 43   |
| Coordination                               | CMPQ@MIL-101                 | XRD, IR, TG, and XRF analyses                             | 123  |
| Coordination                               | Uio-66-C$_2$N$_4$            | Density functional theory calculations and EXAFS analysis | 112  |
| Coordination                               | Uio-66-AO                    | EXAFS analysis                                            | 120  |
| Coordination                               | Uio-66-NH$_2$@CS-PDA         | XPS analysis and element mapping                          | 97   |
| Coordination                               | ZIF-67                       | FTIR and XPS analyses                                     | 76   |
| Coordination                               | JXNU-4                       | Ultraviolet—visible spectra, FTIR, XRD, and XPS analyses | 119  |
| Coordination                               | ECUT-100                     | SEM, EDS and FTIR analyses                                | 103  |
| Coordination                               | PCN-222-PA                   | XPS, EDS mapping, and FTIR spectra                         | 89   |
| Coordination                               | MIL-101-ED                   | FTIR and EXAFS analyses                                   | 52   |
| Coordination                               | MIL-101-DETA                 | FTIR and EXAFS analyses                                   | 52   |
| Coordination                               | MIL-101-NH$_2$               | FTIR and EXAFS analyses                                   | 52   |
| Coordination                               | MOF-2                        | DFT calculations                                          | 42   |
| Coordination                               | MOF-3                        | DFT calculations                                          | 42   |
| Coordination                               | RE-MOFs                      | SEM, XRD, FTIR, $^1$H NMR, and EXAFS analyses            | 90   |
| Coordination                               | Co-3ULU-35                   | TEM, XRD, FTIR, EDS, and XPS analyses                     | 116  |
| Coordination                               | Sz-2/SZ-3                    | XANES, EXAFS, XPS, FTIR analyses, and molecular dynamics simulations | 53   |
| Coordination                               | UPC-K1                       | SEM and XPS analyses                                      | 124  |
| Coordination, electrostatic interactions   | ED grafting MIL-101(Cr)       | XAS analysis                                              | 84   |
| Coordination, hydrogen bonding             | HKUST-1                      | FTIR analysis                                             | 73   |
| Coordination, II−II interaction, ion exchange | Fe$_2$O$_3$@ZIF-8          | XRD and FTIR analyses                                     | 109  |
| Coordination, ion exchange                 | GO-COOH/Uio-66               | Batch experiment, FTIR and XPS analyses                   | 121  |
| Coordination, electrostatic interaction    | MOF-5                        | Batch experiment and XPS analysis                         | 75   |
| Coordination, immobilization               | PCN-222/GO-COOH              | FTIR and XPS analyses                                     | 72   |
| Adsorption and reduction                   | nZVI/Uio-66                  | FTIR and XPS analyses                                     | 31   |
| Binding with carboxyl groups               | carboxyl-functionalized MIL-101 | Batch experiments, molecular dynamics simulation, and density functional theory calculations | 85   |
| Electrostatic interactions and            | Fe$_2$O$_3$@AMCA-MIL53 (Al)  | Batch experiment and EDX analysis                         | 87   |
| Surface complexation, electrostatic        | rGO/ZIF-67 aerogel           | Zeta-potential experiments, FTIR and XRD analyses         | 2    |
Modification methods, such as the use of unsaturated coordination sites in metal centers, chemical bond cooperation in organic chains, control of pores, synthesis of composites with other materials to introduce more functions, and design of MOFs with defects. For instance, after dehydration of MIL-101(Cr) at 423 K, unsaturated coordination bonds appeared at the Cr metal site. At this time, the amine group of ethylenediamine (ED) was grafted on the unsaturated coordination site to yield ED-MIL-101(Cr), which has an adsorption ability to U(VI) stronger than that of the pristine MIL-101(Cr). Li et al. found that the grafted independent carboxyl groups had significantly improved the adsorption of uranyl ions on MIL-101.55 Wang et al. designed and synthesized a MOF functionalized by carboxyl and acylamide groups for adsorption of UO$_2^{2+}$ ions from water.66 This MOF material exhibited excellent ability of extracting UO$_2^{2+}$ ions from water, which is mainly due to the coordination UO$_2^{2+}$ ions by carboxyl groups independently present in the MOF channel. Naushad et al. synthesized magnetic Fe$_3$O$_4$@AMCA-MIL-53 composites with a strong adsorption capacity of U(VI) by chemically modifying the organic chain of MIL-53 with citric acid rich in $\text{COOH}$ and $\text{OH}$ and linking Fe$_3$O$_4$. Addition of modifiers to precursor mixtures can create defects in the MOFs, thereby increasing their specific surface area, pore size, and adsorption sites, which are beneficial for improving the U(VI) adsorption capacity. The maximum capacity of the defective UiO-66-20D was observed to be more than 350 mg·g$^{-1}$ at a solution pH of 5, whereas that for nondefective UiO-66 was found to be below 30 mg·g$^{-1}$.88 Recently, numerous research studies on MOF-based materials for uranium adsorption have been conducted. The adsorption capacities of most reported MOF-based materials are summarized in Table 1, which indicates that the U(VI) adsorption capacities of the MOF-based materials strongly depend on the experimental adsorption conditions, the types of MOFs, their functionalization, and modifications. In general, adsorption capacity of uranium onto MOF-based materials can be improved through functionalization or modification methods. For example, through the introduction of bioinspired phytic acid (PA) into a highly stable MOF (PCN-222), the modified PCN-222-PA has a high density of accessible phosphate groups and exhibits significant U(VI) adsorption.
capacity (401.6 mg·g⁻¹), much higher than the adsorption capacity of PCN-222 (87 mg·g⁻¹). Similarly, mesoporous PCN-222/GO-COOH adsorbent could effectively recover U(VI) and shows an excellent adsorption capacity (426 mg·g⁻¹), which was superior to that of GO-COOH and PCN-222. U(VI) is well-known to be a typical Lewis acid with strong coordination with hard bases such as amidoxime, amine, and oxygen-containing groups. For example, amidoxime-functionalized porous MOF material (MIL-101-AO) shows an adsorption capacity much better than that of MIL-101. In addition, the ionic radius of metal nodes has a rather sensitive influence on the adsorption capacity for uranium(VI). Zhang et al. obtained the maximum U(VI) adsorption capacities (mg/g) of Ln-MOFs to be 265, 274, 371, 467, 478, 515, and 538 mg/g for Sm-MOF, Eu-MOF, Gd-MOF, Tb-MOF, Dy-MOF, Er-MOF, and Y-MOF, respectively, indicating that the U(VI) adsorption capacity continuously increases as the ionic radii of these lanthanide metals decrease.

In conclusion, the adsorption capacities of MOF-based materials for U(VI) mainly depend on their water stability, experimental adsorption conditions, the types of MOFs, and the ionic radii of metal nodes of MOFs. U(VI) adsorption capacity onto MOF-based materials can be generally enhanced through the following methods, such as the adjustment of pore size, the introduction of functional groups onto metal nodes and organic chains, design of defective MOFs, and the composite with other materials.
2.2. Influencing Factors for Uranium Adsorption.

Commonly, U(VI) adsorption by MOF-based materials is influenced by several factors such as the pH value of the solution, adsorption time and temperature, ionic strength, and coexisting ions, etc. Studies on the influencing factors of adsorption process of U(VI) ions by MOF-based materials are helpful to obtain optimized conditions for desirable adsorption performance but also expound the interaction mechanisms between adsorbents and adsorbates on a certain level, which are discussed in the following.

2.2.1. Effect of Solution pH. Generally, solution pH can greatly influence the adsorption process of MOF-based materials as it can affect their surface charge and the chemical properties of uranium(VI) ions. Uranium species are dominated by UO$_2^{2+}$ at lower pH, and the hydrolysis products of uranium such as [UO$_2$(OH)]$^+$ and [(UO$_2$)$_2$(OH)$_3$]$^{2+}$ can be formed with increasing solution pH value. As solution pH value further enhances, precipitation probably occurs depending on uranium concentration. Additionally, uranium can complex with carbonate ion to form negatively charged uranyl carbonate. At the same time, solution pH value can influence the zeta-potential of MOF-based materials and thus determines whether they are positively or negatively charged.

Uranium adsorption properties of the reported MOF-based materials were noticeably affected by solution pH value, as shown in Figure 2a–e. For instance, Liu et al. reported that the uranium adsorption efficiency of MIL-101-AO first increased and then sharply decreased as pH value increased from 3.0 to 11.0, and the adsorption efficiency reached the optimal level at pH 7 (Figure 2a). At low solution pH, the MIL-101-AO was positively charged and uranyl ions existed as electropositive form, and so the electrostatic repulsion between MIL-101-AO with the U(VI) caused the adsorption capacities to be obviously low. When the solution pH increased, the MIL-101-AO became negatively charged, thus electrostatic attraction for uranyl ions by the MIL-101-AO enhanced the adsorption capacities. With further increase in pH value, carbonate ions coordinated with UO$_2^{2+}$ to form [(UO$_3$)- (CO$_3$)$_2$]$^{2-}$, [(UO$_3$)(CO$_3$)$_2$]$^{4-}$, and so on. Thereby, as result of further deprotonation, the negatively charged MIL-101-AO and the uranyl carbonate could lead to repulsion, which caused the adsorption efficiency to decrease. Zhang et al. found uranium(VI) adsorption performance of RE-MOFs to vary at the pH ranging from 2.5 to 5.0 with a maximum U(VI) adsorption at pH 3.0 (Figure 2b). Similar results was obtained from CN-222/GO-COOH (Figure 2c), Fe$_0$@UiO-66-COOH, MOF-76, and Fe$_3$O$_4$@ZIF-8 nanocomposite. Commonly, the pH-induced U(VI) adsorption capacity of MOF-based materials are ascribed to the synergistic effect of the dissociation processes of uranium and the protonation–deprotonation of the functional groups on MOF-based materials.

For uranium adsorption of MOF-based materials, most favorable pH is 3–7, as seen from Table 2. Optimal pH value and variation trend of adsorption capacity depend on the nature of MOF-based materials. For example, acid conditions (pH <6.0) are the optimum pH for PAN/ZIF, whereas the optimal pH for AOPAN/ZIF is in a wide range, which is attributed to the surface modification of AO groups changing the nature of PAN/ZIF (Figure 2d). Analogously, the UiO-66-containing amino group displays higher optimal pH for U(VI)
binding compared to that with other MOF materials (Figure 2e), which could be due to the introduced amino group having protonation at high pH conditions and enhanced the positive electricity of the adsorbent for electrostatic attraction to the electronegativity of $\text{[UO}_2\text{(CO}_3\text{)}_3\text{]}^{-}$. 

2.2.2. Effect of Temperature. The influence of temperature on the uranium by MOF-based materials is always expounded by adsorption isotherms and thermodynamic parameters under specific solution conditions. Adsorption isotherms can provide useful information for evaluating the migration of uranium between liquid and the solid phase. Several adsorption isotherm models such as Langmuir, Freundlich, Dubinin–Radushkevich, Brunauer–Emmett–Teller, and Redlich–Peterson have been used to describe the adsorption behaviors. For example, in order to gain insight into the adsorption mechanism of ZIF-67/SAP$_{0.45}$ for uranium, Bai et al. conducted adsorption experiments with initial U(VI) concentration ranging from 5 to 150 mg L$^{-1}$. They used the Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models to fit their experimental data. The fitting parameters indicated that the Langmuir model was fitted better than the two other models to the equilibrium adsorption curve, illustrating that uranium adsorption onto ZIF-67/SAP$_{0.45}$ was mainly a monolayer process.

Generally, most MOF-based materials for uranium adsorption were followed well by the Langmuir model, as summarized in Table 2, indicating the monolayer adsorption process. In contrast, the adsorption process of a few other MOFs such as La-PDA, nZVI/UiO-66, and Fe@ZIF-8(94) for uranium is better fitted with the Freundlich model, suggesting the multilayer adsorption process.
In addition, thermodynamic parameters including enthalpy change ($\Delta H$), entropy change ($\Delta S$), and Gibbs free energy change ($\Delta G$) can be calculated according to temperature-dependent adsorption isotherms. The thermodynamic parameters are important to determine whether the adsorption process is exothermic or endothermic and spontaneous or nonspontaneous. For example, Wu et al. studied the thermodynamics of uranium adsorption by MOF-5 with the temperature from 298 to 328 K.75 The positive $\Delta H_0$, positive $\Delta S_0$, and negative $\Delta G_0$ values proved that the adsorption of U(VI) onto MOF-5 was endothermic and spontaneous. Also, the $\Delta G_0$ values reduced with increasing temperature, which indicated that higher temperature could be beneficial to the sorption process. A similar result was reported by Li et al. in which the thermodynamics of the uranium adsorption process by PPY/ZIF-8 was an endothermic and spontaneous adsorption.83 In general, uranium adsorption onto most of MOF-based materials was an endothermic and spontaneous adsorption, as shown in Table 1.

### 2.2.3. Effect of Contact Time

The effect of the contact time on the adsorption capacity of the adsorbent is also of vital importance for their practical application for wastewater treatment. Generally, MOF-based nanomaterials for uranium adsorption achieve the adsorption equilibrium within several minutes or hours.2,3,24,43,73,92,94,95,96,116–118 Specifically, defective MOFs or those MOFs functionalized by ingenous ligands with larger pores and active binding sites have been reported to exhibit fast adsorption for U(VI). For example, the U(VI) adsorption of defective UiO-66-20D is quite fast with an adsorption equilibration time within 10 min, which is more than 6 times faster than UiO-66 without defect.90 The faster adsorption is ascribed to the more convenient diffusion of U(VI) into MOFs with the expanded pores and more binding sites created by defects. As an example of MOFs functionalized by ligands, the assembly of Zn(II) mixing with two bridging ligands developed by Wang et al. displayed a very fast adsorption equilibrium reached within 1 min, which was due to the containment of 1D hexagonal channels in the MOF decorated by acylamide and carboxyl.118 Pores and functional sites within MOFs play a significant part in uranium adsorption onto MOFs. Larger pores and more active sites lead to much faster diffusion of uranium into MOFs, which thereby results in a shorter time to achieve adsorption equilibrium.

In order to further explore the adsorption behaviors of MOFs for U(VI), some commonly used kinetic models such as the pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion model have been applied to simulate time-induced adsorption experiment data. The adsorption kinetics of U(VI) onto Fe$_3$O$_4$@AMCA-MIL53(Al) and H–Cu–BTC were simulated by the pseudo-first-order and pseudo-second-order kinetic models.87,99 The results indicated that the U(VI) adsorption of both MOFs was better fitted by the pseudo-second-order equation on the basis of the correlation coefficients. Generally, most of MOF-based materials for uranium adsorption follows the pseudo-second-order model, suggesting that the adsorption process is mainly dominated by chemical reactions between uranium and MOFs.

### 2.2.4. Effect of Coexisting Ions and Ionic Strength

Selectivity is a significant factor for practical application of adsorption materials. High uranium adsorption efficiency depends on high selectivity of its adsorbents. For example, to evaluate the selectivity of dianinomaleonitrile (DAMN)-functionalized double-shelled hollow (DSHM) metal–organic framework of chromium(III) terephthalate (DSHM-DAMN) for U(VI) adsorption, Zhang et al. studied the removal efficiency for U(VI) from an aqueous solution containing coexisting ions such as Ba$^{2+}$, Ca$^{2+}$, Co$^{2+}$, K$^+$, Mg$^{2+}$, Na$^+$, Ni$^{2+}$, and Sr$^{2+}$.101 In comparison to the coexisting ions, DSHM-DAMN exhibited much higher selectivity toward U(VI) (Figure 3a). The high selectivity of U(VI) was attributed to the functional groups that grafted onto the DSHM acting as a hard base and the uranium species acting as a hard acid, which preferentially combines with hard alkalis according to the HSAB principle.19 Also, a series of coexisting ions including Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, and Fe$^{3+}$ were investigated for the interference of coexisting ions on the adsorption efficiency of MSONS-5 (a melamine-induced heterostructured framework through the combination of MOFs and supramolecular organic frameworks). The experiment results indicated that these five coexisting ions with extremely high concentrations (250, 500, and 1000 mg/L) had no essential effect on U(VI) removal by MSONS-5 (Figure 3b), which revealed that MSONS-5 could be regarded as a powerful adsorbent to capture U(VI).86 The effect of the coexisting ions (Ca$^{2+}$, Mg$^{2+}$, Hg$^{2+}$, and Zn$^{2+}$) on the removal of U(VI) by a Cu$_3$(btc)$_2$ encapsulating H$_3$PW$_{12}$O$_{40}$ hybrid94,101,116 materials (HKUST-1-H$_3$PW$_{12}$O$_{40}$) was also investigated. The results showed that the adsorption efficiency of U(VI) did not significantly change in the existence of these coexisting ions, which implied that HKUST-1-H$_3$PW$_{12}$O$_{40}$ could effectively and selectively adsorb U(VI) from aqueous solution with other metal ions. This can be ascribed to two main reasons: first the sequence of hydration radius of metal ions is Hg$^{2+}$ < UO$_2^{2+}$ < Ca$^{2+}$ < Zn$^{2+}$ < Mg$^{2+}$. Thereby, Hg$^{2+}$ and UO$_2^{2+}$ can easily enter the pores of the HKUST-1-H$_3$PW$_{12}$O$_{40}$. Second, functional groups such as $-$COOH on the HKUST-1-H$_3$PW$_{12}$O$_{40}$ can form stronger complexes with UO$_2^{2+}$ than other metal ions.102 Similarly, several other MOF-based materials, such as Fe$_3$O$_4$@ZIF-8 nanocomposites,109 rGO/ZIF-67 aerogels,7 UiO-66-NH$_2$,95 and GO-COOH/UiO-66,121 indicated good selectivity for UO$_2^{2+}$ from aqueous solution with other metal ions (Figure 3c–f).

It is well-known that the salt concentration in wastewater or seawater is high. Therefore, it is important to assess the feasibility of MOF-based adsorbents applied in the adsorption of U(VI) from water with different salt concentrations. For the effect of ionic strength, Wu et al. studied U(VI) adsorption onto MOF-5 with 0.1, 0.01, and 0.001 mol/L NaNO$_3$ under different pH values. The results indicated that the ionic strength had no effect on the adsorption of U(VI) on MOF-5 under the experimental conditions, indicating that the U(VI) adsorption behavior of MOF-5 was mainly dominated by the complexation on the inner surface of the spheres.75 Similarly, the impact of ionic strength on U(VI) adsorption on UiO-66 and UiO-66-NH$_2$ was studied in the presence of NaClO$_4$. The results show that the increase of NaClO$_4$ concentration had no significant effect on the adsorption of U(VI) on UiO-66 and UiO-66-NH$_2$.75 There was also no relationship between the ionic strength on the adsorption effect of U(VI) on PPY/ZIF-8 and JXNU-4, indicating the U(VI) sorption behavior was mainly dominated by the complexation on the inner sphere surface.

In conclusion, these reported results indicated that MOF-based materials display better selectivity after the introduction other functional groups (such as amino, carboxyl, amidoxime,
and phosphoryl groups, etc.) or the combination with other functional materials. However, strong competitive ions (such as V\(^{3+}\) and Fe\(^{3+}\)) and ions with high concentration (such as Na\(^+\), K\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\)) coexisting in water make it still a great challenge for adsorption and recovery of uranium from aqueous solution, especially in seawater with ultralow uranium concentration. It is necessary to design and explore MOF-based materials with excellent selectivity to extract uranium in severe environments.

2.3. Adsorption Mechanism. The adsorption mechanism of uranium by MOF-based materials is extremely important in the exposition of the reaction process, which is conducive to the optimization of adsorption conditions and performance. The mechanistic research has been conducted with various techniques including batch experiments, spectroscopy analysis, and theoretical calculations. The possible adsorption mechanisms of uranium onto MOF-based materials are summarized in Table 2. In different experimental conditions, uranium exists in various species, and different MOF-based materials exhibit different physical–chemical properties. Thereby, uranium interaction with MOF-based materials expressed various adsorption mechanisms, including coordination, ion exchange, electrostatic interactions, chemisorption, hydrogen bonding, and reduction mechanisms. The main adsorption mechanisms could be proposed to be coordination, ion exchange, and electrostatic interaction processes as discussed below.

2.3.1. Coordination. Coordination with functional groups is the dominant absorption mechanism between uranium and MOF-based materials. Generally, functional groups are introduced into MOFs using organic linkers, functionalization with specific functional groups, and modification by specific molecules or other functional materials. MOFs modified by specific functional groups can provide additional binding sites and then coordinate with adsorbates such as uranium. Liu et al. used the adenine and 4,4’-biphenyldicarboxylate (BPDC\(^{2-}\)) ligands to modify a zinc-MOF of JXNU-4 for capturing U(VI) and then one-dimensional channels of JXNU-4 functionalized by the uncoordinated carboxylic acid oxygen atoms which offered the binding sites for U(VI). Thereby, U(VI) adsorption onto JXNU-4 could be ascribed to the coordination reactions between U(VI) and the oxygen atoms and carboxylate oxygen atoms exposed on the channels. Uio-66-AO decorated by UiO-66-AO showed above, functional groups introduced into MOFs played an extremely important role in coordinating with U(VI). Therefore, modification of MOFs with specific functional groups is a superior method to improve uranium adsorption capability and selectivity.

2.3.2. Ion Exchange. As listed in Table 2, ion exchange is another U(VI) adsorption mechanism on MOF-based materials due to their highly ordered structures. Ion exchange between U(VI) CO\(_2\)\(^{-}\) anions and ED\(_3\)\(^{2-}\) in Co-SLUG-35 was evidenced by Li et al. through X-ray diffraction (XRD), FTIR, energy-dispersive spectroscopy (EDS), XPS, and transmission electron microscopy (TEM) analysis. Yang et al. found that the ion exchange between U(VI) and the hydrogen ions of COOH took place when U(VI) was adsorbed onto GO-COOH/UiO-66 composites (Figure 5). The new peak appearing at 920 cm\(^{-1}\) in Figure 5a is due to the asymmetric stretching vibration of O=U=O. The peaks at 1660 and 3300 cm\(^{-1}\) show a red shift, which clearly indicates the coordination or π−π interaction between U(VI) and −COOH and −OH on the GO-COOH/UiO-66 surface. As shown in Figure 5b, the pH changes slowly before and after U(VI) adsorption, which indicates that there is a small amount of ion exchange between U(VI) and hydrogen ions of COOH, and chelon plays the main role. The XPS analysis results shown in Figure 5c,d also confirm the above conclusion.

Zhang et al. also found that U(VI) adsorption onto RE-MOFs dominantly occurred via an ion-exchange process between Me\(_2\)NH\(_4\)+ and hydrated uranyl cations, which was depicted through structural representations of RE-MOFs shown in Figure 6a. This ion-exchange process was confirmed by molecular dynamics simulations (Figure 6b,c) and EXAFS spectra (Figure 6d,e) combined with scanning electron microscopy (SEM), XRD, FTIR, and \(^{1}H\) NMR. Also, Figure 6d,e shows that the spectrum of the U-loaded sample of Eu-MOF (Eu-U) from EXAFS measurements is similar to that of the U(VI) in aqueous solution, which indicates that the coordination of U(VI) in Eu-MOF is apparently similar to that of U(VI) in aqueous solution, indicating that the absorption of uranium(VI) in Eu-MOF occurs mainly through ion exchange between Me\(_2\)NH\(_4\)+ and hydrated uranyl cations. In addition, zirconium phosphate MOFs have been found as ion-exchange materials for the elimination of heavy metal contamination, especially uranium and cesium. For example, Zheng et al. found that a 3D structure of SZ-2 should be a great candidate for the ion-exchange application. When SZ-2 was used to remove uranium, the ion-exchange process between C4mpyr+ and hydrated uranyl cations played an essential role in the adsorption mechanism, which was confirmed by X-ray absorption near-edge structure (XANES), EXAFS, XPS, and IR spectra along with molecular dynamics simulations. The removal percentage of uranium could reach 62.4% by the ion-exchange reaction even at a low pH of 1.0 due to the enhanced stability and elevated porosity of SZ-2. These highly robust zirconium phosphate MOF materials exhibited potential ion-exchange applications under harsh conditions.

2.3.3. Electrostatic Interactions. When the pH value of the uranium-containing solution is different from the isoelectric point (pH\(_{\text{iep}}\)) of MOF-based materials, their surface will be protonated or deprotonated to be either positively or negatively charged. Similarly, U(VI) can also become positively or negatively charged at different pH values. Thus, the electrostatic interactions between U(VI) and MOFs may occur and influence the adsorption of U(VI) in the solution. For example, when the pH increased from 1.50 to 5, electrostatic attraction occurred between UO\(_2\)\(^{2-}\) and negatively charged UO\(_2\)\(^{2-}\) anions and ED\(_3\)\(^{2-}\) in Co-SLUG-35 was evidenced by Li et al. through X-ray diffraction (XRD), FTIR, energy-dispersive spectroscopy (EDS), XPS, and transmission electron microscopy (TEM) analysis. Yang et al. found that the ion exchange between U(VI) and the hydrogen ions of COOH took place when U(VI) was adsorbed onto GO-COOH/UiO-66 composites (Figure 5). The new peak appearing at 920 cm\(^{-1}\) in Figure 5a is due to the asymmetric stretching vibration of O=U=O. The peaks at 1660 and 3300 cm\(^{-1}\) show a red shift, which clearly indicates the coordination or π−π interaction between U(VI) and −COOH and −OH on the GO-COOH/UiO-66 surface. As shown in Figure 5b, the pH changes slowly before and after U(VI) adsorption, which indicates that there is a small amount of ion exchange between U(VI) and hydrogen ions of COOH, and chelon plays the main role. The XPS analysis results shown in Figure 5c,d also confirm the above conclusion.

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charged rGO/ZIF-67 aerogel, leading to a rapid increase in the removal efficiency.\textsuperscript{6} Feng et al. confirmed that the uranium adsorption process on MOF material (HKUST-1) was controlled by not only coordination but also electrostatic interactions.\textsuperscript{73} Analogously, electrostatic interaction took place between uranium ions and electron-rich oxygen of Fe$_3$O$_4$@rGO/ZIF-67 aerogel, leading to a rapid increase in the short detection time, low cost and convenience, easy sample preparation, high sensitivity, real-time detection, and high quantum yield. The luminescence intensity of MOFs is limited by the forbidden f–f transition which is effectively avoided through the antenna effect of lanthanide elements, transition metal elements as central atoms, or combined with carbon nanomaterials such as carbon quantum dots, graphene quantum dots, etc.

3.1. Luminescent MOF-Based MOFs. Recently, luminescent MOF-based materials synthesized through lanthanides as metal nodes have been revealed as potential luminescent sensors.\textsuperscript{147} Owing to the electronic transitions within 4f shell of lanthanides, Ln-MOF materials display several excellent luminescence properties such as long-lived lifetime, characteristic sharp emission, high quantum yield, and large Stokes shift.\textsuperscript{148} The direct excitation of the metal center which is limited by the forbidden f–f transition is effectively avoided through the antenna effect of Ln-MOFs, thus greatly improving the light absorption and energy transfer efficiency.\textsuperscript{149} The attractive light-emitting traits of 4f lanthanides make Ln-MOF material a tunable luminescent sensor for detection of analytes such as UO$_2^{2+}$\textsuperscript{150} ions. Up to now, the reported luminescent Ln-MOF sensors for UO$_2^{2+}$\textsuperscript{151} ion detection have mainly used Eu$^{3+}$ and Tb$^{3+}$ as central atoms. Commonly, the Ln-MOF sensors can detect UO$_2^{2+}$\textsuperscript{152} ion by quenching mechanisms.

With Eu$^{3+}$ as the central metal ion, the MOF-based luminescent sensor [Eu$_2$(MTBC)(OH)$_2$(DMF)$_3$(H$_2$O)$_4$]·2DMF/7H$_2$O was constructed by Liu et al. for the detection of UO$_2^{2+}$\textsuperscript{153} ions (Figure 7a–e).\textsuperscript{154} The luminescence intensity of this MOF-based sensor decreased sharply with the increase of uranium concentration (Figure 7d). The quenching process can also be described quantitatively by plotting the quenching ratio (denoted as $(I_0 - I)/I_0$\% versus uranium concentration.

Table 3. Detection Parameters and Effects of MOF-Based Sensors

| MOF-based sensors | center atom | limit of detection | interfering ions | detection mechanism | refs |
|-------------------|-------------|--------------------|------------------|---------------------|-----|
| Cd(II)-MOF        | Cd          | 0.9 µg/L           | Na$^+$, K$^+$, Mg$^{2+}$, Br$^-$, I$^-$, NO$_3^-$, Cl$^-$, Zn$^{2+}$, Na$^+$, Cd$^{2+}$, F$^-$, CO$_3^{2-}$, Al$^{3+}$, Fe$^{3+}$ | fluorescence quenching | 44  |
| [Zn(HBTC)(BMOPE)-DMF-H$_2$O]$_n$ | Zn          | 5878.6 µg/L        | Li$^+$, Na$^+$, Ag$^+$, Ca$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, Ni$^{2+}$, Mg$^{2+}$, Al$^{3+}$, Cr$^{3+}$, Fe$^{3+}$, F$^-$, Br$^-$, Cl$^-$, SCN$^-$, HCO$_3^-$, NO$_3^-$, SO$_4^{2-}$, CO$_3^{2-}$, PO$_4^{3-}$, Cr$_2$O$_7^{2-}$, Cr$_3$O$_4^{2-}$ | fluorescence quenching | 135 |
| [Zn(HL)(bipy)$_{0.5}$(H$_2$O)]·2H$_2$O | Zn          | 95.2 µg/L          | Ca$^{2+}$, K$^+$, Mg$^{2+}$, Na$^+$, Ag$^+$, Ni$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Cr$^{3+}$, Co$^{2+}$ | fluorescence quenching | 136 |
| Pt$_2$Ru$_2$Pcs/GCE | Zr          | 5.712 µg/L         | Pb$^{2+}$, Cu$^{2+}$, Sr$^{2+}$, Ni$^{2+}$, Pd$^{2+}$, Eu$^{3+}$, Ce$^{3+}$, La$^{3+}$, Sm$^{3+}$, Cl$^-$, NO$_3^-$ | fluorescence quenching | 134 |
| Zn$_2$C$_{11}$N$_2$O$_{13}$H$_{19}$ | Zn          | 2.856 µg/L         | Na$^+$, K$^+$, Mg$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Pb$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, VO$_4^{3-}$ | fluorescence quenching | 55  |
| [Eu$_3$(MTRC)(OH)$_2$(DMF)$_3$(H$_2$O)$_4$]·2DMF/7H$_2$O | Eu          | 309.2 µg/L         | Na$^+$, Mg$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Pd$^{2+}$, Sr$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ | fluorescence quenching | 137 |
| [Eu$_3$(TBTBC)(DMF)$_4$] | Eu          | 5540 µg/L          | Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Mn$^{2+}$, Mg$^{2+}$, K$^+$, Ca$^{2+}$, Na$^+$, Ba$^{2+}$, Fe$^{3+}$, Fe$^{2+}$, Al$^{3+}$ | fluorescence quenching | 138 |
| [Eu$_3$(TATAB)$_2$]·4H$_2$O·6DMF | Eu          | 214.2 µg/L         | Na$^+$, Mg$^{2+}$, K$^+$, Ca$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, La$^{3+}$, Ce$^{3+}$, Sm$^{3+}$, Gd$^{3+}$, Yb$^{3+}$ | fluorescence quenching | 139 |
| terbium(III)-based MOF | Tb          | 0.9 µg/L           | Th$^{4+}$, Eu$^{3+}$, Sr$^{2+}$, Cs$^-$, Al$^{3+}$, Ca$^{2+}$, K$^+$, Cl$^-$, CO$_2^{−}$ | fluorescence quenching | 54  |
| [Tb(BPDC)$_2$]·(CH$_3$)$_2$NH$_2$ | Tb          | 8.34 µg/L          | Ag$^{+}$, Al$^{3+}$, Cd$^{2+}$, Ce$^{3+}$, Co$^{2+}$, Cr$^{3+}$, Mg$^{2+}$, Na$^{+}$, Ni$^{2+}$, Pb$^{2+}$, Pd$^{2+}$, OAC$^-$, Br$^-$, Cl$^-$, CN$^-$, F$^-$, OH$^-$, NO$_3^-$ | fluorescent quenching | 45  |
The quenching process is also well described by the Langmuir model with $R^2 = 0.95$. The detection limit of this sensor for uranium is $309.2 \mu g/L$, relatively higher than that of the previously reported MOF luminescent ones, which may be caused by the inefficient energy transfer from the ligand to the guest $UO_2^{2+}$ ion. The application of this sensor is still promising in some areas with high uranium contamination.

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transfer between UO$_2^{2+}$ and the MOF-based sensing material, which could lead to fluorescence quenching.

A MOF-based sensor (coordination polymer CP-1) with Eu$^{3+}$ as the central metal ion (Figure 7f,g) was also synthesized for the detection of UO$_2^{2+}$ ions. The fluorescence quenching efficiency of CP-1 for UO$_2^{2+}$ was much higher than that of other different metal cations (Figure 7h), which indicated that CP-1 has a good selectivity of UO$_2^{2+}$ ion detection. CP-1 has a significant fluorescence quenching effect for different concentrations of the UO$_2^{2+}$ ion (Figure 7i,j). The detection limit and $K_{SV}$ of CP-1 for UO$_2^{2+}$ ion were calculated to be 0.011 mM and 4000 M$^{-1}$. The mechanism for the detection of UO$_2^{2+}$ ions by CP-1 is that the interaction between the UO$_2^{2+}$ ion and the ligand of the coordination polymer can weaken the energy transfer from the ligand to Eu$^{3+}$ ion to cause fluorescence quenching.

Incorporating a sufficient number of amino (−NH$_2$), hydroxyl (−OH$_2$), or pyridyl (−C$_6$H$_5$N) groups into porous MOF structures, these unsaturated or open Lewis base sites (LBSs) can promote different binding abilities to achieve selective responses to specific metal ions. Li et al. designed and synthesized a luminescent Eu-MOF with abundant LBSs for binding uranyl ions (UO$_2^{2+}$) through a one-step solvothermal synthetic route (Figure 8a). This Eu-MOF displayed specific recognition toward UO$_2^{2+}$ and the best selectivity among all of these potentially interfering cations (Figure 8b). The fluorescence intensity of the Eu-MOF gradually decreased with increasing concentration of UO$_2^{2+}$ (Figure 8c). A low detection limit of 0.9 μM was achieved with a rapid response. This Eu-MOF exhibited characteristic fluorescence of Eu$^{3+}$ and could detect UO$_2^{2+}$ in solution based on a turn-off mechanism. UO$_2^{2+}$ in solution diffuses into the pores of the Eu-MOF and interacts with the unsaturated nitrogen atoms acting as LBSs, the empty orbitals on the UO$_2^{2+}$ accepted electrons from the nitrogen atoms, resulting in a decrease in the electron density on the ligand. Moreover, the interactions between UO$_2^{2+}$ and these binding sites might greatly affect the energy transfer process from the ligand to the Eu$^{3+}$.
metal on the MOFs,\textsuperscript{54} which in turn alters the fluorescence properties of Eu\textsuperscript{3+} and leads to fluorescence quenching.

When MOF materials are applied to the detection of uranium ions in aqueous solutions, one of the primary problems is that the majority of MOFs are not water stable; that is, they are prone to phase transitions or structural decomposition, which often results in poor reproducibility and low sensing efficiency of MOFs. In addition, the cross-sensitivity of MOFs to other metal ions can greatly interfere with the fluorescence selective response of UO\textsubscript{2}\textsuperscript{2+} ions. To overcome these shortcomings, Li et al.\textsuperscript{139} designed a hydrolytically stable mesoporous Tb-MOF, whose channels are equipped with plenty of exposed LBSs (Figure 8d). The luminescence intensity of this Tb-MOF can be efficiently and selectively quenched by uranyl ions (Figure 8e,f). The detection limit (0.9 μg/L) of this Tb-MOF in deionized water is much lower than the maximum contamination standard of 30 μg/L in drinking water set by the United States Environmental Protection Agency. This tremendous detection capability stems from the selective binding of uranyl ions onto the LBSs of the MOF material. Selective binding of uranyl ions to the Lewis basic sites further leads to an effective energy transfer between the uranyl ions and the MOF skeleton, thus quenching fluorescence.

Also, Ye et al. developed a water-stable dual-channel luminescent Tb-MOF (DUT-101) sensor (Figure 9a,b).\textsuperscript{45} DUT-101 can first display luminescence quenching and enhanced dual-channel response to the UO\textsubscript{2}\textsuperscript{2+} ion with high sensitivity and selectivity (Figure 9c,d). The low UO\textsubscript{2}\textsuperscript{2+} detection limit of 8.34 μg/L indicates that DUT-101 is one of the effective detectors reported so far for the UO\textsubscript{2}\textsuperscript{2+} ion.

Nevertheless, to date, only a few lanthanide metals such as Eu\textsuperscript{3+} and Tb\textsuperscript{3+} have been focused on to be used for the synthesis of MOF sensors for UO\textsubscript{2}\textsuperscript{2+} ions. Other lanthanide metal MOF-based sensors with desirable properties require further investigation for the detection of UO\textsubscript{2}\textsuperscript{2+} ions.
3.1.2. Transition-Metal-Based MOFs. Compared with the scarcity and high cost of lanthanide metal MOF-based sensors, most of transition-metal MOF-based sensors are highly economical and abundant. The development of transition-metal-based MOF sensors has been a popular research direction in the detection of uranium ions. It deserves to be further developed in the future.

Recently, various luminescent MOF sensors based on transition metal ions (Co^{2+}, Zn^{2+}, or Cd^{2+}) have been developed for UO_2^{2+} sensing. Generally, luminescence intensity of these sensors can be quenched by UO_2^{2+} ions. For example, a Co(II) MOF sensor (Figure 10a−d) was synthesized to be used for UO_2^{2+} detection. With the increase of UO_2^{2+} concentration, the luminescence intensity at 400 nm gradually decreased (Figure 10e). Based on the linear Stern−Volmer curve (Figure 10f), the detection limit of the sensor for UO_2^{2+} was calculated to be a low value of 13.2 μM. In the detection process, the UO_2^{2+} ion acting as an electron acceptor accepts electrons from the coligand in the framework through electrostatic and host−guest interactions and then reduces or blocks the electron flow within the molecule, leading to quenching of the luminescence.

Liu et al. designed a transition metal ion (Cd^{2+}) as a metal center for constructing the MOF sensor [Cd_3(L)_2(bipy)-(H_2O)_2]·H_2O, with the structure shown in Figure 11a−d. The fluorescence intensity of this MOF sensor decreased with the addition of uranium ions and was almost quenched after the addition of 180 μL of UO_2^{2+} ions with a quenching efficiency of 96% (Figure 11e). The fluorescence quenching was caused by the resonance energy transfer (RET) from MOF to UO_2^{2+} ions. As shown in Figure 11f, except for Fe^{3+} ions, the interfering ions have little effect on the fluorescence intensity of the sensor, so this MOF sensor can selectively detect UO_2^{2+} ions.

Among the reported transition metal MOF sensors, there are probes that can not only selectively detect uranium ions but also detect other cations or anions. Chen et al. designed the first isomorphous MOF-based probe with two different metal ions (Zn^{2+} and Co^{2+}) that can simultaneously detect Fe^{3+}, Cr^{3+}, UO_2^{2+}, CrO_4^{2−}, and Cr_2O_7^{2−} ions in aqueous solution. Hou et al. synthesized a [Zn(HL)(bipy)]_α·(H_2O)]·2H_2O sensor, with its structure shown in Figure 12a,b. The fluorescence intensity of this Zn-MOF sensor gradually decreases with the addition of UO_2^{2+} and Pb^{2+} ions (Figure 12c,d). It exhibits high selectivity and sensitivity for the detection of Pb^{2+} and UO_2^{2+} ions in aqueous solutions. Considering cost savings and convenience, it is a good research direction to design and develop more bi- and multifunctional...
MOF sensors that can simultaneously detect uranium and other pollutants.

For transition metal MOF-based luminescent sensors for uranium detection, only a few transition metals such as Cd$^{2+}$, Zn$^{2+}$, and Co$^{2+}$ as metal centers for MOFs have been developed. Thus, other transition metal MOF-based sensors with desirable properties also need to be designed and developed for the detection of uranium. In addition, during the synthesis process of luminescent MOF probes using transition metals, the problem of secondary contamination by toxic transition metal center ions such as Cd$^{2+}$ and Co$^{2+}$ needs to be taken into account, so nontoxic or less toxic transition metal centers should be preferred to avoid secondary pollution.

3.1.3. Carbon-Nanomaterial-Combined MOFs. Carbon nanomaterials such as carbon dots (CDs), graphene quantum dot (QDs), and their derivatives including graphene oxide QDs and reduced graphene QDs have been used as fluorescent probes for metal ion sensing, biomolecular sensing, and bioimaging applications due to their excellent photoluminescence properties.\textsuperscript{143,153−155} Of the combined excellent photoluminescence properties of carbon nanomaterials with the several merits of MOFs as mentioned previously, luminescent MOF sensors with carbon nanomaterials have promising potential applications for uranium detection. For example, Guo et al. designed multifunctional hybrid MOF composites made of a magnetic core and a zeolite imidazolate framework (ZIF-8) shell embedded with CDs, and the new adsorbent has the ability to simultaneously detect, separate, and recover uranium from aqueous solutions. These MOF composites not only display obviously luminescent response to U(VI) but also enhance U(VI) adsorption properties with the assistance of the loaded carbon dots.

The development of carbon nanomaterials/MOF-based sensors for the detection of uranium is still in the very early stage. There are very few reports in this area. Therefore, more efforts need to be made to design novel and effective carbon nanomaterials/MOF-based sensors for the detection of uranium and explore their detection mechanism.

3.2. Electrochemical Sensors. The working principle of electrochemical sensors is based on the redox reaction of analyte in the electrochemical system. The amount of analyte in the redox reaction can be determined by measuring the electric potential, current, or other electrical signal-sensing surface modifiers due to their good absorbability, high surface area, abundant pore volume, and eminent catalytic activity.\textsuperscript{64,156}

Due to the unique properties of MOFs, i.e., high surface area, tailorable pore size, and high catalytic activity, MOF-based platforms have potential for electrochemical sensing for uranium. However, most MOFs have some disadvantages such as micron size, poor electrical conductivity, and relatively high instability in aqueous solution, which has limited the application of MOFs as electrochemical sensors. A commonly applied method to overcome these limitations is to combine MOFs with other functional materials that have high electrical conductivity while preserving their unique pore structure. Meanwhile, the preparation of functional porous carbon materials by carbonization of MOFs has been widely used in the construction of electrochemical sensors. For example, the TiO$_2$/C900 porous material derived from MOF was used as an electrochemical sensor for the simultaneous determination of...

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Figure 12. [Zn(HL)\_\((bipy)\_0.5(H\_2O)\] \cdot 2H\_2O: Views of the (a) asymmetric unit and (b) 3D topology. Emission spectra upon the addition of (c) UO$_2^{2+}$ ions (10$^{-3}$ M) and (d) Pb$^{2+}$ ions (10$^{-3}$ M). Reproduced with permission from ref 136. Copyright 2018 Elsevier.
hydroquinone and catechol. \(^{157}\) Yan et al. \(^{158}\) carbonized ZIF-8 nanopolyhedrons to obtain nitrogen-doped porous carbon nanopolyhedrons (N-PCNPs) for the simultaneous determination of three biomolecules of ascorbic acid, dopamine and uric acid.

For the detection of UO\(_{2}^{2+}\) ions, MOF-derived porous carbons loaded with PtRu bimetallic nanoparticles (PtRu-PCs) were synthesized by first loading the PtRu particles into a UiO66-NH\(_2\) matrix and then following a calcination process at high temperatures (Figure 13a). \(^{134}\) The XRD patterns (Figure 13b) show that the carbonization at 600 °C leads to the decomposition of the UiO66-NH\(_2\) framework and the formation of ZrO\(_2\), and the characteristic peak of Pt shifted positively with the increase of Ru content, indicating the formation of PtRu alloys. As shown in Figure 13c, the reduction peak current increases with the gradual increase of U(VI) ion concentration. The sensors based on PtRu-PCs showed excellent sensitivity to UO\(_{2}^{2+}\) with a detection limit of only 0.024 μM. Figure 13d shows the \(i-t\) curve for investigating the anti-interference performance of PtRu-PCs/GCE, and 100-fold concentration of interference ions displayed the negligible current responses, illustrating a good anti-interference performance of the PtRu-PCs/GCE. These results show that PtRu-PCs/GCE can be used as a promising platform for the quantitative determination of U(VI) ions with great sensitivity and selectivity. However, PtRu-PCs/GCE is the only example reported thus far of utilized MOF-derived electrochemical sensors to detect uranyl ions in solution. More novel MOF-derived sensors for electrochemical sensing of uranyl ions need to be developed, and their sensing mechanism for uranyl ions by MOF-derived electrochemical sensors need to be clarified.

In summary, MOF-based sensors for uranium have recently attracted more and more attention. Various luminescent MOF-based sensors complexing with carbon nanomaterials or using Co(II), Cd(II), Tb(III), Zn(II), and Eu(III) as metal center ions have been developed for uranium detection commonly based on luminescence quenching effects. The mechanism behind the quenching effect has been found to be due to the interaction between UO\(_{2}^{2+}\) and organic ligands of MOFs leading to an energy or electron transfer between the UO\(_{2}^{2+}\) and the MOF skeleton, thus hindering the energy or electron of the ligand to metal central ions of MOFs. In addition, the combination with high conductive materials such as noble metals endows MOFs with better electroconductivity can be designed and used as electrochemical sensors for uranium detection. However, only one MOF-derived electrochemical sensor was reported to detect uranyl ions so far, indicating that the development of MOF-based electrochemical sensors needs to be further carried out.

Moreover, there are still some limitations and great challenges in the design of MOF-based sensors to detect

![Figure 13.](http://pubs.acs.org/journal/acsodf)
The application of MOF-based sensors in real water is still lacking in-depth and systematic research. Enhancing anti-interference ability to interfering ions is a tough task in future construction of MOF-based sensors. Although most MOF-based sensors show high selectivity over various common metal ions, some specific metal ions such as V(V), Th(IV), and Cu(II) can still affect their detection selectivity. The sensitivity and stability of some reported sensors are still insufficient for detecting uranyl ions at ultralow concentration. New synthesis methods or functional modification are needed to tune the MOF structure and improve their sensing sensitivity and stability as the MOF’s structure is important for sensing properties. Electrochemiluminescence (ECL) technology is also a favorable way to obtain UO_2^{2+} sensors with high sensitivity owing to the avoidance of autofluorescence background or scattered light as compared to other luminescent sensors. However, the development of MOF-based ECL sensors with desirable properties is a great prospective research field. We introduced the structure design, bifunctional performance, and mechanism of uranium detection and adsorption of the reported MOF-based materials with the hope it would be helpful for the further development and application of such materials in the future.

With the coefficients between fluorescence and active sites of CDs and the porous structures of magnetic ZIF-8, FeO_2-CMC@ZIF-8@CDs can simultaneously adsorb and detect uranium in aqueous solution (Figure 14a). In the uranium detection test of FeO_2-CMC@ZIF-8@CDs, the fluorescence intensity decreased with the increase of uranium concentration in the solution, as shown in Figure 14b. The detection limit of FeO_2-CMC@ZIF-8@CDs was approached at the uranium concentration of 100 mg/L in the solution. To investigate the U(VI) adsorption ability, the adsorption isotherms of Freundlich, Langmuir, and Dubinin–Radushkevich models were used to fit the adsorption data of U(VI) on FeO_2-CMC@ZIF-8@CDs at T = 298 K (Figure 14c–f). FeO_2-CMC@ZIF-8@CD materials fit well with Langmuir models. The maximum U(VI) adsorption amount (606.06 mg/g) of FeO_2-CMC@ZIF-8@CD composites with the Langmuir model indicates that the composites display outstanding adsorption performance for uranium. XPS (Figure 14g–j) and FTIR investigations showed that the interactions between U(VI) and FeO_2-CMC@ZIF-8@CDs may include the diffusion and coordination mechanisms.

Considering that the amide groups on N-pyridin-4-ylpyridine-4-carboxamide ligands (NPYC) and two uncoordinated carboxyl oxygen atoms on pyromellitic acid ligands (PMA) can provide potential uranium-binding sites, NPYC as a synergistic ligand was coordinated with PMA to coordinate with Zn(II) to synthesize a fluorescent Zn-MOF (HNU-50) (Figure 15a–c) for the effective detection and removal of U(VI). HNU-50 can selectively and efficiently catch uranyl ions, achieving a maximum adsorption capacity of 632 mg/g with the Langmuir model (Figure 15d,e). Meanwhile, the U(VI) adsorption leads to fluorescence quenching of HNU-50, thus U(VI) can be selectively detected by the change of fluorescence intensity (Figure 15f,g). HNU-50 displays a very low U(VI) detection limit (1.2 × 10^{-8} M), which is less than the World Health Organization maximum contamination standards for drinking water (6.3 × 10^{-8} M). Through XPS
Figure 15. (a) Coordination mode of the asymmetric unit in HUN-50. (b) Single-layered structure in HUN-50. (c) View of the 3D framework of HNU-50 along the b-axis (color code: red, O; gray, C; dark blue, N; light blue, Zn). (d,e) Balanced data for U(VI) adsorption by HNU-50 (m_{sorbent}/V_{solution} = 0.2 g/L, t = 12 h, pH = 3). (f) Emission spectra of HUN-50 dispersed in water upon the addition of U(VI) ions (λ_{ex} = 312 nm). (g) Correlation between U(VI) concentration and [(I_{0} - I)/I_{0}]. XPS spectra of (h) U 4f, (i,j) N 1s, (k) C 1s, and (l,m) O 1s of HUN-50 before and after U(VI) ion adsorption. Reproduced from ref 55. Copyright 2020 American Chemical Society.
and IR analyses, carboxylate and amide groups coordinating with U(VI) ions could account for the selectivity and sensitivity toward U(VI), leading to an efficient energy transfer from HNU-50 to U(VI) ions to causing fluorescence quenching. Therefore, HNU-50 can realize concurrent adsorption and sensing for U(VI).

MOF-76, constructed by 1,3, 5-benzenetricarboxylate (BTC) and the ligand lanthanide ion, has one-dimensional channels of about $6.6 \times 6.6$ Å$^2$ along the [001] direction (Figure 16a). Its aperture is large enough to trap UO$_2^{2+}$. The luminescence intensity of MOF-76 decreased significantly with increasing UO$_2^{2+}$ concentration (Figure 16b). It showed high sensitivity for the detection of U(VI) and also had a high U(VI) adsorption capacity of 298 mg/g at a low pH of 3.0. Furthermore, MOF-76 displays high selectivity for U(VI) adsorptive uptake over a range of competing metal ions.$^{47}$

By adopting postsynthetic modification (PSM) strategies, Sravani et al. synthesized a series of PSM isoreticular metal–organic framework-3 (IRMOF-3) with various functional groups (Figure 17) for the recovery and detection of elemental uranium in aqueous solutions. $^{160}$ All of the MOFs exhibit excellent adsorption capacity toward U(VI) (>90%), and maximum uptake was observed at pH 6. The fluorescence sensing studies of U(VI) via IRMOF-3 and its PSM MOFs revealed high sensitivity and selectivity toward U(VI) over other competing rare earth metal ions, wherein IRMOF-GA displayed an impressive detection limit of 0.36 mg/L for U(VI).

Generally, the strategies used for preparing the reported bifunctional MOF-based materials mentioned above are to introduce functional groups with strong binding affinity for U(VI), to tailor channels and porous structures of MOF, or to combine with materials such as CD with fluorescence and active sites, etc. The functional groups coordinating with U(VI) or the aperture being large enough to trap U(VI) could prompt the adsorption of U(VI), consequently leading to an efficient energy transfer from MOF skeleton to U(VI) ions to cause fluorescence quenching and thus realizing concurrent adsorption and sensing for U(VI).

5. CONCLUSIONS AND PERSPECTIVES

In summary, we provide a systematic review of recent developments in MOF-based materials for adsorption and detection for uranium in aqueous solution. The adsorption mechanisms of MOF-based materials, including coordination, ion exchange, electrostatic interactions, chemisorption, hydrogen bonding, and reduction mechanisms, are demonstrated using multi-techniques such as macroscopic batch experiment, microscopic spectroscopy analysis, and theoretical calculations. MOF-based sensors relying on luminescent and electro-
chemical signals are introduced in detail. Commonly, various luminescent MOF-based sensors detect uranium based on luminescence quenching effects. In addition, the combination with high conductive materials such as noble metals endows MOF with better electroconductivity are designed and used as electrochemical sensors for uranium detection. Moreover, the bifunctional MOF-based materials used to simultaneously detect and remove U(VI) from aqueous solution are introduced. In general, the strategies of designing bifunctional MOF-based materials to introduce functional groups, to tailor the structures of MOFs, or to combine with materials with fluorescence and active sites, etc. Despite great advances achieved over the years, there are still some challenges and unsolved problems for the application of MOF-based materials for uranium removal and detection in water.

(1) Further efforts should be put onto improving the water stability of MOF-based materials, especially in strong acidic and alkaline solutions, and successive exploration of their practical applications.

(2) Most of the reported MOFs were synthesized in organic solvents via solvothermal methods. Recycling the used solvent to minimize the environment pollution should be considered. Meanwhile, developing environmentally friendly aqueous phase or solvent-free synthesis methods is needful.

(3) Improving the sensitivity and anti-interference ability is a further research direction in the future construction of MOF-based adsorbents and sensors due to the low concentration of uranyl ions, high ionic strength, and coexisting ions in actual wastewater and seawater.

(4) The pore structure of MOFs is crucial for their adsorption and sensing applications. Tuning the pore size of MOFs to enhance their adsorption and sensing properties is a future research direction.

(5) More novel electrochemical MOF-derived sensors for uranyl ions need to be developed, and their sensing mechanism for uranyl ions needs to be clarified. The development of MOF-based electrochemiluminescence sensors for UO₂²⁺ is valuable to further broaden the category of MOF-based sensors with new and excellent properties.

(6) The existing synthesis process for MOFs mostly stay at the laboratory research level. Improving synthesis methods for MOFs to achieve industrial-level mass production and commercialization should be given an extreme emphasis.

(7) The uranium adsorption and sensing mechanisms of different MOF-based adsorbents and sensors, including pristine MOFs, MOF composites and MOF derivative, are different and complex, still unclearly understood at present, and thus should be further and systematically revealed.

(8) The development of portable MOF-based detection test paper or devices should be attached importance to realize quick, real-time, on-site and visual detection of uranium, and promote further commercial applications.

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Notes

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