Review Article

Magnetic Nanoparticles@Metal-Organic Framework Composites as Sustainable Environment Adsorbents

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Metal-organic frameworks (MOFs) are an intriguing class of porous inorganic-organic hybrid networks synthesized from metal ions with multidentate organic ligands. MOFs have uniform and tunable cavities and tailorable chemistry, making them promising materials for hazardous component removal from the environment. Controllable integration of magnetic nanoparticles (NPs) and MOFs is leading to the creation of many novel multifunctional MOF-based composites, which exhibit advanced performance that is superior to both of the individual units. This review summarizes the recent significant advances in the development of MOF-based magnetic heterostructure materials for the removal of hazardous contaminants from the environment. The successful methods reported till date for the magnetic MOF synthesis are also provided. In the final section, we provide our views on the future development of the magnetic MOF heterostructure materials for the pollution management.

1. Introduction

In recent years, environmental pollution is increasing and posing serious threat to the ecosystem and human health [1]. Inorganic pollutants such as heavy metal ions in water have drawn much attention due to their long half-life and nonbiodegradability. For these reasons, numerous technologies have been developed for water purification, such as ion exchange [2], biological treatment [3], chemical precipitation [4], and reverse osmosis [5]. Although these technologies are effective, their practical applications are usually hampered by the high cost and poor selectivity. On the other hand, dyes are considered as serious organic pollutants, which are produced by various industrial wastewater such as textile, leather, printing, plastics, cosmetics, pharmaceutical, and food wastewater [6, 7]. The presence of dyes not only gives rise to high visibility but also can reduce the solubility of gas in water and even more has a strong toxicity and carcino-

genicity to the human body. Therefore, the removal of inorganic and organic pollutants from wastewater is very necessary for water safety and human health protection. Compared with these methods, adsorption is considered as an ideal pollution treatment method due to its low cost, strong universality, and simple operation [8]. Traditional adsorbents, such as zeolite, metal oxide, and activated carbon, cannot show satisfactory adsorption capacity or require long contact time [9, 10]. Hence, the development of a novel high efficiency adsorbent with large capacity will be an important challenge.

Metal-organic frameworks (MOFs) are constructed by ditopic or polytopic organic ligands and transition metal ions or clusters [11]. Owing to their diverse structures, adjustable aperture, large surface area, and coordinated unsaturated metal sites, MOFs have been widely used in social and industrial fields, such as gas storage [12], separation [13], catalysis [14], sensing [15], and drug delivery [16]. In particular,

adsorption is one of the most potential applications for MOFs during the past 20 years. Compared with traditional adsorbents, MOFs have huge porosity and tunable pore sizes, endowing highly selective adsorption of hazardous contaminants from the environment [17]. However, these novel MOF-based adsorbents are difficult to be recycled from the mixture solution. To overcome this problem, combining MOFs with magnetic nanoparticles (NPs) has been made due to their high adsorption capacity, easy functionality, and easy isolation with an external magnetic field. The methods of preparing magnetic MOF composites include the hydrothermal method [18] and layer-by-layer assembly method [19]. These composite materials have the magnetic response on the basis of magnetic particles, which facilitates product recovery and lower operational cost in MOF separation. Moreover, the components of MOF-based magnetic composites can be easily engineered [20–22]. Hence, compared to conventional adsorbents used in the environmental pollution treatment, the MOF-based magnetic adsorbents are more suitable for industrial applications. Although magnetic composites at the industrial scale are still facing great challenges, numerous magnetic particles are commercially available, making the magnetic MOFs compatible with commercial applications in the near future [23].

In this review, we summarize the recent significant progress in the development of MOF-based magnetic nanocomposites for hazardous contaminant removal from the environment (Figure 1). The structures, properties, and the methods for the synthesis of the magnetic nanocomposites are discussed briefly. Particular challenges of MOF-based magnetic NPs for further development toward adsorption applications are critically discussed.

2. Design and Synthesis of Magnetic NP@MOF Structure

Magnetic metal-organic framework nanocomposites are new functional materials that have emerged in recent years [24]. They are composed of porous MOFs and magnetic NPs. It not only retains the structure and performance of the MOF material but also increases the magnetic properties of the granular material. It can be separated and recovered from the mix aqueous solution or soil by using a magnet and has the advantages of high selectivity, good dispersion, and multiple reuse [25]. It can be recycled again and is in line with the green concept. The synthesis of magnetic NP@MOFs generally can be seen as the following four methods.

2.1. Presynthesized Magnetic NP Template Method. In this method, the presynthesized magnetic NPs are used as seeds to grow MOFs. Firstly, the presynthesized magnetic NPs should be functionalized by capping agents or surfactants. For instance, Li et al. reported MOF-5@SiO₂@Fe₃O₄ core-shell magnetic catalysts, which were prepared through coating the typical MOF-5 on the surface of SiO₂@Fe₃O₄ NPs [26]. The results displayed that the as-synthesized magnetic core-shell nanocomposites can be easily separated from the mixture reaction system by a magnet. Zhao et al. also reported the synthesis of magnetic Fe₃O₄@MOF and demon-

FIGURE 1: Schematic illustration of magnetic NP@MOF heterostructure for hazardous contaminant removal from the environment.

strated as an immobilization vector for enzymes [27]. Fe₃O₄ NPs were functionalized by the polydopamine (PDA) layer, and then Cu₃(btc)₂ was synthesized on the surface of Fe₃O₄@PDA by introducing Fe₃O₄@PDA into an ethanol solution containing copper acetate and 1,3,5-benzenetricarboxylic acid (Figure 2). The MOF shell has a large surface area to ensure high load carrying capacity. Due to the strong affinity for the enzyme, the Fe₃O₄@PDA@[Cu₃(btc)₂]-enzyme composites achieved excellent digestion efficiency, good reusability, durability, and reproducibility.

2.2. Step-by-Step Method. Our group fabricated a series of Fe₃O₄@MOFs (e.g., Fe₃O₄@Cu₃(btc)₂, Fe₃O₄@MIL-100(Fe), and Au-Fe₃O₄@MIL-100(Fe)) core-shell nanocomposites with a controllable MOF shell thickness by the versatile step-by-step strategy (Figure 3) [28–30]. Functionalization of magnetic Fe₃O₄ core with the mercaptoacetic acid (MAA) before the coating process was vitally important during the initial stage of the step-by-step assembly, because no core-shell structures could be obtained using the unfunctionalized magnetic Fe₃O₄ core [28]. The growth of MOF shell on the MAA-functionalized Fe₃O₄ core can be initiated by first the metal ions binding to the MAA on the Fe₃O₄ surface, to which then the organic ligands from the solution bind. The thickness of the MOF shell can be facile controlled by tuning the number of step-by-step assembly cycles. Zhang et al. also prepared the novel porous Fe₃O₄@MIL-100(Fe) core-shell nanospheres by this method to achieve large enrichment capacity and high size exclusion selectivity for phosphopeptides [31].

2.3. Self-Template Method. In the self-template method, the magnetic metal or metal oxide composites will provide metal ions by sacrificing themselves and then coordinate to organic ligand. For example, Fe₃O₄@SiO₂@HKUST-1 magnetic core-

FIGURE 2: Schematic illustration of $\text{Fe}_3\text{O}_4@\text{PDA}@[Cu_3(\text{btc})_2]$ microspheres and the procedure for enzyme immobilization. Reprinted from Ref. [27] with permission of the Royal Society of Chemistry.

shell composite has been obtained by the self-template strategy in which magnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2$ were first coated with $\text{Cu}(\text{OH})_2$ shell as the sacrificial template and then HKUST-1 grew around the core [32]. Here, $\text{Cu}(\text{OH})_2$ shell not only was the sacrificial template but also provides copper ion sources for the formation of HKUST-1 [32]. Compared to other template strategies, this approach shows decisive economy advantage and does not require additional surface modification. Moreover, the Bi-I-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{HKUST-1}$ magnetic composite exhibited excellent adsorption for Hg^{2+} from water (Figure 4). By using this method, Cai and coworkers also reported the novel magnetic Prussian blue (PB) composite using the self-template method [33]. PB cube was used both as the sacrificial template and as the iron source of Fe_3O_4 for the formation of PB- Fe_3O_4 composite.

2.4. Dry Gel Conversion Method. Tan et al. demonstrated a dry gel conversion (DGC) method to fabricate HKUST-1/ Fe_3O_4 composites for desulfurization and denitrogenation applications [34]. In this method, the solvent is first separated from the mixed Fe_3O_4 and MOF precursors, and then solvent vapor is generated into the mixture to induce MOF formation around magnetic NPs. With this simple method, HKUST-1/ Fe_3O_4 composites have been successfully constructed without blockage of the MOF pores (Figure 5). Significantly, the obtained magnetic porous adsorbents not only can undergo efficient adsorption of various aromatic sulfur and nitrogen compounds from model fuels but also can be easily separated from mixture by an external magnetic field.

3. Applications of Magnetic NP@MOF Composites in the Environment

MOF-based magnetic nanostructures have been widely used for many applications due to their outstanding physicochem-

ical performance [24]. In this review, we are particularly interested in applying these magnetic composites as sustainable environment adsorbents. Environmental pollution has become one of the major problems worldwide at present. Due to the decline of water quality, water bodies continue to deteriorate, leading to the suspension of relevant factories and agricultural production. The adverse social impact and economic loss caused threaten the sustainable development of society and the healthy development of mankind. There are a large number of organic, inorganic, and biological pollutants in water and soil, such as herbicides [35] and dyes [36]. The advantages of magnetic NP@MOF composites for the adsorption of hazardous materials from the environment will be discussed in later sections. Further, we will also point out the state-of-the-art progress in magnetic NP@MOF composite adsorption applications categorized by the hazardous compound type.

3.1. Adsorption of Organic Contaminants. Magnetic NP@MOF composites are promising porous adsorbents for the adsorption of organic contaminants from the environment due to their magnetic core for easy magnetic separation along with porous MOF shell for highly selective removal of contaminants. For example, Zhou et al. developed a novel magnetic $\text{Fe}_3\text{O}_4@\text{MIL-100}(\text{Fe})$ NPs for mechanochemical magnetic solid phase extraction (MCMSPE) of organochlorine pesticides from tea leaves [37]. $\text{Fe}_3\text{O}_4@\text{MIL-100}(\text{Fe})$ magnetic NPs were synthesized by the step-by-step method and further successfully used for the separation of organochlorine pesticides from tea. Moreover, $\text{Fe}_3\text{O}_4@\text{MIL-100}(\text{Fe})$ magnetic NPs can be reused with no significant changes in the organochlorine pesticide recovery after five adsorption cycles. The results indicated that such magnetic NPs are ideal recyclable adsorbents for removal of organochlorine pesticides from plant samples. In the same time, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Zr-MOF}$ magnetic composites were also reported for

FIGURE 3: Schematic representation of the step-by-step assembly strategy (a) and TEM images of $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{btc})_2]$ core-shell magnetic microspheres after (b) 10, (c) 20, (d) 25, (e) 30, (f) 40, and (g) 50 assembly cycles at 25°C . Reprinted from Ref. [28] with permission of the Royal Society of Chemistry.

the effective removal of pharmaceutical compounds from water [38]. The obtained $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{UiO}-66\text{-NH}_2$ displayed a high adsorption capacity and rapid separation rate for the adsorption of salicylic acid (SA) and acetylsalicylic acid (ASA) due to the magnetic NPs in combination with porous Zr-MOF (Figure 6). The saturated magnetization value of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{UiO}-66\text{-NH}_2$ was measured to be 25.4 emu g^{-1} . The easy separation, high capacities, and reusability of the magnetic Zr-based MOF make it as superior adsorbents for removal of pharmaceutical contaminants.

Based on a similar process, four other magnetic composites, $\text{magG}@\text{SiO}_2@\text{ZIF}-8$ [39], $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MOF}/\text{TiO}_2$ [40], $\text{Fe}@\text{SiO}_2@\text{MOF}-5$ [41], and $\text{Fe}_3\text{O}_4@m\text{-SiO}_2/\text{PSA}@\text{Zr-MOF}$ [42], were successfully synthesized based on the magnetic NPs coated with a layer of SiO_2 . The magnetic NPs@ SiO_2 cores help adsorption of metal ions and organic linkers for the growth of outer shell of MOF layers. The $\text{magG}@\text{SiO}_2@\text{ZIF}-8$ composites displayed high extraction efficiency and reusability for adsorption of phthalate esters with the linear range of $50\text{--}8000 \text{ ng mL}^{-1}$ and up to 92% recoveries [39]. $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MOF}/\text{TiO}_2$ [40] and $\text{Fe}@\text{SiO}_2@\text{MOF}-5$ [41] core-shell nanocomposites were used as efficient adsorbents for MSPE of five triazole fungicides as well as N- and S-containing polycyclic aromatic hydrocarbons from contaminated water. Here, TiO_2 immobilized on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MOF}$ could enhance the adsorption properties of magnetic MOF with the detection and quantification limits of $0.19\text{--}1.20 \text{ ng L}^{-1}$ and $0.61\text{--}3.62 \text{ ng L}^{-1}$, respectively [40]. The $\text{Fe}@\text{SiO}_2@\text{MOF}-5$ exhibited a good adsorption for N- and S-containing polycyclic aromatic hydrocarbons with LODs in the range of $0.025\text{--}0.033 \text{ } \mu\text{g L}^{-1}$ [41]. In addition to these, Xu and coworkers developed a novel $\text{Fe}_3\text{O}_4@m\text{-SiO}_2/\text{PSA}@\text{Zr-MOF}$ magnetic nanocomposite for bifenthrin determination from water [42]. Considering the outstanding performance and limitless

of MOFs, it is expected that such MOF-based magnetic core-shell nanocomposites will open a new doorway in the field of adsorption of organic contaminants from the environment.

3.2. Adsorption of Dyes from Wastewater. Dye has become an important industrial hazardous contaminant in water. In recent years, with the development of the dye industry, it has a great adverse impact on the environment and human health. Therefore, it is crucial to devise a strategy for the treatment and removal of these dyes from polluted water. Wang et al. reported the use of magnetic $\text{Fe}_3\text{O}_4/\text{MIL}-101(\text{Cr})$ composite for effective adsorption of two dyes, acid red 1 (AR1) and orange G (OG) [6]. They fabricated $\text{Fe}_3\text{O}_4/\text{MIL}-101(\text{Cr})$ magnetic composites by a reduction-precipitation method with large surface areas, strong magnetism, and excellent dispersion effect. The adsorption capacities of AR1 and OG with $\text{Fe}_3\text{O}_4/\text{MIL}-101(\text{Cr})$ were 142.9 and 200.0 mg g^{-1} , respectively [6]. The authors suggested that the adsorption of AR1 and OG was spontaneous, exothermic, and randomness decreased with monolayer adsorption during this process. Very recently, perfect $\text{MgFe}_2\text{O}_4@\text{MOF}$ [43] and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Zn-TDPAT}$ [44] core-shell magnetic materials were reported by the presynthesized magnetic NP template method. The $\text{MgFe}_2\text{O}_4@\text{MOF}$ magnetic composites were fabricated by a mercaptoacetic acid- (MAA-) functionalized MgFe_2O_4 NPs as the template method [43]. The obtained $\text{MgFe}_2\text{O}_4@\text{MOF}$ hybrid nanomaterials displayed excellent removal of Rhodamine B (RB, 219.78 mg g^{-1}) and Rhodamine 6G (Rh6G, 306.75 mg g^{-1}) from wastewater. Moreover, these magnetic hybrid nanomaterials showed good reusability even after 10 times reused. The as-synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Zn-TDPAT}$ core-shell magnetic material also displayed a high performance activity in adsorption of polluted dyes [44]. The adsorption efficiencies can reach 100 and 99% for Congo red (CR) and methylene blue (MB) by this

FIGURE 4: Scheme of the preparation of Bi-I functionalized Fe₃O₄@SiO₂@HKUST-1 composites. Reprinted from Ref. [32] with permission of the Royal Society of Chemistry.

magnetic material, respectively. Significantly, such Fe₃O₄@-SiO₂@Zn-TDPAT core-shell magnetic material can be stable under different acid-alkaline conditions. The results suggested that MOF-based magnetic core-shell materials are promising adsorbents for dye removal from wastewater.

These MOF-based magnetic composites have high capacity toward a certain dye; the application of selective removal of specific dye from a mixture of multiple dye-polluted water needs more development. In 2018, Yang et al. reported a novel Fe₃O₄-PSS@ZIF-67 magnetic core-shell composite for selective adsorption of methyl orange (MO) from MO and methylene blue (MB) mixed solution (Figure 7) [45]. The results demonstrated that the adsorption capacity of the magnetic composites for MO was measured to be 738 mg g⁻¹ with the separation rate of up to 92%. The selective adsorption mechanism can be attributed to charge-selectivity between the dye molecule and the MOF. The sizes of the MO and MB molecules are 1.54 × 0.48 × 0.28 nm³ and 1.38 × 0.64 × 0.21 nm³, while ZIF-67 has pore cage of 1 nm. Therefore, MO and MB molecules can be adsorbed in the pore cage of Fe₃O₄-PSS@ZIF-67. Furthermore, the negatively charged MO can be adsorbed with the Lewis base of Co²⁺ centrals because of the electrostatic attraction while the positively charged MB is hard to be adsorbed because of the electrostatic repulsion.

3.3. Adsorption of Heavy Metal Ions. Recently, MOF-based magnetic composites have been also used as porous adsor-

bents for the removal of heavy metal ions from the environment. MOF-based magnetic composites are promising adsorbents for the removal of heavy metal ions because of their easy modification and isolation. Karimi et al. reported a chemical bond between the NHSO₃H-functionalized Fe₃O₄ and the HKUST-1 method for the synthesis of magnetic Fe₃O₄-NHSO₃H@HKUST-1 nanocomposites for the adsorption of lead ions (Pb²⁺) from wastewater [46]. According to this work, the maximum adsorption capacity of Pb²⁺ with Fe₃O₄-NHSO₃H@HKUST-1 was 384.6 mg g⁻¹, which corresponds to 46.3% of the magnetic adsorbent occupied sites. After the adsorbent is separated by the magnet and washed with 0.1 M of HCl and distilled water, it can be used for another adsorption experiment. As a result, Fe₃O₄-NHSO₃H@HKUST-1 could be reused four times without significant loss of adsorption activity (>90%). Huang et al. reported two amino-modified Zr-based magnetic MOF composites (Fe₃O₄@SiO₂@UiO-66-NH₂ and Fe₃O₄@SiO₂@UiO-66-Urea) for the extraction of heavy metal ions [47]. Fe₃O₄@SiO₂@UiO-66-NH₂ and Fe₃O₄@SiO₂@UiO-66-Urea were prepared by a simple one-pot strategy with different precursors. The obtained amine-decorated magnetic composites exhibited high adsorption for heavy metal ions compared to pure magnetic composites. In particular, Fe₃O₄@SiO₂@UiO-66-NH₂ showed the highest adsorption capacity for Pb²⁺ (102 mg g⁻¹). The authors concluded that the improvement in the removal of Pb²⁺ by the amine-decorated magnetic composites compared with Fe₃O₄@SiO₂@UiO-66 is due to

FIGURE 5: SEM and TEM images of (a, b) Fe_3O_4 , (c, d) HKUST-1, and (e, f) the HKUST-1/ Fe_3O_4 composites. Reprinted from Ref. [34] with permission of Elsevier.

the fact that the $-\text{NH}_2$ groups on the magnetic composites provide more binding sites for the adsorption of Pb^{2+} by chelating. Further, hierarchically HPU-13@ Fe_3O_4 ($\text{HPU-13} = \{[\text{Cu}_3(\text{L})_2] \cdot \text{OH} \cdot 2\text{CH}_3\text{CH}_2\text{OH} \cdot 10\text{H}_2\text{O}\}_n$; $\text{HL} = 2-(5\text{-pyridin-4-yl-2H-[1,2,4]triazol-3-yl)pyrimidine}$) magnetic hybrid composites were synthesized for high removal and excellent reuse of Cr(VI) ions from water [48]. HPU-13@ Fe_3O_4 showed high adsorption capacities for $\text{Cr}_2\text{O}_7^{2-}$ (398.41 mg g^{-1}) and CrO_4^{2-} (471.69 mg g^{-1}). The results proved that oxidation of Cu(I) to Cu(II) on the magnetic adsorbents occurred during the adsorption process and partial reduction of Cr(VI) to Cr(III) in the solution at the same time. Finally, the authors revealed that the high adsorption of Cr(VI) under these conditions is due to the synergistic reaction of Cr(VI) reduction and adsorption [48].

The radioactive elements are also a major issue to the environment such as U(VI) and Th(IV) . These radioactive metal ions can create numerous diseases including liver and

lung cancers. In this case, the adsorption of these metal ions from the environment is a challenge and critical issue for the environmental remediation. Alqadami et al. prepared an Al-based magnetic MOF nanocomposite ($\text{Fe}_3\text{O}_4@\text{AMCA-MIL53(Al)}$) for the adsorption of U(VI) and Th(IV) from wastewater [49]. The adsorption capacities for U(VI) and Th(IV) were measured to be 227.3 and 285.7 mg g^{-1} , respectively. The adsorption equilibrium time of $\text{Fe}_3\text{O}_4@\text{AMCA-MIL53(Al)}$ for both radioactive metal ions was demonstrated within 90 min. The results suggested the adsorption mechanism for U(VI) and Th(IV) over $\text{Fe}_3\text{O}_4@\text{AMCA-MIL53(Al)}$ through the electrostatic interactions between the organic part of the magnetic nanocomposite and the radioactive metal ions and coordinate interactions between the metal ions and nitrogen in the framework. Min et al. reported a novel $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ magnetic nanocomposite for selective removal of UO_2^{2+} from water, which showed a high adsorption capacity of $523.5 \text{ mg U g}^{-1}$ [50]. Furthermore,

FIGURE 6: Scheme of (a) the preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Zr-MOF}$ composites and (b) the adsorption of SA and ASA. Reprinted from Ref. [38] with permission of the American Chemical Society.

the selective separation of the UO_2^{2+} from lanthanide results indicated that the obtained $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ displayed remarkable selectivity performance for UO_2^{2+} in the presence of lanthanides at pH 3.

Selectivity is one of the most primary issues of a good adsorbent in the practical application. In order to solve this problem, magnetic adsorbents can be modified by various functional groups for the removal of target metal ions. The functional groups can be easily introduced into the MOF-based magnetic composites by a facile postsynthetic modification (PSM) method. Very recently, we prepared thiol-functionalized $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{btc})_2$ core-shell magnetic microspheres and investigated their application in selective adsorption of heavy metal ions in the presence of other background ions from water [51]. $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{btc})_2$ core-shell magnetic microspheres were synthesized by a step-by-step assembly fashion. Further, $\text{Cu}_3(\text{btc})_2$ shell of the magnetic microspheres was modified by thiol groups of dithioglycol using such PSM method (Figure 8). Significantly, the thiol-functionalized $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{btc})_2$ showed high selective adsorption for Pb^{2+} ($K_d = 1.23 \times 10^4 \text{ mL g}^{-1}$) and Hg^{2+} ($K_d = 5.98 \times 10^4 \text{ mL g}^{-1}$) in the presence of background ions of Ni^{2+} , Na^+ , Mg^{2+} , Ca^{2+} , Zn^{2+} , and Cd^{2+} [51].

4. Adsorption Mechanism

The adsorption method is widely accepted for the removal of hazardous pollutants from the environment [52]. Magnetic MOF composites are superior to the traditional porous materials, due to their rational design, tunable porosity, controllable dimensions, large internal surface area, and easy isolation. Particularly, the pore shape and size of the magnetic MOFs can be controlled to selective adsorption of targeted hazardous molecules [53]. The mechanism for the removal of hazardous pollutants can be summarized as the four major types [17, 53]: (I) The hazardous molecules can be bound to the coordinatively unsaturated metal centers of magnetic MOFs. (II) The hazardous molecules can be adsorbed by π - π stacking interactions between the organic part of the MOFs and the hazardous molecules. (III) There are electrostatic interactions between the hazardous molecules and the magnetic MOFs. (IV) There is molecule bonding between the decorate functional groups on ligands of magnetic MOFs and the hazardous molecules. With the rapid new multifunctional MOF development, the mechanisms for the adsorption of pollutants over the magnetic MOFs become increasingly clear.

FIGURE 7: (a) Scheme of selective adsorption of MO from the mixed MO/MB solution by Fe₃O₄-PSS@ZIF-67 magnetic composites; photographs (b) and UV-vis spectra (c) of the mixed MO/MB solution before and after magnetic separation. Reprinted from Ref. [45] with permission of Elsevier.

FIGURE 8: Scheme of the preparation of thiol-functionalized Fe₃O₄@Cu₃(btc)₂ and its use for selective removal of Pb²⁺ and Hg²⁺ from the mixed heavy metal ion solution. Reprinted from Ref. [51] with permission of Elsevier.

5. Conclusion and Outlook

Here, we summarize a review of recent developments in the MOF-based magnetic nanocomposites for the removal of hazardous contaminants from the environment. The design and synthesis of the magnetic core-shell MOF composites are promising methods to achieve synergies of magnetic particle core and porous MOF shell. Compared with traditional adsorption materials, magnetic MOF adsorbents have a larger specific surface area and more surface active sites and

can be quickly and easily recovered by an external magnetic field, which is in line with the modern green concept. Because of these excellent properties, magnetic MOF adsorbents have great application prospects in the removal of hazardous materials from the environment. The magnetic MOF composites with highly selective adsorption of target toxic compounds can be constructed by chemical modification, which will further improve the removal efficiency. This review has demonstrated several synthetic methods for the MOF-based magnetic core-shell composites. However, the

current challenge is that most of the reported magnetic MOFs are still in the small-scale application stage and the far distance from large-scale industrial production and application to safeguard the environment. In addition, the incorporated magnetic particle shape and size are highly desirable, which are key issues for the application in adsorption with high capacity and selectivity. Meanwhile, the understanding of the electronic structure and interactions present between the magnetic core and MOF shell remains a challenge. Furthermore, the exact mechanism of enhanced adsorption activity by the magnetic MOF composites is still unclear. Although challenges still exist, it is expected that with the in-depth development and discussion of the magnetic MOF composites at home and abroad, it will show a broad prospect in the future practical application.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Gege Zhao and Nianqiao Qin contributed equally to this work.

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