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REVIEW ARTICLE

Overview on recent advances of magnetic metal–organic framework (MMOF) composites in removal of heavy metals from aqueous system

Mayuri Dutta[1] · **Jyotismita Bora**[1] · **Bolin Chetia**[1]

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Abstract

Developing a novel, simple, and cost-effective analytical technique with high enrichment capacity and selectivity is crucial for environmental monitoring and remediation. Metal–organic frameworks (MOFs) are porous coordination polymers that are self-assembly synthesized from organic linkers and inorganic metal ions/metal clusters. Magnetic metal–organic framework (MMOF) composites are promising candidate among the new-generation sorbent materials available for magnetic solid-phase extraction (MSPE) of environmental contaminants due to their superparamagnetism properties, high crystallinity, permanent porosity, ultrahigh specific surface area, adaptable pore shape/sizes, tunable functionality, designable framework topology, rapid and ultrahigh adsorption capacity, and reusability. In this review, we focus on recent scientific progress in the removal of heavy metal ions present in contaminated aquatic system by using MMOF composites. Different types of MMOFs, their synthetic approaches, and various properties that are harnessed for removal of heavy metal ions from contaminated water are discussed briefly. Adsorption mechanisms involved, adsorption capacity, and regeneration of the MMOF sorbents as well as recovery of heavy metal ions adsorbed that are reported in the last ten years have been discussed in this review. Moreover, particular prospects, challenges, and opportunities in future development of MMOFs towards their greener synthetic approaches for their practical industrial applications have critically been considered in this review.

Keywords Magnetic metal–organic framework (MMOF) · Heavy metal ions · Water contamination and remediation · Magnetic solid phase extraction · Adsorption removal

Introduction

The world's aquatic systems are continuously being threatened by the continuous explosion of world population together with urbanization as well as industrial and agricultural revolution (Crini and Lichtfouse 2019). It is a mandatory requirement to have access to clean water for proper survival and development of living beings. Serious health issues to humans and other living organisms caused by chemical risk factors in aqueous environments have been increased in recent years (Crini et al. 2019). The types of pollutants discharged to the aqueous media, their quantities, and difficulties in detection as well as removal have been a major concern for both researchers and environmental organizations all over the world. Most of the heavy metal ions including lead (Pb), arsenic (As), mercury (Hg), cadmium (Cd), and chromium (Cr), inorganic acids, oxycations/oxyanions, and inorganic anions, organic contaminants including agricultural products, organic industrial wastes, organic dyes, pharmaceuticals, and personal care products discharged to water streams are ubiquitous source of water contamination (Mon et al. 2018; Rashid et al. 2021).

Heavy metal ions have versatile applications in different industrial activities including metal planting, mining, chemical and power generation companies, electronic device manufacturing, painting, and plumbing and thereby introduced to the water bodies through industrial effluents (Zargoosh et al. 2013). High-grade toxicity, potential bioaccumulation in the living cells, and non-biodegradability of the

Responsible Editor: Angeles Blanco

✉ Bolin Chetia
bolinchetia@dibru.ac.in

Mayuri Dutta
rs_mayuridutta@dibru.ac.in

Jyotismita Bora
rs_jyotismitabora@dibru.ac.in

[1] Department of Chemistry, Dibrugarh University, Dibrugarh, Assam 786004, India

existing heavy metal ions even in trace amount have been continuously exerting atrocious impact on living organism by entering into the food chain and food webs (Almomani et al. 2020). Long-term exposure of these toxic heavy metal ions even in ppb level can cause progressive adverse effects to the living organisms by deteriorating the central nervous system, kidney, brain, lungs, etc. (Shams et al. 2016). As stated by the International Agency for Research on Cancer (IARC) and United State Environmental Protection Agency (U.S. EPA), the heavy metals like arsenic (Rahaman et al. 2021), cadmium (Sharma et al. 2015), mercury (Zahir et al. 2005), lead (Hall 1972), and chromium (Tsenget al. 2019) are categorized as either probable or known carcinogenic elements on the basis of their experimental and epidemiological studies (Pratush et al. 2018). In this context, reduction or elimination of existing heavy metal ions from coastal and inland contaminated water is garnering attention worldwide among the scientists (Ledezma et al. 2021; Bhateria and Singh 2019; Wen et al. 2018).

Existing technologies for removal of heavy metal ions

Till now several technologies are demonstrated for removal and recovery of heavy metal ions with different degree of success including membrane filtration (Zhang et al. 2018; Zhao et al. 2022; Peng and Guo 2020; Yang et al. 2020a, b, c), coagulation/flocculation (Sun et al. 2021; Liang et al. 2014; Nguyena et al. 2021), advanced oxidation processes (Zhang et al. 2022a, b, c, d; Kim et al. 2018; Ikhlaq et al. 2022; Mahtab et al. 2021), chemical precipitation (Mavhungu et al. 2021), adsorption (Chaudhry et al. 2022; Sharma et al. 2021; Lata and Samadder 2016), nanotechnologies (Bhat et al. 2022; Lai et al. 2022; Rani et al. 2021; Wadhawan et al. 2020), and biological processes (Singh et al. 2022; Bhatt et al. 2022; Pazdzior et al. 2019). Although these currently used conventional technologies for wastewater monitoring and remediation have their own advantages, they suffer some inconveniences such as high installation and maintenance cost, generation of secondary contaminants, complicated and prolonged processing time, and poor accuracy and are incapable of eliminating the entire waste of contaminated water (De Gisi et al. 2016; Martini 2021; Yahya et al. 2018).

Among all the methods available for wastewater treatment, adsorption technique with organic or inorganic porous materials has been established as the most reliable and competitive one due to its simplicity, high efficiency, and cost-effectiveness (Soylak et al. 2021; Burakov et al. 2018). However, the challenging task for practical application is to discover a highly efficient and cost-effective adsorbent. In this perspective, different types of adsorbents such as mesoporous clays (Marangu et al. 2022; Yadav et al. 2019), mesoporous silica (Han et al. 2018; Yaftian et al. 2019a, b; Yaftian et al. 2018, 2016, 2018), zeolites (Ugwu et al. 2022; Irannajad and Haghighi 2021; Zhang et al. 2022a, b, c, d), nanoporous materials (Ghani et al. 2021; Phukan and Chetia 2016; Liu et al. 2020), nanofibers (Wirzal et al. 2020; Doan et al. 2021), carbon-based materials (Mahesh et al. 2022; Ugwu and Agunwamba 2020; Wong et al. 2018), and biopolymers (Pillay et al. 2021; Liu et al. 2022a; Sarode et al. 2019) have extensively been studied and employed to remove heavy metal ions from water ecosystem to a considerable extent.

However, inconveniences related to the conventional sorbent materials include lack of synthetic procedures to develop recoverable adsorbents with tailorable structures/pores, precise control on adsorption kinetics, high capacity, and selectivity of contaminants (Al-Othman et al. 2021). Thus, addressing novel approaches for complete removal of heavy metal ions from aqueous environments with very high efficiency, high specificity, high selectivity, and high sensitivity has become a priority research topic among the chemists in order to restore a sustainable balance in the ecosystem (Chai et al. 2021; Zhu et al. 2019).

Metal organic frameworks (MOFs)

MOFs also known as porous coordination polymers (PCPs) are organic–inorganic hybrid crystalline materials having fascinatingly diverse properties with highly ordered frameworks of pores in which inorganic nodes (e.g., transition metal ions, alkali and alkaline earth metal ions, and rare earth metal ions/metal clusters) and organic linkers (e.g., carboxylate derivatives, Schiff bases, and pyridyl and ether derivatives) are linked together by coordinate bonds to assemble infinite network structures (Yuan et al. 2018a, b; Khan et al. 2013). Unique structural characteristics in MOFs can be achieved by tuning the building blocks of the frameworks to obtain novel MOFs according to their specified applications. Due to their high crystallinity, permanent porosity, ultrahigh surface area, adaptable pore shape/sizes, tunable functionality, and designable framework topology, MOFs exhibit ever-expanding application scopes in chemistry (Rasheed et al. 2022; Raptopoulou 2021; Kumar et al. 2020; Yang and Gates 2019). MOFs and MOF composites have been extensively studied over the last few years, and researchers have explored their versatile applications in diverse fields including heterogeneous catalysis (Rostamnia and Taghavi 2022a, b; Rostamnia et al. 2020, 2016; Liu et al. 2021; Hu et al. 2018; Cheng et al. 2021a, b; Kaushal et al. 2021; Remya and Kurian 2019), green catalysis (Rostamnia and Alamgholiloo 2018), gas storage and separation (Ghanbari et al. 2020; Lin et al. 2019), sensing (Rasheed and Rizwan 2022; Lv et al. 2022; Safarifard et al. 2020; Soni et al. 2019; Cui et al. 2019), biomedical applications including drug loading and delivery (Wei et al. 2022; Hashemi et al. 2019), enzyme immobilization (Karami et al. 2022; Sheta et al. 2018), luminescence (Zhang et al. 2022a, b, c, d; Xiao et al. 2022), photocatalytic dye adsorption/degradation (Oladoye et al. 2021; Ghosh et al. 2019), removal of environmental pollutants (Rajendran et al. 2022; Saboor et al. 2021; Zhao et al. 2015a, b), proton conduction (Ye Y et al. 2020), and as super capacitors (Byun et al. 2022; Jiao et al. 2017). Zhou et al. in their review article cover different types of Fe-based MOFs in photo-Fenton process for the removal of various organic pollutants (Zhou et al. 2022). In comparison to other MOFs, Fe-MOFs nicely couple with Fenton reagents and show excellent photocatalytic activities. MOF composites have been successfully utilized for the removal of antibiotics from aquatic samples via adsorption and photocatalysis (Yu et al. 2021a, b; Cao et al. 2022; Du et al. 2022; Yu et al. 2021a, b).

Recently, metal single atom catalysts (SACs) supported on MOFs have emerged applications in photocatalytic energy conversions including hydrogen formation reaction and CO_2 reduction owing to their synergistic effects in enhancing photocatalytic activities (Cheng et al. 2022a, b). Water-resistant zirconium-based MOF, UiO-66, with excellent mechanochemical and hydrothermal stability has been modified by functionalization of organic linkers, choosing perfect metal nodes, identifying foreign metal, defect engineering, sensitization of dyes, and combination of semiconductors for various photocatalytic applications including the removal of organic pollutants, reduction of Cr(VI), hydrogen generation, and CO_2 reduction (Cheng et al. 2022a, b). Uniform encapsulation of polyoxometalate (POM) in long-range ordered structure of MOFs (POM@MOF) has gained wide interests as a promising visible light induced photocatalysts for degradation of organic pollutants, photocatalytic water splitting, selective oxidation of organics, and reduction of CO_2 due to their synergistically improved charge transfer and electron redox transformation (Cheng 2021a).

Among all the industrialized and non-industrialized organic and inorganic adsorbents available for removal of heavy metal ions, MOFs are developed to gain the advantages of both inorganic and organic components (Li et al. 2014; Shahid et al. 2022; Xu et al. 2021; Kaushal et al. 2020). Even though several research works have been carried out on development and applications of MOFs, industrialization of MOFs has been limited due to their instability in water (Qin et al. 2021; Meteku et al. 2020). Moreover, challenge in recovery of MOF-based adsorbents from the mixture of solution after their application is another severe drawback (Baskar et al. 2022).

Magnetic nanoparticles (MNPs)

MNPs are typically an emerging class of nanomaterials (solid particles with dimensions ranges between 1 and 100 nm) that exhibit extraordinary chemical, mechanical, and thermal properties along with substantially different and marvelous magnetic properties as compared to conventional micro and mesomaterials (Zhou et al. 2020). Along with excellent surface effect and fascinating magnetic properties, they exhibit outstanding optical, electrical, and catalytic properties as well and offer wide opportunities in chemical synthesis (Chutia and Chetia 2018, 2019, 2020), biomedical applications (Devi et al. 2014; Mohammed et al. 2016), environmental remediation, and sensing (Jiang et al. 2018). However, high surface energy of metallic MNPs thermodynamically destabilizes them and exerts a potential tendency to get aggregate which adversely affect their applications.

Magnetic metal–organic frameworks (MMOFs)

To countervail the deficiencies of both MOFs and MNPs, MNPs ($MnFe_2O_4$, Fe_3O_4, α-Fe_2O_3, γ-Fe_2O_3, $CoFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$, and $ZnFe_2O_4$) can either be immobilized into MOF structures or employed as metal source for building an MOF structure and thereby tuning the magnetic properties of NPs in the MOFs, resulting in an auspicious magnetic composite material in which MOFs serve as a host for the functional guest MNPs (magnetic metal–organic framework, MMOFs) (Ricco et al. 2013; Hu et al. 2013). Consequently, MMOF composites have synergistically enhanced properties including increased surface area, higher adsorption ability, easier functionality, and facile as well as rapid recyclability with an external magnet. The synergistic properties are significantly different from those of individual constituting components and offer promising applications in the removal of heavy metal ions from the aqueous system (Liu et al. 2022c; Peng et al. 2022).

Purpose of the review

Over the last decade, development in the synthesis and applications of MMOF composites in the adsorption of toxic heavy metal ions has widely been reported all over the world (Abdel-Magied et al. 2022; Abdollahi et al. 2022). Several reviews have summarized the fundamentals of MMOF composites and their selected applications in environmental monitoring and remediation by catalysis and adsorption (Moussavi et al. 2022; Gao et al. 2019; Zhao et al. 2019). To the best of our knowledge, comprehensive reviews on this subject matter are not so far focused. However, most of the recent developments in this area from the last three years have not been covered by their articles. In this review, we summarize different synthetic strategies adopted by the researchers for the preparation of MMOF composites, various structural properties that are harnessed for removal of heavy metal ions from contaminated water, and recent applications in removal of toxic heavy metal ions from wastewater with their adsorption capacities as well as limit of detections and their stability and reusability. Finally, future perspectives of MMOF composites in mitigating global environmental pollution are presented. Moreover, particular prospects and challenges in further development of MMOFs towards greener synthetic approaches for their industrial applications have critically been considered in this review.

Classification of MMOF composites

Several authors have adapted different criteria to elaborate the classification of MMOF composites including the type of guest molecule, nature of the MOF structures, and the synthetic approaches depending on the dynamic interactions between MOFs and MNPs (Li and Huo 2015; Espallargas and Coronado 2018). However, it is crucial to understand the synthetic strategies applied for designing various types of MMOF composites according to their specific applications and desired synergistic properties (Yadav et al. 2021). In this review, for more simplicity, MMOF composites have been categorized into two broad classes based on their composition and their synthetic strategies: (a) simple MMOF composites which are solely constructed by MOFs and MNPs and (b) complex MMOF composites which are usually multifunctional composites that are constructed by MNPs, MOFs, and a third component (Fig. 1).

Simple MMOF composites

As mentioned earlier, simple MMOF composites are generally made up of two components: the magnetic component (MNPs) and the framework structure (MOF). The magnetic components are most commonly the oxides of Fe (Fe_3O_4, α-Fe_2O_3, and γ-Fe_2O_3) or the ferrites of Co and Ni ($CoFe_2O_4$, $NiFe_2O_4$, etc.) (Far et al. 2022; Saemian et al. 2019; Zheng et al. 2020). Fabrication processes available for devising simple MMOF composites are quite simplistic involving the encapsulation of MNPs within the MOF structure or the deposition of MNPs on the MOF structure. Till date, several synthetic approaches have been successfully reported to get simple MMOF composites which are deliberately designed towards their specific applications.

Direct mixing, encapsulation, and embedding are the most frequently employed synthetic strategies in developing simple MMOF composites.

Direct mixing strategy for preparing MMOF composites

The mixing method is the simplest technique for generating simple MMOF composites in which separately synthesized MNPs and pre-synthesized MOFs are mixed together in a suitable solvent under sonication to avoid aggregation. MNPs are firmly fixed on the surface of the MOFs by electrostatic interactions (Nadar et al. 2018). In this strategy, neither the surface of MNPs is modified by utilizing functionalizing agents nor are polymer coatings employed to provoke the growth of MOFs over MNPs (Huo and Yan 2012).

For instance, the mixing approach for developing simple MMOF composite was demonstrated very well by Liu and his coworkers in which MIL-100(Fe) was prepared by using trimesic acid as organic linker and iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) as metal source in a Teflon-lined steel autoclave at 200 °C for 8 h. Magnetic MOF composite Fe_3O_4/MIL-100(Fe) was fabricated by simply mixing the pre-synthesized MIL-100(Fe), ferric chloride crystals, and anhydrous sodium acetate with ethylene glycol in an autoclave for 10 h at 200 °C. Fe_3O_4/MIL-100(Fe) composite obtained was collected, washed, and dried under vacuum and was demonstrated as a stable, durable, and reusable adsorbent for rapid extraction and separation of Rhodamine B dye from water (Liu et al. 2016).

Yadav et al. recently prepared a novel magnetically retrievable MMOF catalyst $CoFe_2O_4$/Mn-BDc by using a solvothermal synthetic route, which is involved in the mixing of manganese dichloride tetrahydrate ($MnCl_2{\cdot}2H_2O$) and 1,4-benzene dicarboxylic acid (1,4-BDC) organic linker and resulting solution was stirred for 10 min. The solution was directly mixed with pre synthesized $CoFe_2O_4$ MNPs in 1:4 ratio of DMF:methanol under ultrasonication and then transferred to an autoclave to heat at 120 °C for 10 h (Fig. 2). The synthesized $CoFe_2O_4$/Mn-BDc catalyst was found to exhibit high catalytic activity in click coupling reaction to afford several biologically and pharmaceutically significant 1,4-disubstituted 1,2,3-triazoles with a satisfactory yield (Yadav et al. 2020).

Utilizing the aforementioned synthetic approach, several research groups have synthesized Fe_3O_4/MIL-53(Fe), NH_2-MIL-88B(Fe)/Fe_3O_4, MOF-199/Fe_3O_4, etc. and successfully explored their efficacy in the field of catalysis, sensing, environmental monitoring, and remediation (Cao et al. 2016; Zhang et al. 2015; Samui et al. 2016).

Encapsulation strategy for preparing MMOF composites

Another synthetic technique often utilized for designing simple MMOF composites is encapsulation in which the outer surface of the magnetic nanostructures (i.e., MNPs or fibers) are pre-treated with an interface material such as a polymer,

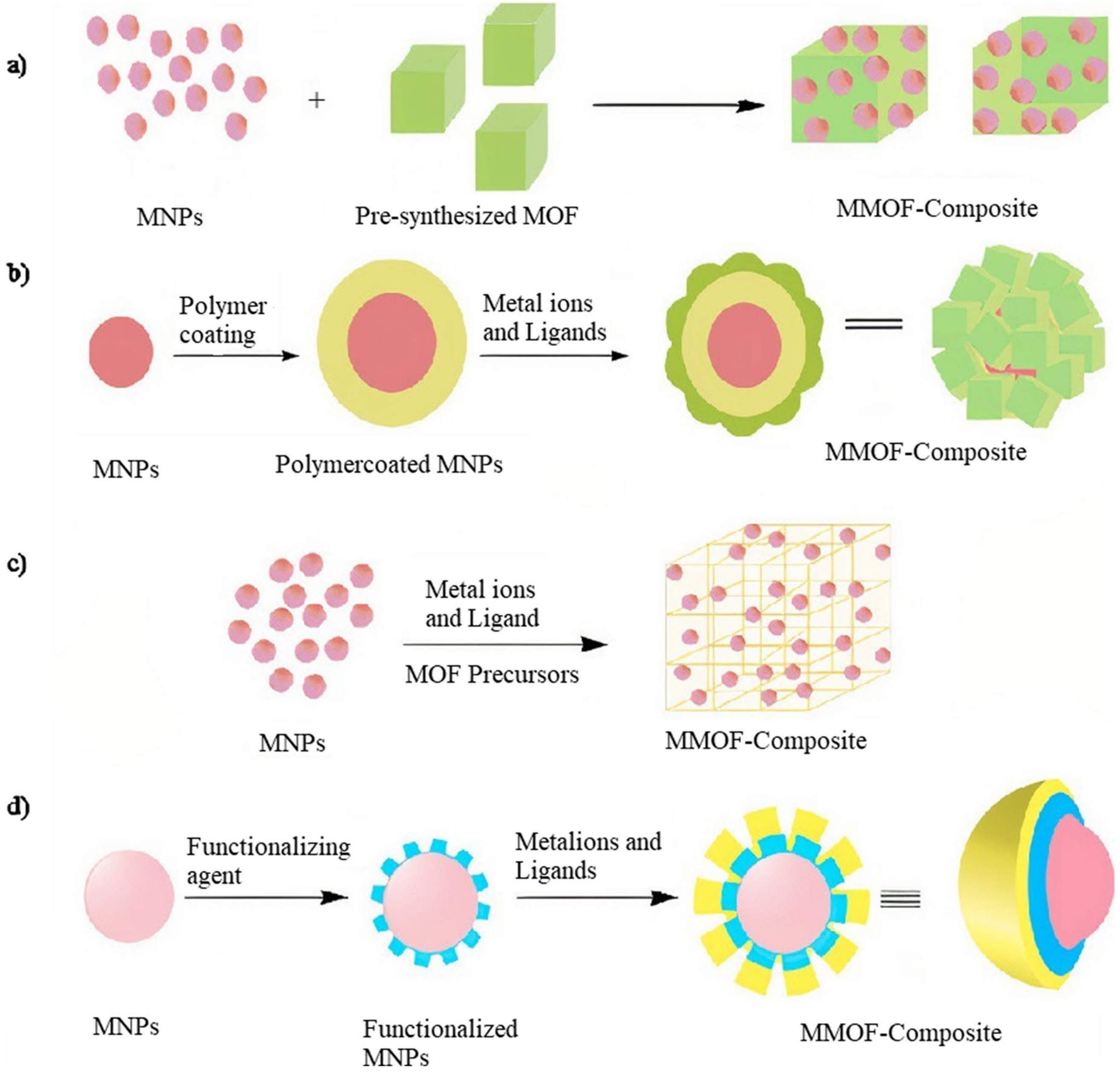


Fig. 1 Different synthetic approaches for designing MMOF composites: **a** mixing, **b** encapsulation, **c** embedding, and **d** layer by layer

silica, or a carbonaceous layer possessing high compatibility towards the fabrication of MOF, thereby generating a magnetic core–shell architecture. The affinity of the MOF shell towards the magnetic part was increased by the polymer shell consisting plenteous functional groups and hydrophilic sites and the magnetic core component that allowed the nucleation and controlled growth of a particular type of MOF. Remarkable examples have been reported in which the surface of magnetic nanostructures is modified by effectively encapsulating within silica (Huo and Yan 2012; Luo et al. 2019), chitosan (Chowdhuri et al. 2016), polyacrylic acid (PAA) (Jin et al. 2015), polydopamine (PDA) (Zhou et al. 2015), polyvinylpyrrolidone (PVP) (Xu et al. 2016), etc. to facilitate a controlled growth of MOF layers.

It is worth to mention here that very recently Yang and his group developed a facile synthetic route for attaining a novel MMOF composite, Fe_3O_4@SiO_2@Zr-MOF, with 2-aminoterephthalic acid as the organic linker and Zr as the metal node and demonstrated it as a potential adsorbent for adsorptive removal of salicylic acid and acetylsalicylic acid from aqueous solution. The elementary step of the above-mentioned synthetic protocol involves the encapsulation

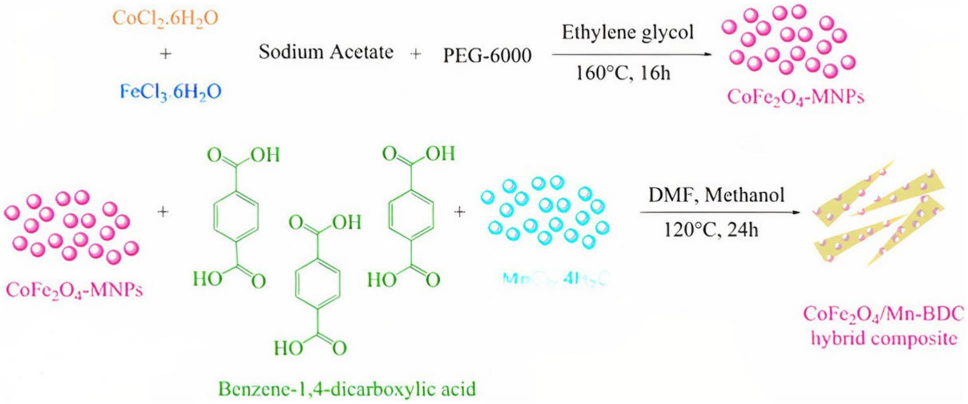


Fig. 2 Synthetic route for $CoFe_2O_4$/Mn-BDC composite

of pre-synthesized Fe_3O_4 MNPs within a coating of silica utilizing tetraethyl orthosilicate (TEOS). $Fe_3O_4@SiO_2@Zr$-MOF magnetic composite was obtained by ultrasonic dispersion of silica-coated MNPs ($Fe_3O_4@SiO_2$) with $ZrCl_4$ salt in DMF followed by addition of separately prepared DMF solution of 2-aminoterephthalic acid under continuous mechanical stirring for 6 h at 120 °C (Fig. 3). The silica coating stabilized the magnetic Fe_3O_4 core and essentially controlled the growth of Zr-MOF on the surface of Fe_3O_4 due to chelating interactions existing between Zr^{4+} ions of the MOF and –OH groups of silica layer (Yang et al. 2018).

A facile solvothermal route for fabrication of a novel MMOF composite, Fe_3O_4@MIL-101(Fe), was successfully illustrated by Yue et al. wherein PVP-coated Fe_3O_4 MNPs were ultrasonically mixed with DMF solution containing MOF salts, i.e., terephthalic acid and $FeCl_3 \cdot 3H_2O$ under 110 °C for 20 h. In the abovementioned protocol, the PVP-coated Fe_3O_4 MNPs are encapsulated within the MIL-101(Fe) nanostructure to yield crystalline Fe_3O_4@MIL-101(Fe) composite which was demonstrated as a stable and recyclable heterogeneous catalyst for the removal of azo dye such as Acid Orange-7 from environmental wastewater (Yue et al. 2016).

In the last decade, following the similar trend, various research groups have developed $Fe_3O_4@SiO_2$UiO-67, Fe_3O_4@PDA@[$Cu_3(btc)_2$], Fe_3O_4@PVP-PEI@MOF-PBA, etc. MMOF composites and illustrated their successful applications in enzyme immobilization, protein capture and release, organic as well as inorganic contaminant removal from environmental samples, etc. (Zhang et al. 2019; Zhao et al. 2015a, b; Yang et al. 2017).

Embedding strategy for preparing MMOF composites

The embedding approach is another important synthetic methodology frequently employed for devising simple MMOF composite. In this approach, pre-synthesized magnetic nanostructures (particles, fibers) are first directly dispersed into the MOF precursor solution comprising the organic linker, inorganic metal salt, and suitable solvent or mixture of solvents. Generally, by employing hydrothermal or solvothermal strategy, MNPs are allowed to get automatically embedded within the pores of MOF matrix without functionalizing or coating the surface of MNPs (Meteku et al. 2020; Ricco et al. 2013).

Very recently, Yadollahi et al. fabricated a novel MMOF composite, $CoFe_2O_4$/TMU-17-NH_2, via an embedding approach. Firstly, $CoFe_2O_4$ MNPs were synthesized by a co-precipitation method (Fig. 4). The synthesized $CoFe_2O_4$ MNPs were directly dispersed into a DMF solution containing 2-amino-1,4-benzenedicarboxylic acid, 1,4-bis(4-pyridyl)-2,3-diaza-2,3-butadiene, and $Zn(NO_3)_2 \cdot 6H_2O$ and allowed to get embedded within the pores of in situ-synthesized TMU-17-NH_2 matrix in an autoclave under 90 °C in 3 days (Yadollahi et al. 2021).

They explored the catalytic activity of the magnetic nanocomposite material $CoFe_2O_4$/TMU-17-NH_2 and established it as an easily recoverable and reusable acid catalyst for synthesis of several dihydropyrimidine derivatives via one pot solvent free multicomponent reaction of aromatic aldehyde, urea or thiourea, and 1,3-diketone.

Saikia and his coworkers followed a quite astounding protocol for embedding Fe_3O_4 MNPs into MIL-101(Cr) matrix

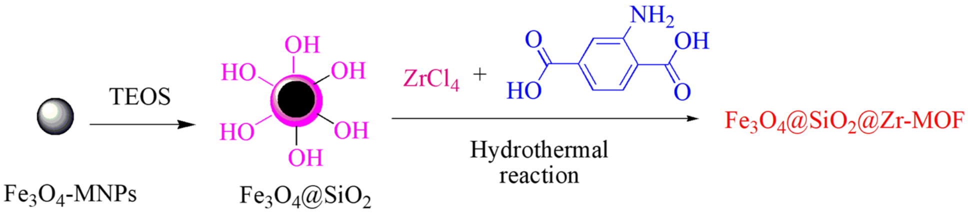


Fig. 3 Synthetic route for $Fe_3O_4@SiO_2@Zr$-MOF composite

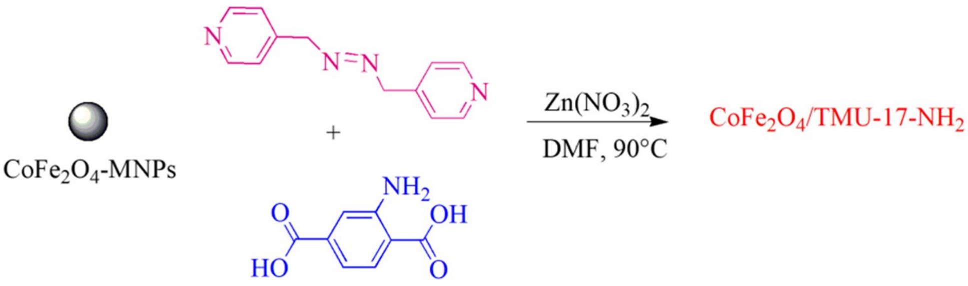


Fig. 4 Synthetic route for $CoFe_2O_4$/TMU-17-NH_2 composite

by adding $FeCl_2·4H_2O$ and $FeCl_3$ salts into an aqueous solution of MIL-101(Cr) under vigorous stirring for 1 h to fabricate Fe_3O_4@MIL-101(Cr) magnetic hybrid composite. The massive surface area of MIL-101(Cr) allows fantabulous dispersion as well as incorporation of MNPs on its surface. Fe_3O_4@MIL-101(Cr) composite was demonstrated as a very efficient catalyst for oxidation of benzyl alcohol to benzaldehyde under solvent-free condition and was recycled up to three catalytic cycles (Saikia et al. 2015).

Till date, embedding technique has successfully been utilized by several research groups to develop simple MMOF composites, e.g., hollow magnetic Fe_3O_4@NH_2-MIL-101(Fe), magnetic Mg-MOF-74, and magnetic MIL-101-SO_3H, whose efficacy has been explored in several prospering applications (Li et al. 2016a, b, c; Boroujeni et al. 2016).

Complex MMOF composites

As mentioned earlier, complex MMOF composites are generally made up of magnetic component (magnetic fibers or MNPs), MOF structure, and most essentially third component(s) such as noble metals, graphene oxide (GO), carbon nanotubes (CNT), carbon dots (CD), or polymers which synergistically improve the formation of the composites. These supporting agents are chosen on the basis of desired properties for their intended applications (Nirumand et al. 2018; Ke et al. 2015). In a similar manner to those of simple MMOF composites, most commonly employed magnetic components are the oxides of Fe (Fe_3O_4, α-Fe_2O_3, and γ-Fe_2O_3) or the ferrites of Co, Ni, etc. (Yin et al. 2019).

A layer-by-layer synthetic methodology is best suited for devising complex core–shell heterostructure where magnetic component is the core and the MOF is the shell. For synthesizing complex core–shell heterostructures, the surface of magnetic core is decorated with certain appropriate functional groups which facilitates a controlled growth of MOF structure resulting in the core–shell MMOF composite (Zhang et al. 2014).

For instance, Ke et al. (2015) reported a complex core shell MMOF composite Au-Fe_3O_4@MIL-100(Fe) via a layer-by-layer strategy. In the synthetic process, pre-synthesized Au nanoparticles were immobilized on the surface of L-cysteine-functionalized Fe_3O_4 MNPs using ascorbic acid to obtain Au-Fe_3O_4. Magnetic Au-Fe_3O_4 was then functionalized with mercaptoacetic acid (MAA) which facilitates layer-by-layer growth of MIL-100(Fe) shell around Au-Fe_3O_4 magnetic core (Ke et al. 2015).

Duo and his coworkers designed a fusiform-like MMOF composite, Fe_3O_4-NH_2@MOF-235, by employing a two-step solvothermal strategy. In the first step, amine-functionalized Fe_3O_4 MNPs, i.e., Fe_3O_4-NH_2, were obtained by the addition of ferric chloride, 1,6-hexanediamine, and ethylene glycol (Fig. 5). The amine-decorated MNPs were dispersed into a DMF solution containing MOF precursors, i.e., terephthalic acid organic linker and $FeCl_3·6H_2O$ metal source under a

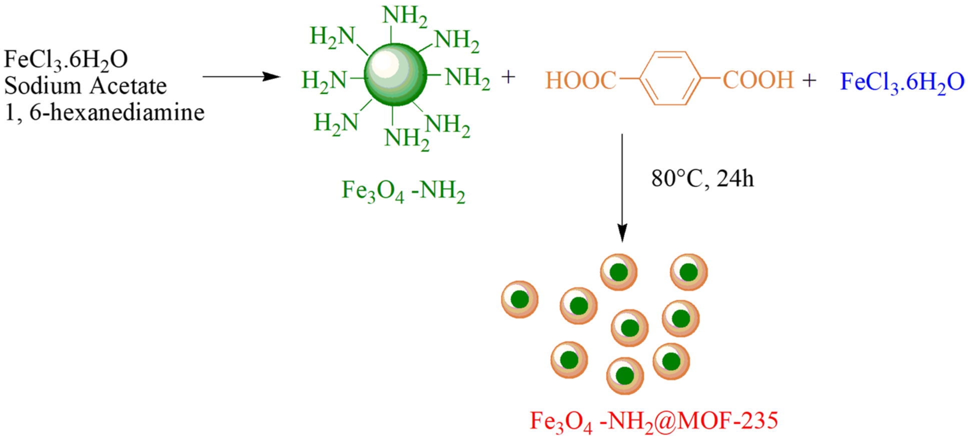


Fig. 5 Synthetic route for Fe_3O_4-NH_2@MOF-235 composite

solvothermal condition which allows the -NH_2 groups to get chelated with Fe^{3+} metal ions on the surface of Fe_3O_4 MNPs and then the chelated Fe^{3+} ions further bind with terephthalic acid forming the core to yield Fe_3O_4-NH_2@MOF-235 composite (Duo et al. 2019).

Tao et al. reported a time-efficient and productive solvent-free strategy for designing magnetic PCN-250 composite exhibiting outstanding CO_2 capture capacity in which citric acid-decorated Fe_3O_4 MNPs were prepared and blended with 3,3′,5,5′-azobenzene tetracarboxylic acid organic linkers and $Fe_2Co(\mu3\text{-}O)(CH_3COO)_6$ metal clusters with a vortex mixer and then transferred to an alternating magnetic field of strength 39 mT. The MNPs in the resulting powder reaction mixture acted as “nanoheaters” and the magnetic induction heat generated mPCN-250 composite after continuous heating of 1.5 h (Tao et al. 2019).

Sepehrmansourie and his group reported a novel MOF-based core–shell nanomagnetic composite Fe_3O_4@Co(BDC)-NH_2 and a range of novel fused pyridines and 1,4-dihydropyridines with pyrazole and pyrimidine moieties were synthesized by using the nanomagnetic composite as an efficient and recyclable catalyst. A simple sonication strategy was employed for the synthesis of Fe_3O_4@Co(BDC)-NH_2. 45.0 mM solution of $Co(NO_3)_2{\cdot}6H_2O$ and 45.0 mM of H_2BDC-NH_2 in DMF were prepared separately. Then, a mixture of pre-synthesized carboxylic acid-functionalized Fe_3O_4 MNPs ($Fe_3O_4@CH_2CO_2H$) and DMF solution of $Co(NO_3)_2{\cdot}6H_2O$ were sonicated. The sonicated mixture was separated by an external magnet and washed with DMF. To that magnetic mixture DMF solution of H_2BDC-NH_2 was added and sonicated for 45 min to obtain Fe_3O_4@Co(BDC)-NH_2 MMOF composites (Sepehrmansourie et al. 2021).

Another synthetic strategy for the synthesis of MMOF composite catalyst (Fe_3O_4@MIL-101(Cr)-N(CH_2PO_3)$_2$) was reported by the same group for the synthesis of pyrazolo [3,4-*b*] pyridines as convenient medicine by condensation reaction of aldehydes, 3-(cyanoacetyl)indole and 5-(1*H*-Indol-3-yl)-2*H*-pyrazol-3-ylamine. MIL-101(Cr)-NH_2 and phosphoric acid-functionalized MIL-101(Cr)-NH_2, i.e., MIL-101(Cr)-N($CH_2PO_3H_2$)$_2$, were synthesized by employing their previously reported simple solvothermal rout (Fig. 6). Then, a mixture of Fe_3O_4 MNPs and MIL-101(Cr)-N($CH_2PO_3H_2$)$_2$ was dispersed in toluene at 80 °C for 12 h. After cooling the reaction mixture, the nanoporous MMOF composite (Fe_3O_4@MIL-101(Cr)-N(CH_2PO_3)$_2$) was collected by an external bar magnet, washed with ethanol, and dried before catalytic application (Sepehrmansourie et al. 2022).

Babaee et al. developed a nanocomposite (MIL-101(Cr)-N($CH_2PO_3H_2$)$_2$) based on MIL-101(Cr)-NH_2 MOF with phosphorus acidic functional groups. The synthesized nanoporous MOF composite acted as a multifunctional heterogeneous catalyst for one-pot synthesis of *N*-amino-2-pyridone and pyrano[2,3-*c*]pyrazole derivatives. MIL-101(Cr)-NH_2 was obtained from an equimolar mixture of 2-aminoterephthalic acid and $Cr(NO_3)_3{\cdot}9(H_2O)$ in the presence of NaOH by heating it in a Teflon-lined autoclave at 150 °C for 12 h. MIL-101(Cr)-NH_2 with phosphoric acidic arms (MIL-101(Cr)-N($CH_2PO_3H_2$)$_2$) was obtained by refluxing MIL-101(Cr)-NH_2, formaldehyde, phosphorus acid, *p*-toluenesulfonic acid, and ethanol (Fig. 6). The amount of phosphorus present in MIL-101(Cr)-N($CH_2PO_3H_2$)$_2$ was found to be 4.56% (Babaee et al. 2020).

Recently, Alamgholiloo et al. demonstrated a highly economic and novel synthetic strategy to fabricate a complex ternary MMOF nanocomposite (Fe_3O_4/Cu-BDC/GO) in which Fe_3O_4 MNPs with open metal site Cu BDC MOF were allowed to grow simultaneously on GO sheets. It was the first ever reported ternary nanocomposite employed as an excellently reusable and efficient catalyst for the aerobic oxidation of alcohols to carbonyls in presence of a stable nitroxide radicals, [2,2,6,6-tetramethylpiperidine-*N*-oxyl] (TEMPO) as a cocatalyst. The synergistic interactions between Fe_3O_4 MNPs and GO as well as active copper in open metal sites of Cu-BDC frameworks synergistically enhanced the catalytic activity of the ternary MMOF-based nanocomposites (Alamgholiloo et al. 2020).

Alamgholiloo and his group in another report demonstrated a novel green solvothermal strategy to fabricate a ternary nanocomposite GO/CuBDC-Fe_3O_4 for fast degradation of ciprofloxacin antibiotics. Microporous Cu-BDC MOF was fabricated by employing a solvothermal route using terephthalic acid as organic linker and copper nitrate trihydrate as metal salts in the presence of polyvinyl alcohol

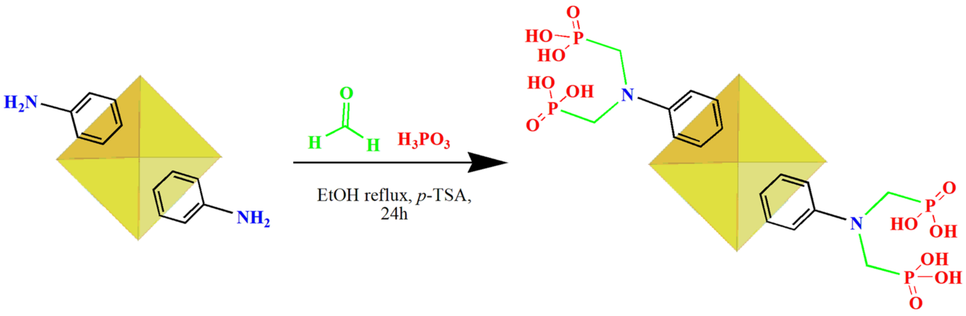


Fig. 6 Synthesis of MIL-101(Cr)-N($CH_2PO_3H_2$)$_2$ MOF composite containing phosphorous acid arms

as modulating agent. Exfoliated GO was used as a platform for the growth of Cu-BDC MOF and magnetic Fe_3O_4 NPs with the aim to create a PMS (peroxymonosulfate) activator. The maximum degradation rate for ciprofloxacin using the new ternary MMOF composite was found to be 98.5% within 24 min with rate constant 0.191 min^{-1} (Alamgholiloo et al. 2021).

Structural characteristics of MMOF composites

MMOF composites exhibit fascinating synergistic physical properties including ultrahigh surface area, high porosity, and outstanding magnetic property that are exploited in environmental monitoring and remediation (Li and Huo 2015).

Surface area

Surface area is one of the most important synergistic physical properties of MMOF composites that are crucial in environmental monitoring and remediation. Most of the environmental contaminants including organic and inorganic pollutants are eliminated from environmental samples through the adsorption process. The extent of adsorption depends on the available surface area on the sorbent materials. MOF, which is a major component of MMOF composites, is well known for its ultrahigh specific surface area that is highly desirable in many potential applications (Mohammed et al. 2016). Moreover, adsorption can be improved by introducing functional groups to the surface and pores of MMOF sorbents according to their intended application which significantly provides active sites for enhanced adsorption. Farha et al. reported two novel MOFs (NU-109 and NU-110) which exhibited record-breaking specific BET surface area of approximately 7000 m^2g^{-1}. Furthermore, theoretical upper limit for the MOF surface area was investigated and a substantially greater hypothetical surface area (14,600 m^2g^{-1}) was observed (2.7 American football fields could be covered by only 1 gm of the material) (Farha et al. 2012).

Each component in MMOF composites has synergistic impact on specific surface area. Recently, Mahmoodi and his group reported MOF-based magnetic adsorbent ZIF-8/$CoFe_2O_4$/GO (ZCG) composites with different amounts of $CoFe_2O_4$/GO (25 mg $CoFe_2O_4$/GO for ZCG-25 and 50 mg $CoFe_2O_4$/GO for ZCG-50) for the removal of pollutants from water. The specific surface area was determined according to the Brunauer–Emmett–Teller (BET) method and was found to possess an excellent BET surface area of 1543 m^2/g and 2490 m^2/g for ZCG-25 and ZCG-50, respectively. The BET surface of magnetic component was recorded to be 52 m^2/g and that of GO was 46 m^2/g. However, introduction of ZIF-8 synergistically enhanced the BET surface area of the entire composite to an outstanding value of 2490 m^2/g. Combination of ZIF-8 synergistically enhanced the BET surface area of the entire composite than the single components (Mahmoodi et al. 2019a,b). Far and his coworkers synthesized a MOF (UiO-66) with record-breaking BET surface area of 1215 m^2/g. Although BET surface area of pristine MOFs decreased from 1215 m^2/g to 507 m^2/g on incorporation of MNPs into UiO-66 structures, there was significant increase in the specific BET surface area of Fe_3O_4 MNPs from 11 to 507 m^2/g. On further coating with PPI dendrimer, the BET surface area was lowered down to a value 120 m^2/g. However, PPI dendrimer functionalization showed a positive impact on adsorption of anionic dyes (DR31 and AB92) due to the introduction of abundant functional groups to the nanoadsorbents which provided active sites for adsorption (Far et al. 2020).

Magnetic properties

Magnetism, the paramount property for recyclability, is an important characteristic of MMOF composites by virtue of which the sorbent material can be recycled efficiently by using an external magnetic field after usage Ease of recycling and regeneration of adsorbents is an important concern from the industrial and “green chemistry” point of view (Gao et al. 2019). MNP is a major component of MMOF composites that is introduced either to the surface or to the pores of MOFs. They not only affect the properties of specific surface area and adsorption capacity of the sorbent but also impart magnetism in it. Thus, introduction of MNPs to MOFs makes the composite economic and less laborious. The MMOF composites can be recycled, regenerated, and reused repeatedly until the magnetic property and adsorption capacity remain intact (Yang et al. 2020a, b, c; Shao et al. 2019).

Recently, Mousavi and his coworkers reported a novel MMOF composite, MIL-101(Cr)/Fe_3O_4@SiO_2@2-ATP, for the separation/pre-concentration of trace amount silver metal present in aqueous system. To explore magnetic characteristics of the individual components and the entire composite, a Vibrating Sample Magnetometer (VSM) was used for each. MOF and other non-magnetic components present in the composite reduce the magnetic property of the composites. As shown in Fig. 7, the magnetization saturation value of Fe_3O_4 (MNPs) kept reducing on addition of extra components from 67 emu/g to 41 emu/g for Fe_3O_4@SiO_2@2-ATP and finally to 26 emu/g for the entire composite, MIL-101(Cr)/Fe_3O_4@SiO_2@2-ATP. The obtained plots and values show that although the magnetization saturation value of the composite MIL-101(Cr)/Fe_3O_4@SiO_2@2-ATP is lesser than that of sole MNPs, the material is superparamagnetic and can be magnetically isolated

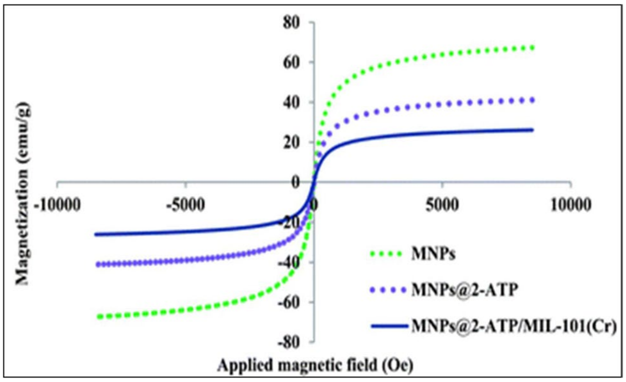


Fig. 7 VSM curves of Fe_3O_4 MNPs, Fe_3O_4@SiO_2@2-ATP MNPs, and MIL-101(Cr)/Fe_3O_4@SiO_2@2-ATP MMOF composite. Reproduced from reference Mousavi et al. 2021 with permission from The Royal Society of Chemist

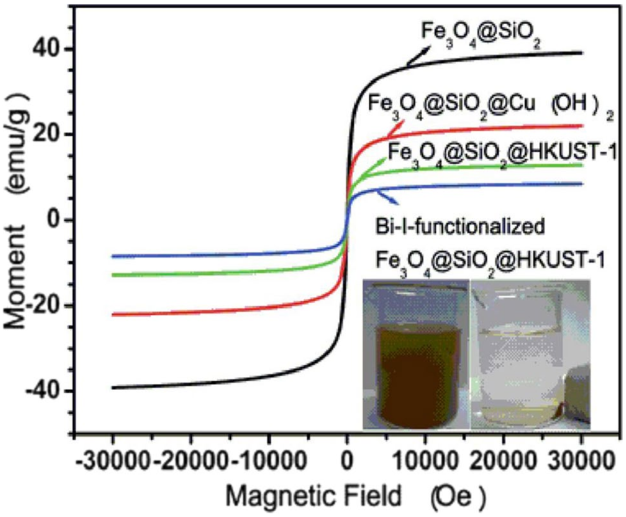


Fig. 8 VSM magnetization curves Fe_3O_4@SiO_2, Fe_3O_4@SiO_2@$Cu(OH)_2$, Fe_3O_4@SiO_2@HKUST-1, and Bi-I-functionalized Fe_3O_4@SiO_2@HKUST-1; and images before and after magnetic separation under an external magnetic field. Reproduced from Reference Huang et al. 2015 with permission from The Royal Society of Chemistry

by employing an external magnetic field (Mousavi et al. 2021).

Huang and his group reported the synthesis and characterization of novel MMOF composites Fe_3O_4@SiO_2@HKUST-1 and Bi-I-functionalized Fe_3O_4@SiO_2@HKUST-1 utilized for selective and efficient removal of Hg^{2+} ion from environmental water samples. The magnetic property of the composites was established by VSM study and their corresponding hysteresis curves are shown in Fig. 8.

The saturation magnetization of Fe_3O_4@SiO_2, Fe_3O_4@SiO_2@$Cu(OH)_2$, Fe3O4@SiO_2@HKUST-1, and Bi-I-functionalized Fe_3O_4@SiO_2@HKUST-1 is 39, 22, 13, and 8 emu/g, respectively. It clearly reveals that after addition of extra components to the MNPs, the magnetic property of resultant composites formed in each step decreases. However, all the composites are superparamagnetic and can be sufficiently separated easily with an external bar magnet (Huang et al. 2015).

Farhadi and his coworkers reported a novel magnetically retrievable nanoporous adsorbent $P_2W_{18}O_{62}$@Fe_3O_4/MIL-101 (Cr) for ultrafast treatment of organic pollutants present in aqueous solutions. The magnetic properties of the Fe_3O_4, Fe_3O_4/MIL-101 (Cr), and $P_2W_{18}O_{62}$@Fe_3O_4/MIL-101 (Cr) were determined by VSM, and the magnetic hysteresis loops depicted are as shown in Fig. 9A.

All the samples were found to be superparamagnetic, and the saturation magnetizations values of the pure Fe_3O_4, Fe_3O_4/MIL101 (Cr), and $P_2W_{18}O_{62}$@Fe_3O_4/MIL101 (Cr) were found to be 72, 35, and 25 emu/g, respectively. The saturation magnetization value of the magnetic $P_2W_{18}O_{62}$@Fe_3O_4/MIL101 (Cr) composite was found to be decreased by approximately 70% as compared with pure Fe_3O_4, which was attributed to the less magnetic source component (Fe_3O_4) present per gram in the composite sample. However, easy magnetic separation of the adsorbent material from aqueous suspension was satisfied by the saturation magnetization value of the composite. The adsorption capacity of the adsorbent for removing pollutants (methylene blue and Rhodamine B) was found to remain intact in every three consecutive adsorption cycles (Fig. 9B) with a maximum adsorption capacity of 98% (Farhadi and Jarrah 2018).

Porosity

MMOFs possess record-breaking porosity as its major constituent; MOFs are extrinsically sophisticated materials with abundant pores. Pores of the material allow the incorporation of guest molecules into its structure in order to achieve different functionalities. The energy released upon the interactions of adsorbents with the pores is the main driving force for this adsorption phenomenon which strongly depends on adsorbate-adsorbent interaction strength. Adsorption is generally influenced by orientation and structural geometry of the pores and pore functionality as well as adsorbate-adsorbent analogy. Adsorption can be maximized by increasing the pores/adsorption sites. Generally, large cavities offer easy incorporation of guest molecules (Zhao et al. 2020). The flexibility and high porosity of MOFs facilitate guest molecules to diffuse into the MOF-bulk structure, and the pore shape/size controls the selectivity over the guests that may be adsorbed. Most of the reported MMOF composites possess microporous structures (pore diameter less than 2 nm) that are advantageous for absorbing small guest molecules including small organic molecules, small coordination complexes, and gas molecules. Cage-like structures

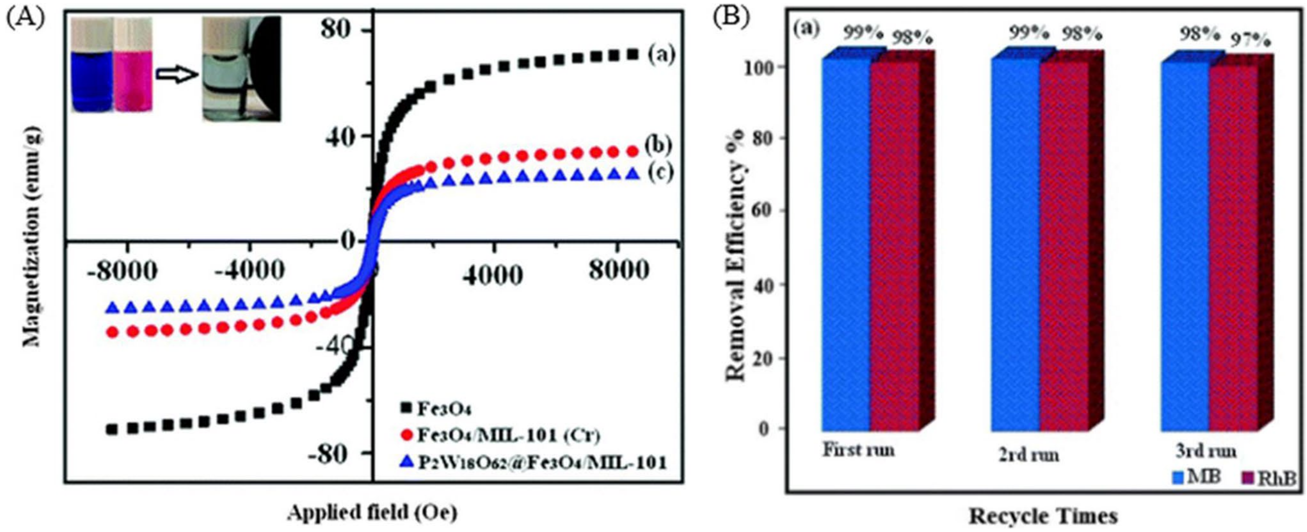


Fig. 9 **A** Magnetic hysteresis loop of (a) Fe_3O_4, (b) Fe_3O_4/MIL-101 (Cr), and (c) $P_2W_{18}O_{62}$@Fe_3O_4/MIL-101 (Cr) at room temperature. The inset shows the behavior of the nanohybrid under an external magnetic field. **B** Recyclability of the $P_2W_{18}O_{62}$@Fe_3O_4/MIL-101 (Cr) hybrid nanomaterial in the removal of MB dye. Reproduced from Reference Farhadi et al. 2018 with permission from The Royal Society of Chemistry

of mesoporous or macroporous (pore diameter 2–50 nm) MMOF composites are highly desired for penetration of larger guest molecules such as biomolecules. Volume of the pores depends on cross-linking density which can be increased by employing slim ligands. Elongated organic linkers are generally employed to increase the pore size through isoreticular expansion (Yuan et al. 2017). Far and his group reported a magnetic metal–organic framework functionalized with PPI dendrimer (Fe_3O_4@MOF@PPI) for sustainable wastewater treatment. The pore size distribution was determined according to the Barrett-Joyner-Halenda (BJH) method and was found to be dramatically increased from 0.014 to 0.58 cm^3/g after coating a layer of MOF (UiO-66) on Fe_3O_4 MNPs. On magnetization, no significant changes in the pore size were observed for the pristine UiO-66 MOFs which was recorded to be 0.54 cm^3/g. However, pore volume was somehow decreased on dendrimer coating to a value 0.25 cm^3/g (Far et al. 2020).

Adsorption mechanism

MMOF composites have been successfully applied as adsorbents for the removal of various heavy metal ions from aqueous medium. In many reports, adsorption/removal of heavy metals was reported as a success story (Hasan and Jhung 2015; Howarth et al. 2015; Li et al. 2016a, b, c). MMOF composites possess many types of organic linkers and have structural and morphological differences. The interaction sites involved in the adsorption mechanism can either be the linkers as well as the metal or clusters. As per reports, interaction mechanism involved in the adsorption of heavy metal ions by MMOF composites may be physical base adsorption such as van der Waals interactions, electrostatic adsorption, hydrogen bonding, π–π conjugation, Lewis acid–base interaction, chelation, or by complexation (Manousi N et al. 2019). In order to improve the selectivity and/or adsorptive capability, pre-/post-synthetic functionalization of the linkers, with various groups such as amino, hydroxyl, carboxylic acid, amide, and thiol, is a well-known and successive strategy. Functionalization of the MMOF frameworks increases the number of N-, O-, or S-containing groups that enhance the adsorption efficiency and selectivity of the targeted metal ions. Lewis acid–base interactions are one of the most common mechanisms for the adsorption of metal ions by MMOF composites (Vu et al. 2015). O-, N-, and S-containing groups present in the linkers act as Lewis bases and metal ions act as Lewis acids. pH of the sample plays the most significant role that influences the kinetics and adsorption process. Organic ligands rich in N, O, and S can bind with metal ions via host–guest complexation (Kobielska et al. 2018). At lower pH value, O, N, and S atoms get protonated and hence adsorption cannot occur due to the repulsive forces between positively charged adsorption sites and the metal cation [53]. However, on increasing the pH of metal ions containing aqueous samples, deprotonation of the donor atoms takes place. This enables the sorption of the targeted analytes by complex formation between the donor atoms of the adsorbent and the metal ions (Jamali et al. 2016; Hassanpour et al. 2015).

Adsorption of metal ions with MMOF composite via complexation can be improved by the chelation mechanism

(Fang et al. 2010). Adsorption capacity of MMOF adsorbents can be enhanced by functionalization of the composite with groups that facilitate the formation of chelating complexes with the metal ions.

For instance, Wang et al., for the first time, reported a reliable and highly selective dithizone-functionalized magnetic sorbent, $Fe_3O_4/Cu_3(BTC)_2$-H_2Dz, for magnetic solid phase extraction and determination of Pb(II) ion from environmental water sample (Wang et al. 2013). BET surface area and pore volume of the composite were determined by N_2 adsorption–desorption isotherm which showed that BET surface area of the composite (753.58 m^2g^{-1}) was decreased than the pristine MOF (933.37 m^2g^{-1}) and pore volume was found to be decreased from 0.62 cm^3g^{-1} to 0.51 cm^3g^{-1} on incorporation of MNPs. However, under the optimized conditions of pH, sample volume, sorbent quantity, and concentration as well as coexisting interfering ions, the maximum Pb(II) uptake was found to be 1.67 mg g^{-1} determined by ETAAS (Electrothermal Atomic Adsorption Spectrometry) with a very low limit of detection 0.0046 μg L^{-1}.

Highly selective chelating agents under controlled experimental conditions may allow various pre-concentration processes that can be carried out for the extraction of lead. Dithizone (Dz, 1,5-diphenylcarbazone) is a commonly used chelating agent that can form highly stable Pb complex via –SH and –NH functional groups. Efficient extraction of Pb can be attributed to the formation of a penta-heterocycle chelating complex between Pb(II) ion and dithizone molecules in the sorbent (Fig. 10A). At lower pH value, protonation of the binding sites of the chelating molecules takes place and hence adsorption cannot occur. With increase in pH up to an optimum value, adsorption capacity increases

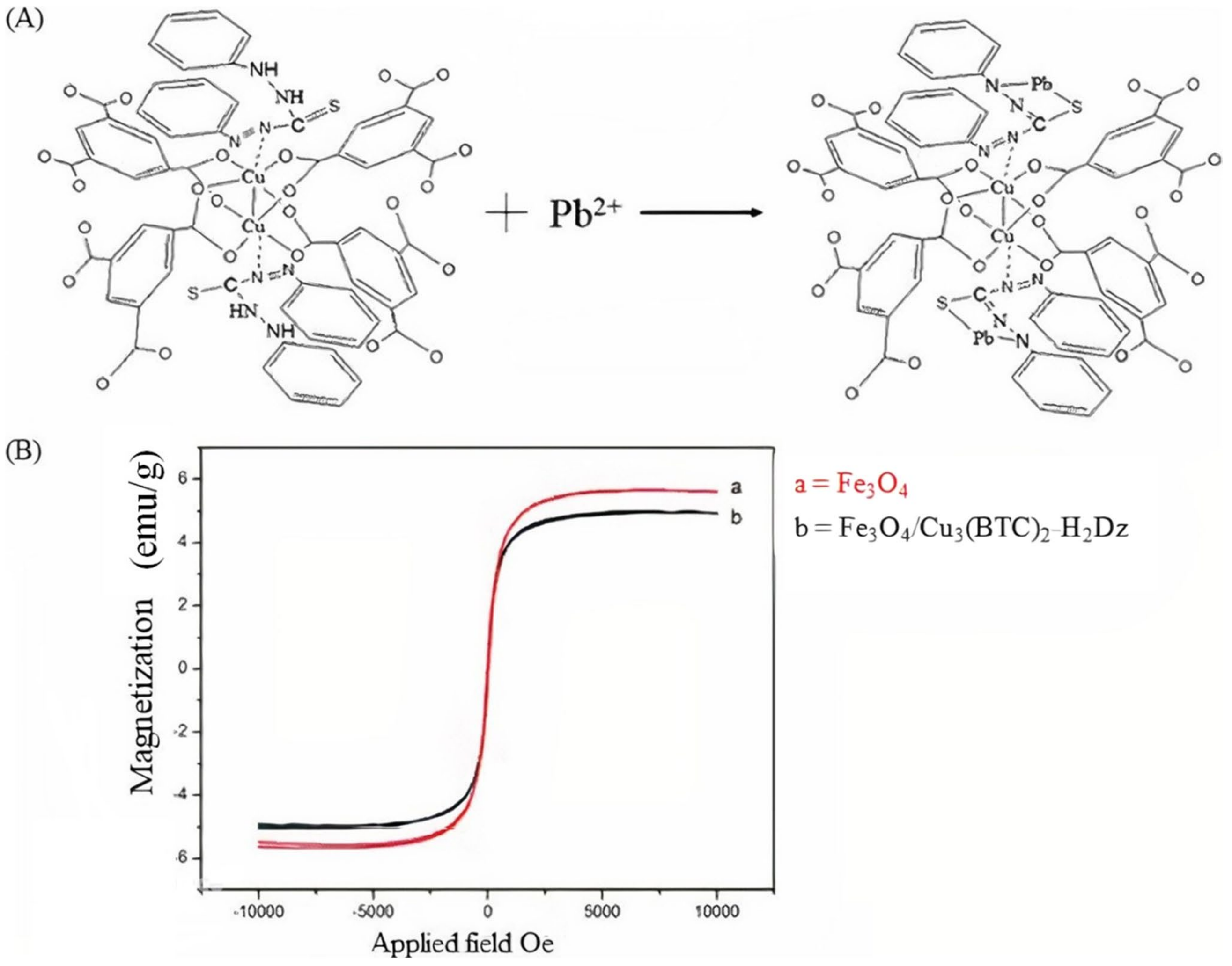


Fig. 10 Schematic representation for **A** adsorption mechanism of Pb(II) on $Fe_3O_4/Cu_3(BTC)_2$-H_2Dz composite and **B** their corresponding VSM magnetization curves (a) VSM magnetization curves for Fe_3O_4 and (b) VSM magnetization curves for $Fe_3O_4/Cu_3(BTC)_2$-H_2Dz. Reproduced from Reference Wang et al. 2013 with permission from The Royal Society of Chemistry

but further increase in pH may cause hydrolysis resulting in the precipitation of target analytes.

Magnetic properties of $Fe_3O_4/Cu_3(BTC)_2$-H_2Dz composite were characterized by hysteresis curves by means of VSM. VSM magnetization curves of $Fe_3O_4/Cu_3(BTC)_2$ and $Fe_3O_4/Cu_3(BTC)_2$-H_2Dz at room temperature are shown in Fig. 10B. The saturation magnetization value for $Fe_3O_4/Cu_3(BTC)_2$ was measured to be 5.48 emu g^{-1} whereas for $Fe_3O_4/Cu_3(BTC)_2$-H_2Dz it was 4.91 emu g^{-1}. The decrease in magnetic strength of $Fe_3O_4/Cu_3(BTC)_2$-H_2Dz as compared to that of $Fe_3O_4/Cu_3(BTC)_2$ was attributed to the presence of the nonmagnetic H_2Dz. However, the MMOF sorbent was still sufficiently magnetic for easy separation with a bar magnet.

In case of physical adsorption, various interactions between the adsorbent and targeted adsorbates may be responsible for the higher adsorption capacity of MMOF composites. The presence of particular functional groups and the net charge on the framework have significant impact on the extent of physical adsorption [61]. The electrostatic interactions between anionic adsorption sites of the adsorbent framework and the cationic adsorbates are the most extensively reported mechanism of adsorption (Rahimi and Mohaghegh 2015). In the MMOF composites, pore size can range from micropores to mesopores. MMOF composites possessing different pore sizes allow adsorption of heavy metal ions with spatial arrangements. The diffusion of the targeted metal ions toward the active sites of the MMOF adsorbent is also an important aspect, and hence the size, volume, and geometry of the pores have paramount significance (Jian et al. 2014).

In many cases, more than one interaction mechanism can be explained for the high adsorptive capacity of MMOFs. For instance, Huang et al. reported a cost-effective and green strategy to develop aluminum metal-based, amino-functionalized MMOF composites (MFC-N-X) by varying the ratio of disodium salt of 2-amionterephthalic acid (NH_2-Na_2BDC) and terephthalic acid (Na_2BDC) ligands (Fig. 11). The nanoscale MFCs were found to possess large pore volume, high surface area, and excellent magnetic response as well as good water and thermal stability. MFC-N-100 with 100% NH_2-Na_2BDC organic ligand was demonstrated as a

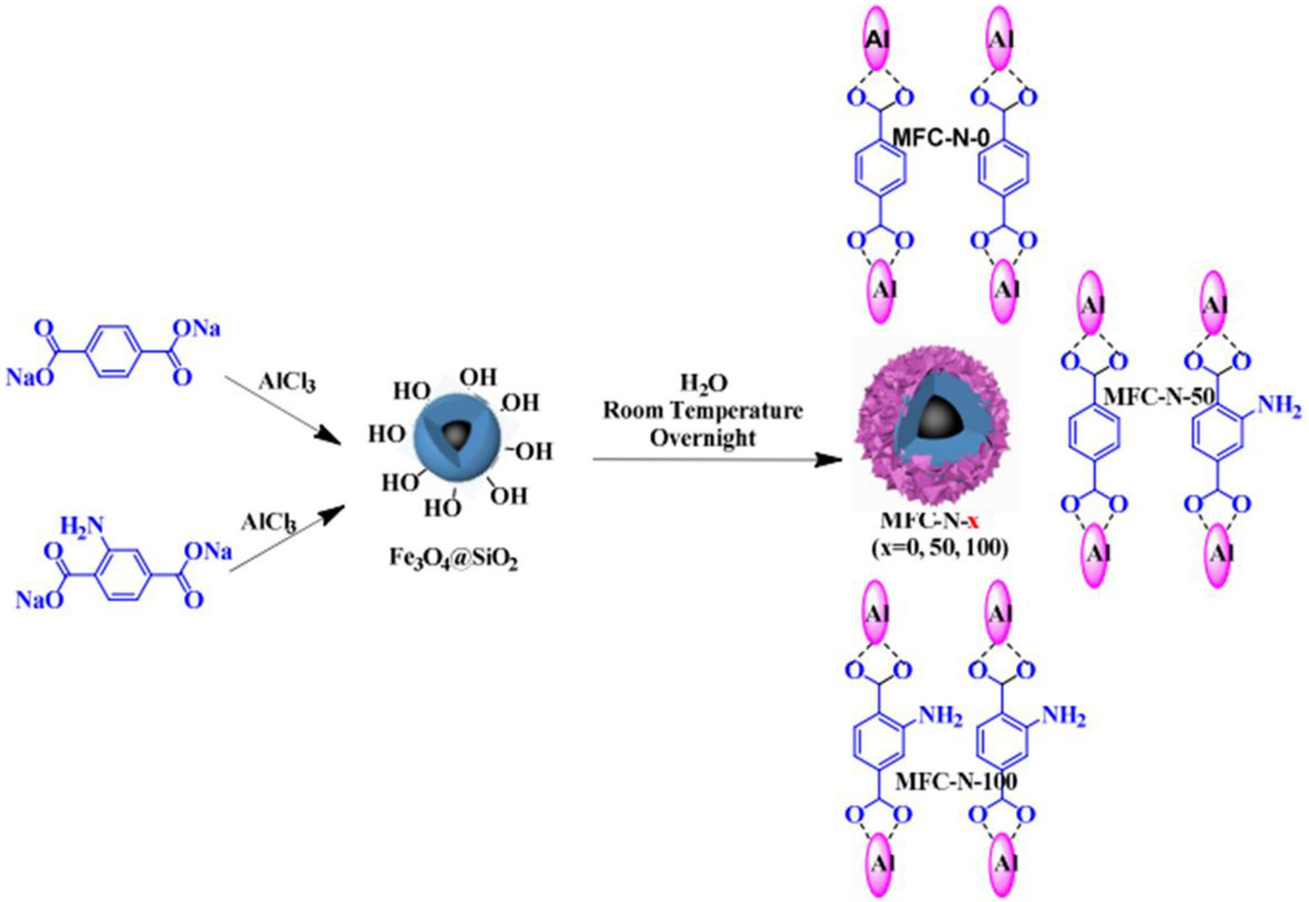


Fig. 11 Schematic diagram of the preparation of MFC-N-X composites. Reproduced from Reference Huang et al. 2018a, b with permission from The Royal Society of Chemistry

fascinating adsorbent for removal of As(V) from different water samples with a high removal efficiency of 71 mg g^{-1} (Huang et al. 2018a, b).

Under pH > 2.2, As(V) mainly exists in anionic forms, i.e., $H_2AsO_4^-$ (2.2 < pH < 7.0), $HAsO_4^{2-}$ (7.0 < pH < 11.5), and AsO_4^{3-} (pH > 11.5) (Mohan and Pittman 2007). There exists an electrostatic repulsion between the negatively charged MFC-N-100 composite and anionic As(V) species above pH 8. However, above pH 8, a quantitative adsorption of As(V) was observed indicating the existence of other mechanisms rather than electrostatic interactions contributing to the adsorption of anionic target As(V) species on MFC-N-100 composite. Hence, the FT-IR analysis of MFC-N-100 composite loaded with As(V) species was performed and the peak at 1237 cm^{-1} verified the appearance of As-O–Al bond, indicating an interaction existing between target As(V) species and hydroxyl groups of octahedral $AlO_4(OH)_2$. Adsorption of As(V) onto MFC-N-100 was further established by elemental mapping images. Moreover, XPS analysis of MFC-N-100 done before and after As(V) loading confirmed the formation of arsenic complexes via the formation of Al-O-As bonds. Further, involvement of -NH_2 groups in adsorption of As(V) was established by shifting of binding energy for N 1 s by an amount ~ 0.5 eV toward high binding energy after the adsorption of As(V) (Li et al. 2018). Hence, the adsorption of As(V) on the MMOF composite MFC-N-100 is based on the As-O–Al interactions as well as electrostatic interactions between $H_2AsO_4^-$ and NH_2 functional groups (Fig. 12).

Advanced computational techniques such as density functional theory (DFT) and molecular dynamics (MD) and sophisticated analytical techniques such as X-ray absorption fine structure (XAFS) and resonant anomalous X-ray reflectivity (RAXR) provide sufficient information and make it possible to understand the in-depth adsorption mechanism.

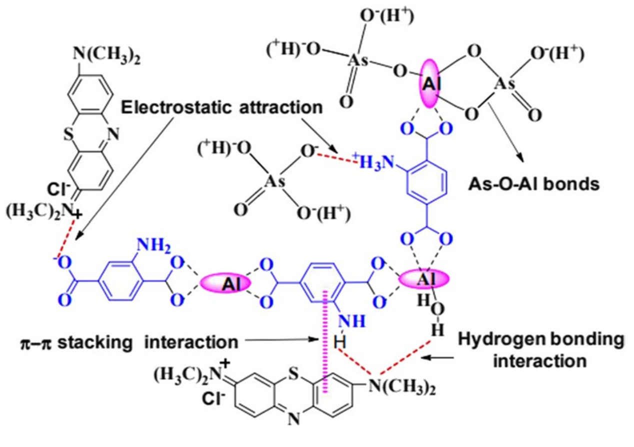


Fig. 12 The possible mechanism for the adsorption of As(V) and MB on MFC-N-100. Reproduced from Reference Huang et al. 2018a, b with permission from The Royal Society of Chemistry

Applications of MMOF composites in removal of heavy metal ions

With rapid development of industries and agricultures, contamination of environmental water by heavy metal ions has become increasingly a severe issue. Heavy metal ions are non-biodegradable and highly biotoxic. Enrichment of heavy metal ions in humans and other organisms via food chain or drinking water can harm normal metabolism and is the greatest threat to human health (Sud et al. 2008; Fu and Wang 2011). Removal of toxic heavy metals by traditional adsorption materials, e.g., metal oxides, activated carbon, zeolite, porous organic polymers, and molecular or ion imprinted polymers, has several limitations owing to their lower specific surface areas, insufficient thermal and chemical stability, poor adsorption performance, poor reusability, and tedious as well as laborious separation process (Zare et al. 2018; Da'na. 2017). In recent years, MSPE done by nanoparticles, nanocomposites, sponges, foam, and beads has been recognized for its easy operation, regenerability, and high efficiency for adsorption of hazardous environmental contaminants including heavy metal ions (Zhang et al. 2022a, b, c, d; Ricardo et al. 2020). MMOF composites have a number of advantages as compared with other conventional adsorbents used for wastewater remediation. These include their multiple types, simple synthetic processes, tunable functionalities, adaptable pore sizes, large specific surface areas, easy recyclability, efficient reusability, and saturated or unsaturated central metal sites. Physicochemical properties of heavy metals can be met by designing the structurally advanced MOFs. MMOF composites successfully replace the conventional adsorbent materials mentioned above for rapid and selective removal of heavy metals from aqueous samples with their outstanding structural characteristics and good adsorption performance. Consequently, MMOF composites have pulled enormous research interest for the removal of toxic pollutants including heavy metal ions from environmental samples via adsorption (Sarker et al. 2017).

Bagheri and his group for the first time introduced a novel MMOF composite (Fe_3O_4-pyridine)/$Cu_3(BTC)_2$ by taking pyridine-functionalized Fe_3O_4 NPs as the magnetic component, Cu(II) ions as the metal node, and trimesic acid as the organic linker, utilizing a facile solvothermal route. The (Fe_3O_4-pyridine)/$Cu_3(BTC)_2$ composite was demonstrated as a magnetic sorbent material for rapid extraction of highly toxic and carcinogenic Pd(II) ions from various matrixes including environmental water sample with a maximum sorption capacity 105.1 mg g^{-1} in an optimum pH value

6.9. The limit of detection for Pd(II) ion was found to be 0.37 ng mL^{-1} without being interfered by other counter ions such as Na^+, K^+, Ca^{2+}, Al^{3+}, Ag^+, Cu^{2+}, Fe^{3+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, and Zn^{2+}. For desorption of Pd(II) ions, Pd(II) ions adsorbed on MMOF sorbent was eluted with 6 mL of 0.01 M NaOH in 9.5 K_2SO_4 solution as an eluent with recoveries of Pd(II) ions in the range between 96.8% and 102% and the desorption amount was determined by FAAS (flame atomic absorption spectrometry). Other acidic eluting solvents such as HCl and HNO_3 were found to decompose the MMOF structures (Bagheri et al. 2012).

Following the same trend, Taghizadeh et al. fabricated a novel MMOF hybrid composite, by immobilizing $[Cu_3(BTC)_2(H_2O)_3]_n$ MOF with dithizone-functionalized Fe_3O_4 MNPs employing a simple solvothermal strategy. The synthesized Fe_3O_4-DHz@HKUST-1 composite was found to be a reproducible adsorbent for fast selective solid phase extraction of Zn(II), Ni(II), Pb(II), and Cd(II) ions from aqueous sample with limit of detection 1.2, 0.98, 0.39, and 0.12 ng mL^{-1}, respectively. Selectivity of the new solid phase towards the heavy metal ions is promoted by the dithizone group presented in the sorbent material. The maximum adsorption capacities in optimum conditions were found to be 206, 98, 104, and 188 mg g^{-1} for Zn(II), Ni(II), Pb(II), and Cd(II) ions, respectively. Based on Box–Behnken design (BBD), concentration and volume of the eluent were found to have positive and significant impacts on effective recovery of the heavy metal ions while elution time showed a positive but non-significant impact. Several eluents (e.g., HNO_3, HCl, NaOH, KCl, K_2SO_4, and thiourea solution and their mixtures) were examined for desorption process keeping other factors constant (extraction time 13 min, dosage of the magnetic adsorbent 25 mg, pH 6.4, elution time 20 min, and eluent volume 5 mL). Decomposition of the framework structure of MMOF nanocomposite was found to occur with NaOH, HCl, and HNO_3 eluents. However, the best quantitative recovery of the metal ions was obtained with 7.8 mL of a 0.9 M thiourea in 0.01 M NaOH solution as an eluent. The clear solution containing the eluted heavy metal ions was introduced to FAAS, and the amount of each ion eluted was calculated (Taghizadeh et al. 2013).

Sohrabi and his coworkers developed a novel MMOF hybrid adsorbent material Fe_3O_4-pyridine@HKUST-1 from pyridine-functionalized Fe_3O_4 MNPs and $Cu_3(BTC)_2$ MOF following a facile solvothermal synthetic route for rapid and selective extraction of trace amount of Cd(II) and Pb(II) ions from aqueous media with a very low limit of detection (0.2 ng mL^{-1} for Cd(II) and 1.1 ng mL^{-1} for Pb(II)) and high enrichment capacity of 190 mg g^{-1} for both the adsorbents. The new solid phase was found to be highly selective towards Cd(II) and Pb(II) ions due to the presence of pyridine groups in the sorbent. Mechanism for the adsorption of Cd(II) and Pb(II) ions was illustrated as shown in Fig. 13.

The adsorption capacity of Cd(II) and Pb(II) ions by the MMOF sorbent was found to be increased with the increase in pH and the sorbent amount. pH of solution, extraction time, and doses of MMOF were found to have a positive and significant impact on the extraction efficiency. Factors affecting the desorption process were optimized (pH value 6.3 extraction time: 14 min; doses of MMOF sorbent: 30 mg; eluent volume: 5 mL; elution time, 25 min). Eluents such as HCl, NaOH, HNO_3, K_2SO_4, KCl, and EDTA solution and their mixtures were examined as the desorption solvent, and the best quantitative recovery of metal ions was achieved with 0.01 M NaOH in EDTA solution without any structural decomposition (Sohrabi et al. 2013).

Xiong and his coworkers (Xiong et al. 2015) prepared a bifunctional porous magnetic γ-Fe_3O_4/C@HKUST-1 composite via two simple steps; the first step involves the microwave-assisted high-temperature strategy to prepare highly porous Fe_3O_4/C magnetic composite from starch via an ionothermal method followed by liquid-phase epitaxial growth of HKUST-1 onto the magnetic composite (Fig. 14). The unique functional groups like –OH and –NH_2 on γ-Fe_3O_4/C were utilized as the support to promote the direct growth of HKUST-1 via the stepwise liquid-phase epitaxy process. Fe_3O_4/C@HKUST-1 composite was demonstrated as an efficient adsorbent for removal of Cr(VI) ion from aqueous solutions with a very high adsorption capacity 101.4 mg.g^{-1}. pH played a significant role on adsorption and reduction of Cr(VI). The highest adsorption capacity was obtained at pH 3.0, and the lowest adsorption capacity was obtained at pH 9.0 indicating a sorption mechanism that involves in surface complexation or bonding. Desorption of Cr(VI) and regeneration of γ-Fe_3O_4/C@HKUST-1 composite were successfully achieved by using 0.01 M NaOH solution. The adsorption capacity of the MMOF composite for removing Cr(VI) was decreased by 10% in 5th cycle as compared within the

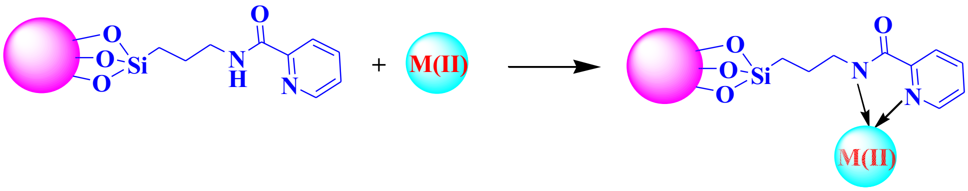


Fig. 13 Proposed mechanism for uptake of Cd(II) and Pb(II) ions on magnetic MOF-pyridine nanocomposite (M = Pb/Cd)

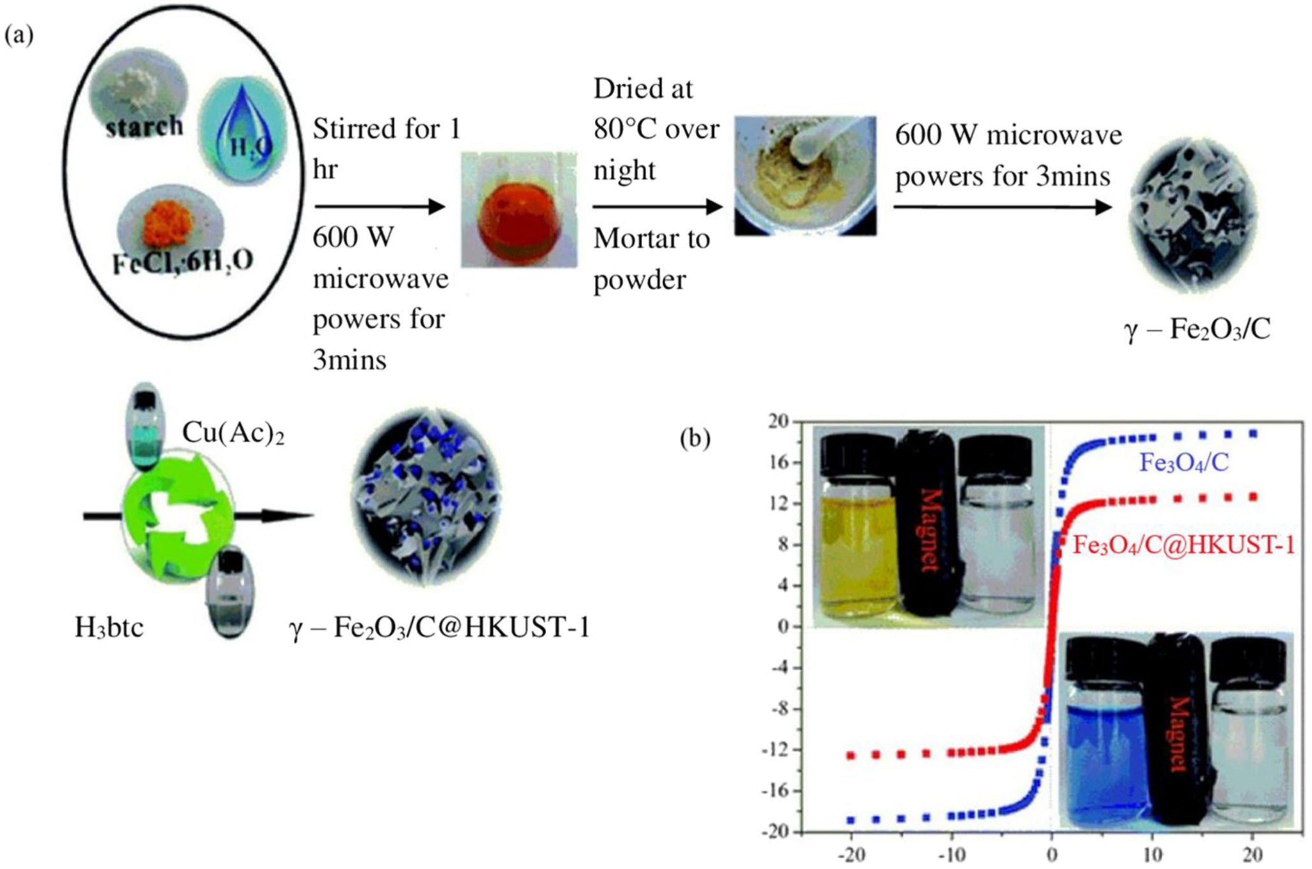
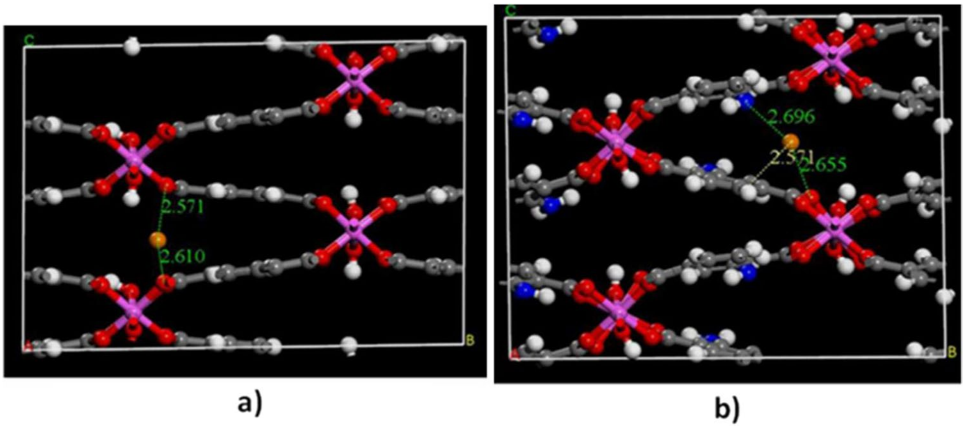


Fig. 14 **a** Schematic representation for synthesis of γ-Fe_3O_4/C@HKUST-1 composite and **b** their corresponding VSM magnetization curves showing separation of samples from solutions under external magnetic field. Reproduced from Reference Xiong et al. 2015 with permission from The Royal Society of Chemistry

1st cycle showing better regenerability and recyclability of the adsorbent.

Ricco et al. successfully designed a series of magnetic framework composite materials using aluminum-based MOFs, MIL-53, and Fe_3O_4 MNPs via an embedding methodology. A series of amino-functionalized MIL-53 MOF were prepared by varying the load of 2-amino terephthalic acid (aBDC) with terephthalic acid from 0%, 50%, and 100% to obtain MIL-53(Al@0aBDC), MIL-53(Al@50aBDC), and MIL-53(Al@100aBDC), respectively. The fully functionalized system, i.e., MIL-53(Al@100aBDC), which resulted from 100% load of 2-aminoterephthalic acid as the starting ligand was found to show superior performance in the removal of Pb(II) ion from contaminated water which was

Fig. 15 DFT optimized locations and binding energies (B.E.) of lead atom in **a** MIL-53(Al) and **b** MIL-53(Al)-NH2 calculated using DFT-D2 method. The distances shown are in angstroms. Color code: C, grey; H, white; N, blue; Al, pink; Pb, orange. Reproduced from Reference Ricco et al. 2015 with permission from The Royal Society of Chemistry



confirmed by density functional theory calculations (DFT) (Fig. 15). A record-breaking lead uptake capability of 492.4 mg/g was achieved with the adsorbent. Increase in Pb(II) uptake with increasing amount of amino group during the synthetic procedure can be attributed to the coordination of N atoms present in the framework structure to the metal ions. To further explore the adsorbent-adsorbate interaction, Langmuir and Freundlich models were considered and the Freundlich model was found to fit slightly better, suggesting a homogeneous uptake of lead cations throughout the entire framework. Desorption of Pb(II) was done by exposing the composite to magnetic heating at 43 °C, and nearly 50% of the lead was released within 2 h. Leaching study showed maximum Al leakage under acidic conditions, where due to acid degradation Al was lost up to 15% (Ricco et al. 2015).

Huang and his group (Huang et al. 2015) reported a green strategy for facile self-template-assisted synthesis of a designable core–shell MMOF composite, Fe_3O_4@SiO_2@HKUST-1 (Fig. 16). The thickness of the MMOF shell can be adjusted by varying the quantity of metal precursor. Moreover, they employed a facile coordination based post-synthetic approach to generate a thermally and chemically stable bismuthiol-functionalized magnetic composite, Bi-I-functionalized-Fe_3O_4@SiO_2@HKUST-1, which was demonstrated as an excellent adsorbent for fast and selective (99%) removal of Hg(II) ions in environmental water with a high adsorption capacity of 264 mg g^{-1} in the presence of other competing ions, e.g., Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+}. About 99% mercury ions were found to be adsorbed within 10 min, indicating that the Bi-I-functionalized-Fe_3O_4@SiO_2@HKUST-1 exhibited a fast adsorption dynamics for the removal of mercury from water. Excellent adsorption capacity of Bi-I-functionalized-Fe_3O_4@SiO_2@HKUST-1 towards Hg^{2+} in a wide pH range was ascribed to the strong interaction between mercury species and -SH functional group. PXRD patterns obtained for MMOFs after loading Hg^{2+} ions within the pH range 3–10 were in accordance with those of the synthesized MMOFs before spiking into the aqueous solution, suggesting a good chemical stability of Bi-I-functionalized Fe_3O_4@SiO_2@HKUST-1 in aqueous solution. For release of mercury, several eluents, e.g., HCl, HNO_3, NaOH, and thiourea solution and their mixtures, were tested as the desorption solvent. However, elution of Hg^{2+} from the adsorbent was found to be difficult due to strong binding forces of -SH with Hg^{2+}, and hence, the utilized MMOF adsorbent was disposable. Although a considerable recovery was obtained with diluted NaOH (0.01 M) solution without any structural damage of the employed adsorbent, it may cause the hydrolysis of Bi-I.

MSPE was done under different pH to investigate the leaching of Cu^{2+} from the prepared Fe_3O_4@SiO_2@HKUST-1 and Bi-I-functionalized Fe_3O_4@SiO_2@HKUST-1 sorbents, and Cu^{2+} concentration in the aqueous solution was determined by ICP-OES. Better chemical stability of

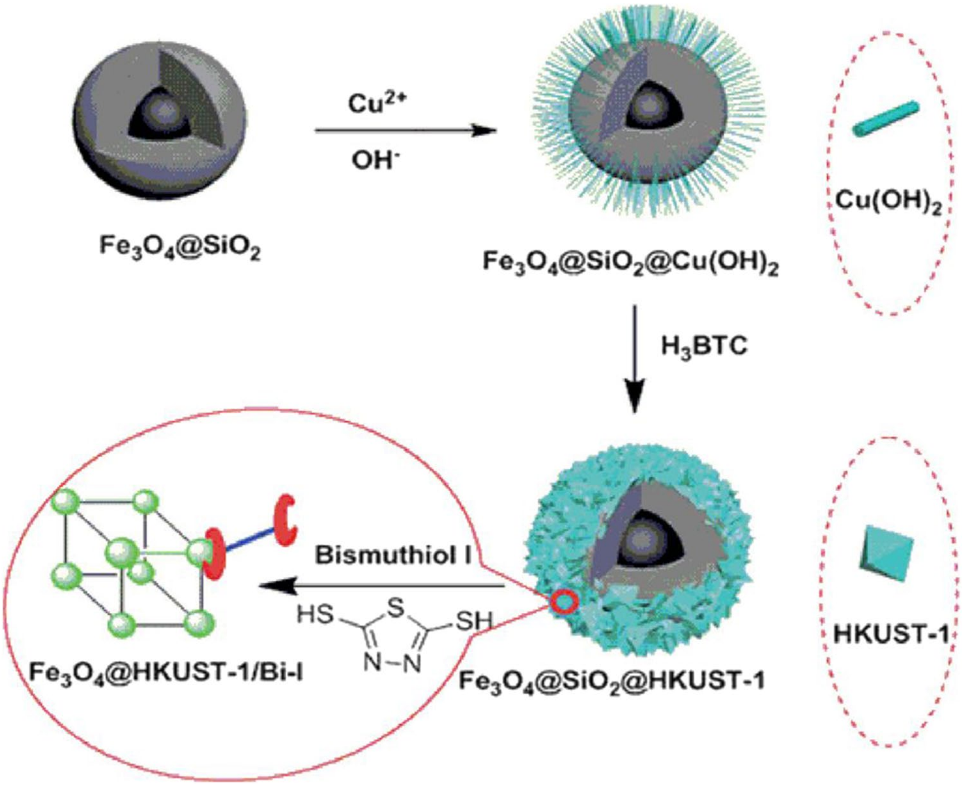


Fig. 16 Schematic representation for synthesis of Fe_3O_4@SiO_2@HKUST-1 composite. Reproduced from Reference Huang et al. 2015 with permission from The Royal Society of Chemistry

Bi-I-functionalized Fe_3O_4@SiO_2@HKUST-1 than Fe_3O_4@SiO_2@HKUST-1 was suggested by the percentage of Cu^{2+} release in acidic condition (at pH 3) which is lesser in the case of Bi-I-functionalized Fe_3O_4@SiO_2@HKUST-1 (20%) compared to that of Fe_3O_4@SiO_2@HKUST-1 (27%).

A selective recyclable and regenerable MMOF-based adsorbent, Fe_3O_4@MIL-101, for removal of As(III) and As(V) ions from surface as well as ground water was successfully demonstrated by K observed by Folens and his group with excellent adsorption capacities of 121.5 and 80 mg g^{-1}, respectively. The magnetic nanocomposite material was synthesized by encapsulating Fe_3O_4-engineered nanoparticles (ENPs) within MIL-101(Cr) framework structure. No significant leaching of Cr and Fe and the retained crystallinity of the magnetic framework structure after adsorption and desorption process indicates the higher stability of the magnetic adsorbent material. To examine the chemical stability of Fe_3O_4@MIL-101(Cr), leaching of Cr and Fe as well as the crystallinity was explored after the adsorption–desorption process. Leaching of 0.3% Cr^{3+} ions and (0.2 ± 0.10) % $Fe^{2+/3+}$ ions was confirmed by ICP-OES measurements after a contact time of 24 h. Preservation of crystal structure of the MMOF composite after the desorption processes was further confirmed by XRPD measurements. NaH_2PO_4 was selected as eluent for the efficient release of As(III) (56.5%) and As(V) (71.1%) which offers efficient exchange of the arsenic ions owing to their tetrahedral chemical structure that resembles the phosphate ion (Folens et al. 2016).

Moradi et al. reported a highly water stable and nontoxic MMOF composite, Fe_3O_4@MOF-235(Fe)-OSO_3H, by loading sulfonated MOF, MOF-235(Fe)-OSO_3H, onto mercaptoacetic acid-functionalized Fe_3O_4 MNPs, utilizing a simple solvothermal strategy (Fig. 17). The MOF-235(Fe)-OSO_3H composite was utilized as a reusable adsorbent for magnetic solid phase extraction of Cd(II) ion present in environmental water sample with limit of detection 0.04 μg L^{-1} and enrichment value 195.0 in the presence of other competing ions such as Al^{3+}, Ca^{2+}, Mg^{2+}, K^+, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cl^-, CO_3^{2-}, and SO_4^{2-} (Moradi et al. 2016). The pH value played a significant role in adsorption of Cd(II) ions due to the influences of pH on the surface properties of the MMOF as well as the ionic form of the Cd(II) ions in solution. Depending on the pH of solution, cadmium exists in various ionic forms including Cd^{2+}, $Cd(OH)^+$, $Cd(OH)_2$, $Cd(OH)_3^-$, and $Cd(OH)_4^{2-}$ in aqueous medium. Over the pH range 2.0–8.0, cadmium predominantly exists in Cd^{2+} form. At pH value greater than 2.0, the surface of

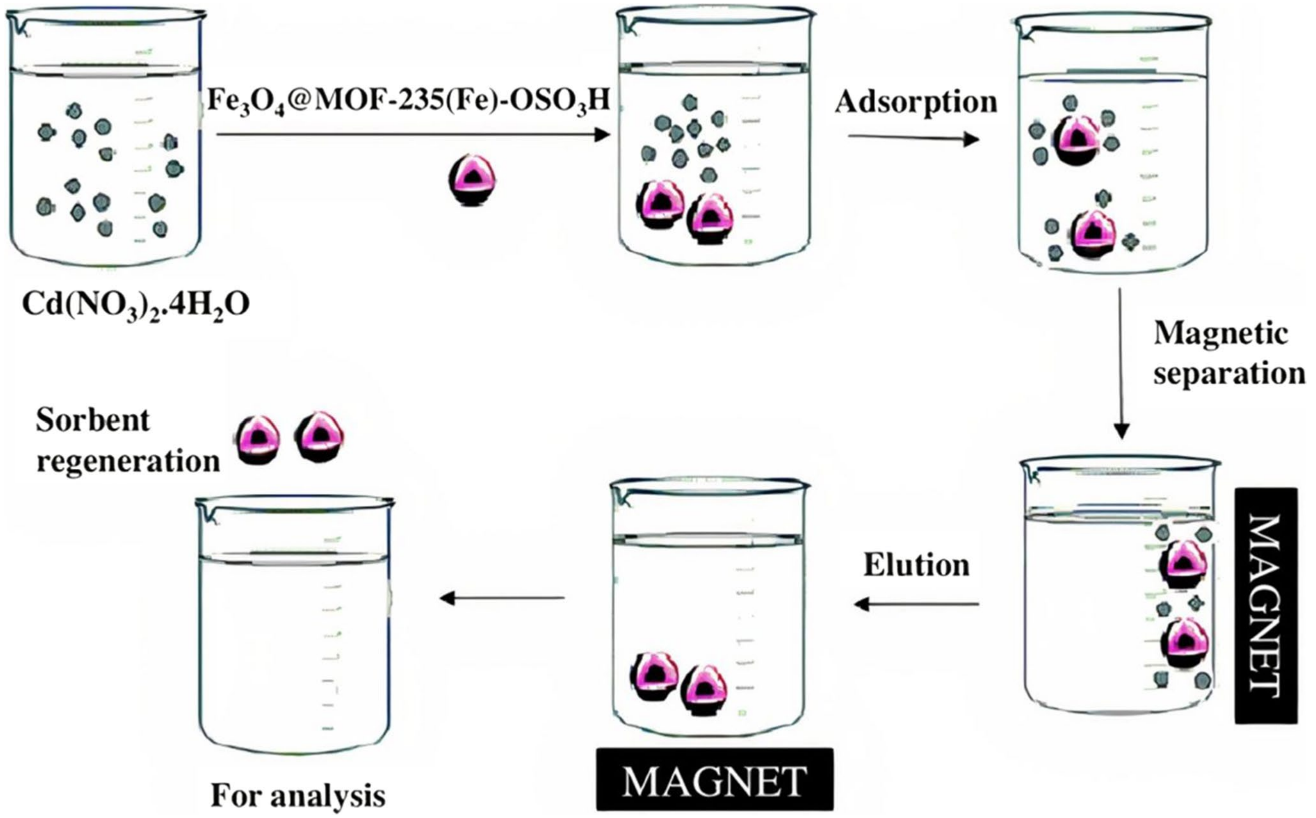


Fig. 17 Schematic representation for adsorption of Cd(II) on Fe_3O_4@MOF-235(Fe)-OSO_3H composites and separation of samples from solutions under external magnetic field. Reproduced from Reference Moradi et al. 2016 with permission from The Royal Society of Chemistry

MMOF sorbent gets negatively charged providing affinity for electrostatic interactions between the sorbent and cationic cadmium species. Experimental data were well fitted to Langmuir isotherm suggesting homogenous monolayer adsorption of cadmium ion onto the sorbents. No significant structural change was observed up to ten adsorption–desorption cycles indicating excellent stability and recyclability. 1 mL of 0.5 M EDTA solution was selected as the best eluent for the desorption of Cd(II) ions.

Yang et al. fabricated a highly porous and beautifully organized core–shell magnetic adsorbent material Fe_3O_4@MIL-100(Fe), using citrate-functionalized Fe_3O_4 MNPs as the crystal seed that facilitated the in situ growth of MIL-100(Fe) shell on its surface via a facile hydrothermal approach. It was the first MMOF composite appraised to remove Cr(VI) ion from aqueous media. Higher extraction yield was obtained at lower pH value ($pH < 3.7$) due to the increased electrostatic interaction between the positively charged surface of Fe_3O_4@MIL-100(Fe) and CrO_4^{2-} ion in acidic solution. Overall optimization study revealed that the magnetic adsorbent material exhibited a maximum adsorption capacity of 18 mg g^{-1} at pH value 2 in 120-min time of duration with 4 mg dose of the magnetic adsorbent (Yang et al. 2016).

Safari et al. developed a synthetic approach for fabricating two pillar MOFs: TMU-8 with azine groups in the middle of pillar ligand [4-bpdb (1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene)] and TMU-9 with 4,4′-bipyridine (4,4′-bipy) pillar ligand. Lewis basic azine-functionalized pores of TMU-8 were found to exhibit more extraction efficiency for heavy metal ions as compared to that of TMU-9 which do not contain any azine group. TMU-8 was chosen as an effective adsorbent for the extraction and pre-concentration of trace amounts of some heavy-metal ions including Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Pb(II), and Cd(II) ions from contaminated aqueous system. TMU-8 was fabricated with magnetic component (Fe_3O_4) by employing two strategies—in situ synthesis of magnetic nanocomposites and core shell. Results showed that magnetic Fe_3O_4@TMU-8 composite synthesized via core–shell strategy provides more binding sites for the adsorption of heavy metal ions and magnetic proprieties.

Magnetic solid-phase extraction of heavy metal ions was done by adding 10 mg of sorbent (Fe_3O_4@TMU-8) to 185 mL of spiked sample solution at a pH of 10. After adsorption, Fe_3O_4@TMU-8 was by using an external magnet. For pre-concentration, 500 µL of 0.5 M HNO_3 solution was added as eluent to desorb the metal ions from the adsorbent surface by fierce vortex and was determined by ICP-AES (inductively coupled plasma-atomic emission spectroscopy) technique (Safari et al. 2017).

Huang and his coworkers reported a facile solvent-assisted ligand exchange (SALE) strategy to obtain Zr-MOF composite (MFC-S), in which terephthalate ligand present

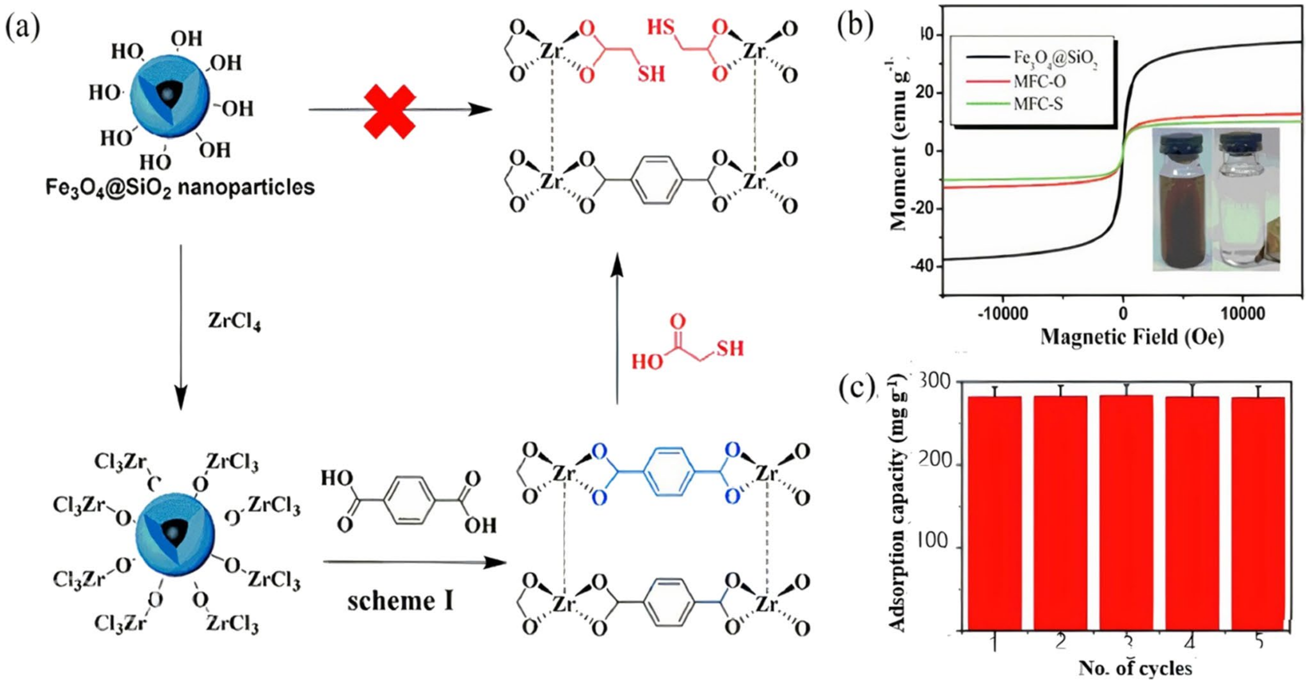


Fig. 18 **a** Schematic representation for synthesis of MFCs and **b** their corresponding VSM magnetization curves showing separation of samples from solutions under external magnetic field; **c** recyclability test. Reproduced from Reference Huang et al. 2016 with permission from The Royal Society of Chemist

in UIO-66 was replaced with flexible mercaptoacetic acid ligand in aqueous solvent under mild reaction condition (Fig. 18). The porosity, crystallinity, and supermagnetic properties of mercapto-functionalized Zr-MOF were maintained well during the process of SALE. The MFC-S was found to exhibit higher stability and enhanced adsorption capacity of 282 mg g^{-1} towards the removal of Hg(II) ions from environmental water sample (Huang et al. 2016). A mixture of 0.1 M HCl with 0.1% thiourea was used as eluent for regeneration of the adsorbents at pH 1.8. Regenerated MFC-S was reused for the removal of target contaminants, and the adsorption capacity was found to remain intact up to 5 cycles. To examine the leaching of Zr^{4+} from the MFC-S, magnetic solid phase extraction was done under different pH and ICP-OES result showed that less than 0.5% of the total Zr^{4+} was present in the supernatant. PXRD patterns of the MFC-S after 5 adsorption/elution cycles of Hg^{2+} suggested excellent chemical stability of the synthesized sorbent. Moreover, high specific surface areas (571 m^2 g^{-1}) of the employed MFC-S after the 5th cycle were established by N_2 adsorption–desorption isotherms. Furthermore, unchanged morphology and core–shell structure of prepared MFC-S after 5 adsorption/elution cycles of Hg^{2+} were supported by TEM investigation.

Naeimi et al. synthesized [$Cu_3(BTC)_2$] (HKUST-1) MOFs impregnated with potassium nickel hexacyanoferrate (KNiFC) to obtain MOF/KNiFC. Further, it was magnetized with Fe_3O_4 MNPs to obtain MOF/Fe_3O_4/KNiFC composite. MOF/KNiFC and MOF/Fe_3O_4/KNiFC were utilized as adsorbent for efficient removal of hazardous Cs(I) radionuclide present in wastewater in the presence of other background ions like Na(I) and K(I) with adsorption capacities 153.0 and 109.0 mg g^{-1}, respectively. Lower adsorption capacity of MOF/Fe_3O_4/KNiFC than MOF/KNiFC may be attributed to the addition of magnetic component (Fe_3O_4) to MOF/KNiFC which had no significant effect on the adsorption of Cs^+. However, the presence of Fe_3O_4 facilitated magnetic separation of the used sorbent from the solution. Adsorption mechanism was ascribed by the exchange of K^+ in KNiFC with Cs^+ in solution. At higher pH value, deprotonation of the adsorbents surface occurs which facilitates electrostatic interactions between the adsorbent surface and ingoing cation. At lower pH, hydronium ions compete with Cs^+ for the exchange sites lowering the uptake. Experimental data for adsorption was found to fit better with Langmuir model suggesting homogeneous monolayer adsorption of Cs^+ ions on the surface of MOF/Fe_3O_4/KNiFC without any interactions between the adsorbed ions. Decrease in adsorptive capability with increase in the dose of adsorbents was attributed to the concentration of Cs^+ which was not enough to occupy all the sites available for adsorption and to the surplus adsorption sites remained unemployed. For regeneration, 25 mL of 1 M HNO_3 solution was added to 0.1 g of the sorbent and kept for 24 h. Negligible concentration of iron in the supernatant indicated that Fe_3O_4 was perfectly protected against acidic conditions. The adsorption-regeneration process was repeated up to five cycles. Incomplete Cs^+ desorption and leaching of KNiFC from the adsorbent surface lower the adsorption capacity of the magnetic sorbent after regeneration. 70% and 80% of initial adsorption capacity of MOF/Fe_3O_4/KNiFC and MOF/ KNiFC were retained up to five adsorption-regeneration cycles (Naeimi and Faghihian 2017).

A step-by-step assembly strategy was reported by Ke et al. (2017) for fabrication of a novel core–shell MMOF composite with Fe_3O_4 MNPs as the magnetic core and porous $Cu_3(BTC)_2$ MOF as shell which was further thiol-functionalized by a facile post-synthetic modification approach to obtain thiol-functionalized Fe_3O_4@$Cu_3(BTC)_2$ composite (Fig. 19). The thiol-functionalized magnetic adsorbent was demonstrated as an efficient recyclable adsorbent for almost complete removal of highly toxic Pb(II) and Hg(II) ions from wastewater containing mixed heavy metal ions with maximum adsorption capacities of 348.43 and 215.05 mg g^{-1}, respectively. Excellent adsorption capacity of thiol-functionalized Fe_3O_4@$Cu_3(btc)_2$ toward Pb^{2+} and Hg^{2+} ions over a wide pH range was ascribed by the strong interaction between the thiol group and the analyte ions. For desorption, the Fe_3O_4@$Cu_3(btc)_2$ sorbent with adsorbed Pb^{2+} and Hg^{2+} ions was collected by an external magnet from the mixture, washed three times with 5 mL 0.01 M NaOH solution, and sonicated. Adsorption capacity of regenerated thiol-functionalized Fe_3O_4@$Cu_3(btc)_2$ was tested with the same initial conditions, and no significant losses in the adsorption capacity for Hg^{2+} ion and only minute changes in the adsorption capacity for Pb^{2+} ion were observed up to four adsorption-regeneration cycles which

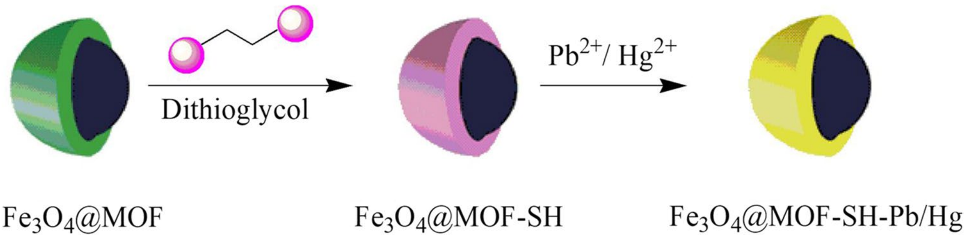


Fig. 19 Application of thiol-functionalized Fe_3O_4@$Cu_3(BTC)_2$ composite for removal of Pb(II) and Hg(II) ions

indicated excellent long-term stability of the magnetic core–shell microspheres (Ke et al. 2017).

Yang et al. developed a highly stable magnetic core–shell nanocomposite $CoFe_2O_4$@MIL-100(Fe), for rapid and effective removal of both As(III) and As(V) from contaminated water with maximum removal capacities 143.6 mg g^{-1} and 114.8 mg g^{-1}, respectively. Adsorption kinetics, adsorption isotherms, and thermodynamics of iAs on $CoFe_2O_4$@MIL-100(Fe) were examined to illustrate the adsorption mechanism of iAs. Both Langmuir and Freundlich models were studied for the adsorption of iAs on $CoFe_2O_4$@MIL-100(Fe) to propose the adsorption mechanism. The Langmuir model fitted better with the adsorption of As(V) on $CoFe_2O_4$@MIL-100(Fe) suggesting a homogeneous monolayer adsorption process. Adsorption of As(III) was appropriately fitted with the Freundlich isotherm model indicating heterogeneous multilayer adsorption which was attributed to H-bonding between H_3AsO_3 molecules. However, an inner-sphere complex mechanism was attributed to the adsorption of both As(III) and As(V) to form the Fe–O-As microstructure via hydroxyl exchange with the deprotonated arsenite and arsenate. $CoFe_2O_4$@MIL-100(Fe) sorbent with adsorbed As(V) or As(III) was added to 5 mL of ultrapure water, ultrasonicated, and centrifuged at high speed. Higher concentration (22.3 mg L^{-1}) of As(III) in the supernatant than that of As(V) (1.1 mg L^{-1}) indicated weak adsorption of As(III) on the absorbent. High chemical stability, fast adsorption kinetics, high adsorption capacity, wide pH range, and capability of tolerating interfering ions of the adsorbent facilitated it to be validated by two different wastewater treatment processes for simultaneous removal of iAs; one is a simple filtration strategy and another one is batch magnetic separation strategy (Yang and Yin 2017).

For the first time, Min and his group reported an expedient and powerful method for fast and efficient removal of UO_2^{+2} ion from aqueous solution with an unprecedented maximum adsorption capacity of 523.5 mg g^{-1} by utilizing Fe_3O_4@ZIF-8 nanocomposite. Adsorption mechanism of UO_2^{2+} ions on Fe_3O_4@ZIF-8 was ascribed by coordination between Zn atoms of the framework and UO_2^{2+} ions as well as the hydrogen bonding. For desorption, U-absorbed sorbent was eluted by 0.1 M Na_2CO_3 solution and the desorption percentage was found to be 77%. PXRD patterns of samples after adsorption and desorption of UO_2^{2+} suggested excellent chemical stability of the nanocomposite. Moreover, the magnetic sorbent possessed extraordinary selectivity toward lanthanides over actinides. Excellently high porosity, outstanding thermal and chemical stability of ZIF-8, and possibilities of easy and fast magnetic separation established it as a fantabulous adsorbent for wastewater treatment (Min et al. 2017).

It is worth to mention here that Zhu and his coworkers fascinatingly designed a core-double-shell magnetic polydopamine@ZIF-8 nanocomposite (MP@ZIF-8) with supermagnetic Fe_3O_4 NPs as the magnetic core, polydopamine (PDA) as the inner shell, and porous ZIF-8 structures as the outer shell by employing a facile and green synthetic route. The PDA shell not only provides colloidal stability to the MNPs but also prevents them from undergoing corrosion. The MP@ZIF-8 composite was used to achieve a high adsorption capacity of 136.56 mg g^{-1} in the removal of Cr(VI) ions from Cr-contaminated aqueous media as well as partial reduction of highly toxic Cr(VI) ions to low toxic Cr(III) ions. Along with adsorption, Cr(VI) ions were in situ reduced to Cr(III) ions and enabled to get immobilized on the adsorbent via the reduction of N containing groups on ZIF-8 and PDA. Adsorption of Cr(VI) is not an ordinary and single process mechanism but occurs in multisteps—(i) adsorption of water molecules on ZIF-8 in aqueous solution ($pH = 5.0$) producing active sites including protonated N atoms groups and the Zn – OH sites, (ii) adsorption of Cr(VI) at active sites and their partial reduction to Cr(III) by the groups containing nitrogen atoms on ZIF-8, (iii) retarded diffusion of Cr(VI) to PDA and reduction of Cr(VI) into lesser toxic Cr(III) by amine groups, and (iv) chelation of Cr(III) onto imino groups, as well as chemical bonding between Cr(VI) with the hydroxyl groups on PDA. After adsorption of Cr(VI), the sorbent with adsorbed metal was immersed in 6 mL 0.05 M NaOH solution, agitated for 12 h, centrifuged and washed multiple times with Milli-Q water for regeneration, and reused up to five adsorption–desorption cycles. A slight decrease in Cr(VI) removal efficiency was observed after regeneration in the fifth cycle. The slight decreases in uptake efficiency were attributed to the incomplete desorption of adsorbate from the surface of the sorbent (Zhu et al. 2017).

Wang and his group reported a simple mechanical agitation strategy to combine magnetic cellulose nanocrystal (MCNC) and metal organic framework composite (Zn-BTC) to obtain a novel magnetic adsorbent material (MCNC@Zn-BTC) at room temperature. Briefly, MCNC were synthesized by a simple co-precipitation technique followed by its surface coating with Zn-BTC structures via an Et_3N-catalyzed reaction under mild reaction condition (Fig. 20). Within 30 min, a maximum adsorption capacity of 558.66 mg g^{-1} of the MCNC@Zn-BTC composite was achieved at room temperature for the removal of Pb(II) ions. More than 80% Pb(II) ion was removed even after five cycles of adsorption–desorption cycles. Adsorption mechanism was ascribed by electrostatic interactions between negatively charged COO^- ions present on the surface of composite and positive Pb(II) ions. Pseudo-second-order kinetics model was fitted better by the experimental data suggesting chemisorptions. For desorption, 20 mL 0.1 M HCl solution was added as eluent to Pb(II)-loaded MCNC@Zn-BTC and shaken for 4 h. The magnetic sorbent was separated by an external magnet and washed with deionized water. After releasing Pb(II)

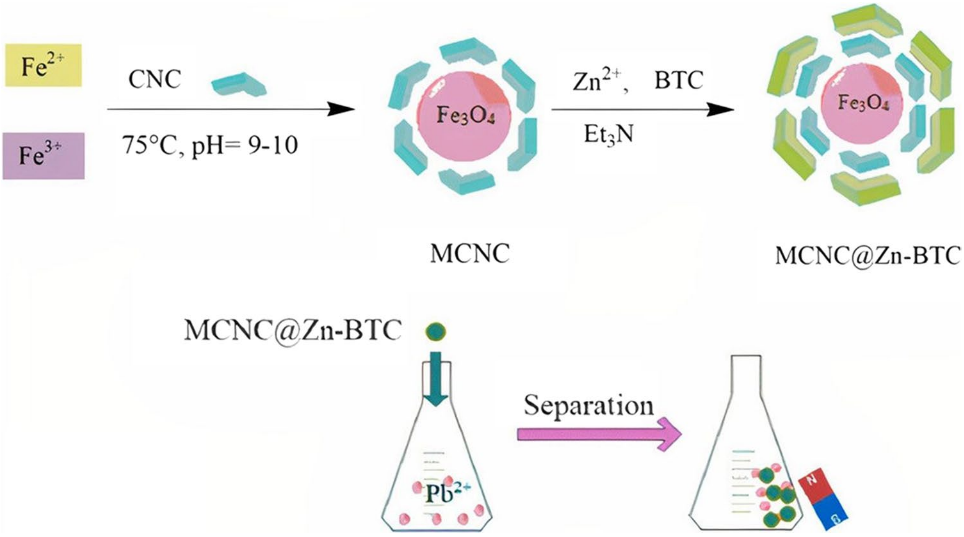


Fig. 20 Synthesis and application of MCNC@Zn-BTC composite for removal of Pb(II)

ions, MCNC@Zn-BTC was reused up to five cycles. However, slight decrease in Pb(II) uptake from 198.18 ± 0.54 to 163.31 ± 1.89 mg/g was observed but Pb(II) removal ratio remained intact at 82.07 ± 0.31% (Wang et al. 2017).

Huang and his group synthesized an amino decorated Zr-MOF-based core–shell magnetic framework composite Fe_3O_4@SiO_2@UiO-66-NH_2 (MFC-N), with adjustable shell thickness by employing a facile and efficient protocol. It was found that the MFC-N exhibited a maximum of 102 mg g^{-1} adsorption capacity and fast adsorption kinetics for Pb(II) ions under optimized conditions. Enhanced adsorption was attributed to more binding sites for Pb^{2+} provided by free -NH_2 groups as well as chelation of Pb^{2+}ions with free -NH_2 groups present on MFC-N and MFC-U. Regeneration of adsorbent was achieved by using 0.5 M HNO_3 solution as eluent. No significant loss of adsorption capacity was observed up to 6 cycles, implying good regenerability of all the MFCs for water treatment. Stability was further confirmed by leaching test, and ICP-OES result showed negligible concentration of Zr (< 0.5 mg L^{-1}) in the supernatant indicating good stability of the sorbent. Furthermore, original appearance of TEM images and XRD patterns of the adsorbent after five adsorption–desorption cycle demonstrated the structural stability of the prepared MFCs during the extraction process (Huang et al. 2018a, b).

Li and his coworkers fabricated hierarchically engineered microporous Cu-(I)-MOF-based magnetic hybrid material HPU-13@Fe_3O_4 for efficient removal of Cr(VI) from contaminated water. The HPU-13@Fe_3O_4 composite was demonstrated as an effective and reusable adsorbent for the removal of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions in the presence of other competitive ions including F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}, and HPO_4^- with record-breaking maximum removal capacities of 398.41 mg g^{-1} and 471.69 mg g^{-1}, respectively. In the plausible adsorption mechanism, the low valent Cu(I) was found to exhibit a high affinity towards Cr(VI) ions and reducibility of Cu(I) in HPU-13@Fe_3O_4 enabled the adsorption of Cr(VI) via a redox reaction. The adsorbent was recovered successfully by soaking it in saturated aqueous solution of $NaNO_3$ for 12 h. The adsorption–desorption process was repeated for 6 cycles without any significant changes in adsorption capacity. Unchanged PXRD pattern indicated the recyclability and reversibility of HPU-13@Fe_3O_4 sorbent in remediation of Cr(VI)-polluted water (Li et al. 2018).

Shi et al. reported an in situ synthetic route for developing Cu-MOFs followed by doping with Fe_3O_4 MNPs to obtain a MMOF composite, Cu-MOF/Fe_3O_4, and utilized it for efficient removal of Pb(II) ion from lead-contaminated water with a maximum removal capacity of 219 mg g^{-1} and 90% removal efficiency. The adsorption of Pb(II) ion was attributed to the formation of chemical bonds between Pb(II) ions and N-atoms of amino groups in the organic ligand. Desorption of the adsorbed metal ions to regenerate the Cu-MOFs/Fe_3O_4 composite is done by treating them separately with acetone and 0.1 M EDTA solution as eluent. Although the strong Pb^{2+}adsorption with over 85% removal efficiency was obtained up to three adsorption–desorption cycle, on further adsorption, the removal efficiency was reduced to 50% (Shi et al. 2018).

A supermagnetic cation-exchange Al-based MOF, Fe_3O_4/MIL-96(Al), was reported by Mehdinia and his group for efficient removal of Pb(II) ion from environmental water sample. MIL-96(Al) synthesized using Al^{3+} metal source and 1,3,5-benzene tricarboxylic acid as organic linker under hydrothermal condition was magnetized by Fe_3O_4 MNPs via an embedding technique to obtain a novel adsorbent possessing large adsorptive size with high adsorption capacity, active anionic surface, weak Lewis acid sites, and positive response to magnetic field as well as available enclosed space for trapping of bulky analytes. The electrostatic interactions between hydrated Pb(II) ions and anionic surface of the adsorbent facilitated the adsorption mechanism. In addition, water molecules interacted by the Lewis acidic sites of MIL-96(Al) acted as active sites for adsorption of Pb^{2+} ions. Under the optimized conditions, a maximum adsorption capacity of 301.5 mg g^{-1} was resulted due to the presence of high percentage of OH groups on the Fe_3O_4/MIL-96(Al) surface. Prior to extraction, 32.4 mg of Fe_3O_4/MIL-96(Al) sorbent was activated by dispersing it in 3 mL of 1 M NaOH solution followed by sonication for 10 min. The activated sorbent was dispersed in aqueous solution containing Pb(II) ions for extraction. After extraction, the sorbent was regenerated by using 2.5 mL of 0.2 M HNO_3 solution as eluent. Good adsorption capacity of Fe_3O_4/MIL-96(Al) after two extraction-regeneration cycles suggested better regeneration of the sorbent. XRD pattern of Fe3O4/MIL-96(Al) before and after activation process suggested excellent stability of Fe_3O_4/MIL-96(Al) during the activation process (Mehdinia et al. 2018).

Huo et al. developed a convenient method to prepare a stable and high surface area (1133 m^2g^{-1}) magnetic core–shell hybrid composite Fe_3O_4@ZIF-8 containing supermagnetic Fe_3O_4 NPs as the core and microporous ZIF-8 structures as the shell. Fe_3O_4@ZIF-8 was applied as an excellently regenerable adsorbent in wastewater treatment for efficient removal of As(III) ions from contaminated water and an outstanding maximum removal capacity of 100 mg g^{-1} was obtained (Table 1). In aqueous medium, some water molecule get adsorbed on the surface ZIF-8 which further produce several external active sites (Zn-OH) by dissociating water. Subsequently, interaction between As(III) and Zn-OH groups occurs facilitating the formation of monodentate mononuclear or bidentate binuclear complex via the ligand exchange interactions. A new strong band in FTIR spectra of spent adsorbent was ascribed to Zn–O-As vibration indicating an inner-sphere complexation mechanism between arsenic anions and the adsorbent via the ligand exchange which is responsible for the primary adsorption of As(III) ions. However, the arsenite uptake was significantly hindered by the presence of phosphate and carbonate which was due to the formation of inner-sphere complexes between these ions and the adsorbent that competed with the arsenite for the active sites thereby reducing As(III) the adsorption. For regeneration, used sorbent was collected by an external magnet and dispersed 0.2 M of NaOH eluent solution, shaken at 200 rpm for 6 h. The adsorption capacity was found to be decreased with increase in the cycle numbers (from 100 to 50% for 1st to 5th, respectively). Decreased adsorption capacity was attributed to the decreased active sites due to partial recovery of occupied H_3AsO_3 and falling off of ZIF-8 from the composites. Experimental data (PXRD, SEM, FTIR, etc.) suggested that the spent adsorbent did not undergo any morphological change indicating the stability of the MMOF composite (Huo et al. 2018).

In another approach, Yuan and his group fabricated a glucose-functionalized Zr-based MMOF composite, Fe_3O_4@SiO_2@UiO-66-NH_2-Glu, and utilized it to reduce the Co(II) level in contaminated water. The maximum adsorption capacities at 288 K, 298 K, and 208 K were found to be 178.6, 222.2, and 270.3 mg g^{-1}, respectively. More than 90% adsorption was observed to occur in initial 8 h and then gradually equilibrium was reached. The kinetic and thermodynamic data were well fitted to the Langmuir isotherm model, and the removal kinetics was observed to be pseudo-second-order. Adsorption mechanism was attributed to the coordination effect of O-atoms on glucose linkers and SiO_2 surface with Co(II) ions which was supported by XPS analysis data. To examine the reusability performance, 0.1 M HCl solution was used as the eluent to regenerate Fe_3O_4@SiO_2@UiO-66-Glu and adsorbent was found to show excellent adsorption capacity and stability up to five adsorption-regeneration (Yuan et al. 2018a, b).

A highly water stable MMOF composite was constructed by Venkatewarlu and his group by uniformly embedding biocompatible polymer-capped Fe_3O_4 MNPs (PFe_3O_4) on the surface of NH_2-MIL-125(Ti) MOF structures which was controlled by hydrothermal strategy by varying the precursor of PFe_3O_4. The biopolymer coating on Fe_3O_4 MNPs was introduced by utilizing the extract of potato peels which not only acted as a capping agent but also as a reducing agent. Unique functionalities of both nanoporous MOF and biopolymer on PFe_3O_4 particles synergistically enhanced the adsorption of Pb(II) ions on the surface of PFe_3O_4@NH_2-MIL-125(Ti) composite with a maximum removal capacity of 561.7 mg g^{-1}. Experimental data (XPS and FTIR) indicated the coordination of Pb(II) via O and N atoms present in the PFe3O4@NH2-MIL-125 composite. The polymer coating not only introduced higher adsorption efficiency but also a better stability for recycling the composite which was successfully recycled up to six cycles without significant loss of their initial properties and successfully desorbed by utilizing 0.1 M EDTA solution. Excellent regenerating ability of EDTA without leaching of adsorbent was attributed to the strong chelation of EDTA with Pb(II). Maximum removal efficiency (99.1%) was obtained at pH 5 at 298 K temperature (Venkatewarlu et al. 2018).

In another report, Huo and his group reported a facile and green approach to fabricate a magnetic core–shell composite Fe_3O_4@UiO-66 possessing large surface area (124.8 m^3g^{-1}) and plenteous micropores with pore volume 0.121 cm^3g^{-1} by employing a direct epitaxial strategy. Abundant carboxyl groups on the surface of Fe_3O_4 microspheres (Fe_3O_4–COOH) enabled further epitaxial growth of the unique core shell by strongly coordinating with Zr(IV) metal nodes. Fe_3O_4@UiO-66 composite was utilized to eliminate

Table 1 Selected MMOF composites in removal of toxic heavy metal ions

MMOF composites	Magnetic component	MOF component	Heavy metal ion removed	Initial concentration	Maximum adsorption capacity (mg/g)	Metal recovery (%)	Recyclability (no. of cycles)	Techniques used to check stability	Ref
Fe_3O_4-(pyridine)/$Cu_3(BTC)_2$	Fe_3O_4	$Cu_3(BTC)_2$	Pd(II)	5 µg L^{-1}	105.1	98	–	TGA	Bagheri et al. 2012
Fe_3O_4/$Cu_3(BTC)_2$-H_2Dz	Fe_3O_4	$Cu_3(BTC)_2$	Pb(II)	5 µg L^{-1}	1.67	99–102	80		Wang et al. 2013
Fe_3O_4-DHz@HKUST-1	Fe_3O_4	$Cu_3(BTC)_2$	Zn(II)	5 ng mL^{-1}	206	98–102	–	TGA	Taghizadh et al. 2013
			Ni(II)	5 ng mL^{-1}	98	94–99	–		
			Pb(II)	5 ng mL^{-1}	104	94–104	–		
			Cd(II)	5 ng mL^{-1}	188	94–100	–		
Fe_3O_4-(pyridine)@HKUST-1	Fe_3O_4	$Cu_3(BTC)_2$	Cd(II)	5 mg L^{-1}	190	97–99	–	–	Sohradi et al. 2013
			Pb(II)	5 mg L^{-1}	190	98	–	–	
γ-Fe_3O_4/C@HKUST-1	Fe_3O_4/C	HKUST-1	Cr(VI)	–	101.4	–	5	–	Xiong et al. 2015
Fe_3O_4@MIL-53(Al@100aBDC)	Fe_3O_4	MIL-53	Pb(II)	100 ppm	492.4	–	–	Leaching	Ricco et al. 2015
Bi-I-Fe_3O_4@SiO_2@HKUST-1	Fe_3O_4	HKUST-1	Hg(II)	10 mg L^{-1}	264	–	1	TG, PXRD Leaching	(Huang et al. 2015)
Fe_3O_4@MIL-101	Fe_3O_4	MIL-101	As(III)	10 mg L^{-1}	121.5	56.6	8	PXRD	(Folens et al. 2016)
			As(V)	10 mg L^{-1}	80	7	8	Leaching ADF-STEM	
Fe_3O_4@MOF-235(Fe)-OSO_3H	Fe_3O_4	MOF-235(Fe)	Cd(II)	2.5 µg L^{-1}	195.0	98.7–102.1	10	TGA	(Moradi et al. 2016)
Fe_3O_4@MIL-100(Fe)	Fe_3O_4	MIL-100(Fe)	Cr(VI)	50 ppm	18	–	–	TGA	(Yang et al. 2016)
MFC-S	Fe_3O_4	UIO-66	Hg(II)	10 mg L^{-1}	282	–	5	PXRD, TGA	(Huang et al. 2016)
[$Cu_3(BTC)_2$/Fe_3O_4/KNiFC]	Fe_3O_4	$Cu_3(BTC)_2$	Cs(I)	–	153	–	5	Leaching	(Naeimi and Faghihian 2017)
Thiol-functionalized Fe_3O_4@$Cu_3(BTC)_2$	Fe_3O_4	$Cu_3(BTC)_2$	Pb(II)	0.5 mM	215.05	–	4	Leaching	(Ke et al. 2017)
			Hg(II)	0.5 mM	348.43	–	4	–	
$CoFe_2O_4$@MIL-100(Fe)	$CoFe_2O_4$	MIL-100(Fe)	As(III)	–	143.6	–	–	–	(Yang et al. 2017)
			As(V)	–	114.8	–	–	Leaching	
Fe_3O_4@ZIF-8	Fe_3O_4	ZIF-8	UO_2^{2+}	250 mg L^{1}	523.5	77	–	Leaching	(Min et al. 2017)
MP@ZIF-8	Fe_3O_4	ZIF-8	Cr(VI)	60 mg L^{-1}	136.56	–	5	PXRD	(Zhu et al. 2017)
MCNC@Zn-BTC	CNC	Zn-BTC	Pb(II)	200 mg L^{-1}	558.66	–	5	–	(Wang et al. 2017)
MFC-N-100	Fe_3O_4	MIL-53-NH_2	As(V)	500 µg L^{-1}	71	–	5	–	(Huang et al. 2018a, b)
Fe_3O_4@SiO_2@UiO-66-NH_2	Fe_3O_4	UiO-66-NH_2	Pb(II)	50 mg L^{1}	102	–	6	TGA, FTIR, XRD, leaching	(Huang et al. 2018a, b)

Table 1 (continued)

MMOF composites	Magnetic component	MOF component	Heavy metal ion removed	Initial concentration	Maximum adsorption capacity (mg/g)	Metal recovery (%)	Recyclability (no. of cycles)	Techniques used to check stability	Ref
HPU-13@Fe_3O_4	Fe_3O_4	HPU-13	$Cr_2O_7^{2}$	100 mg L^{1}	398.41	–	6	Leaching	(Li et al. 2018)
			CrO_4^{2-}	100 mg L^{1}	471.69	–	6	PXRD, TGA	
Cu-MOF/Fe_3O_4	Fe_3O_4	Cu-MOF	Pb(II)	–	219	–	3		(Shi et al. 2018)
Fe_3O_4/MIL-96(Al)	Fe_3O_4	MIL-96(Al)	Pb(II)	–	301.5	–	2	–	(Mehdinia et al. 2018)
Fe_3O_4@ZIF-8	Fe_3O_4	ZIF-8	As(III)	27 mg L^{-1}	100	–	5	XRD	(Huo et al. 2018)
Fe_3O_4@SiO_2@UiO-66-NH_2-Glu	Fe_3O_4	UiO-66-NH_2	Co(II)	10 mg L^{-1}	270.3	–	5	TGA	(Yuan et al. 2018a, b)
PFe_3O_4@NH_2-MIL-125(Ti)	PFe_3O_4	MIL-125(Ti)	Pb(II)	10 mg L^{-1}	561.7	97.9	6	–	(Venkatewarlu et al. 2018)
Fe_3O_4@UiO-66	Fe_3O_4	UiO-66	As(V)	27 mg L^{-1}	73.2	–	5	Leaching, TGA	(Huo et al. 2019)
Fe_3O_4-NH-SO_3H@-HKUST-1	Fe_3O_4	HKUST-1	Pb(II)	5 mg L^{-1}	384.6	–	4	TGA, FTIR, XRD	(Karimi et al. 2019)
Fe_3O_4@UiO-66@UiO-67/CTAB	Fe_3O_4	UiO-66@UiO-67	Cr(VI)	50 ppm	932.1	–	5	–	(Li et al. 2020)
								TGA	
UiO-66/Fe_3O_4	Fe_3O_4	UiO-66	Cs(I)	60 mg L^{-1}	57.29	–	3		(Feng et al. 2019)
UiO-66/Fe_3O_4/GO	Fe_3O_4	UiO-66	Cs(I)	60 mg L^{-1}	62.07	–	3	–	
Fe_3O_4@TA@UiO-66		UiO-66	As(III)	10 mg L^{-1}	97.8	–	–	–	(Qi et al. 2019)
Fe_3O_4@ZIF-8	Fe_3O_4	ZIF-8	U(VI)	20 mg L^{-1}	539.7	–	5	–	(Wu et al. 2019)
	Fe_3O_4		Eu(III)	20 mg L^{-1}	255	–	5	TGA, XRD	
ZIF-67@Fe_3O_4@ESM	Fe_3O_4	ZIF-67	Cu(II)	15 mg L^{-1}	344	–	6	FTIR	(Mahmoodi et al. 2019a, b)
								XRD, SEM/EDS	
Fe_3O_4@MIL-88A(Fe)/APTMS	Fe_3O_4	MIL-88A(Fe)	Pb(II)	0.1 mol L^{-1}	532.66	94.73	5	ICP	(Mahmoud et al. 2020)
			Cd(II)		693.0	91.81	5	TGA,	
			Cr(VI)		1092.2	95.46	5		
PAA-Fe_3O_4-NPs-Cu MOF	Fe_3O_4	Cu-MOF	Pb(II)	-	610	–	–		(Goyal et al. 2020)
Fe_3O_4-Car-MOF	Fe_3O_4	Car-MOF	As	20–40 mgL^{-1}	94.33	–	4	TGA, XPS, leaching	(Keykhaee et al. 2020)
Fe_3O_4@UiO-66@Ppy	Fe_3O_4	UiO-66	Cr(VI)	50 mg L^{-1}	259.1	–	4	FTIR	(Zhou et al. 2021)
								XRD, FTIR	
$Ni_{0.6}Fe_{2.4}O_4$-UiO-66-NH_2/PEI	$Ni_{0.6}Fe_{2.4}$	UiO-66-NH_2	Cr(VI)	10 mg L^{-1}	428.6	–	5	Leaching	(Wang et al. 2021a)
	O_4		Pb(II)	10 mg L^{-1}	273.2	–	5	TGA,	

Table 1 (continued)

MMOF composites	Magnetic component	MOF component	Heavy metal ion removed	Initial concentration	Maximum adsorption capacity (mg/g)	Metal recovery (%)	Recyclability (no. of cycles)	Techniques used to check stability	Ref
Fe_3O_4/cysteine/NH_2-MIL-53(Al)	Fe_3O_4	NH_2-MIL-53(Al)	Pb(II)	100 mg L^{-1}	361.53	71	3	Leaching	(Nasiri et al. 2021)
Fe_3O_4@UIO-66-2COOH	Fe_3O_4	UIO-66-2COOH	Sb(III)	100 mg L^{-1}	56.49	–	–	SEM, TEM	(Zhu et al. 2021)
mag-MOF-NH_2	Fe_3O_4	MIL-101(Cr)	U(VI)	10 ppm	80	–	1	Leaching, TGA	(Chen et al. 2021)
Fe_3O_4/ZIF-67@AmCs	Fe_3O_4	ZIF-67	Cr(VI)	50 mg L^{-1}	119.05	–	7	Leaching,, TGA	(Omer et al. 2021)
MIL-101(Cr)/Fe_3O_4@SiO_2@2-ATP	Fe_3O_4	MIL-101(Cr)	Ag(I)	5 ng mL^{-1}	103	89–103	6	–	(Mousavi et al. 2021)
Fe_3O_4@ZIF-8	Fe_3O_4	ZIF-8	Cu(II)	100 mg L^{-1}	301.33	–	4	TGA	(Jiang et al. 2021)
			Pb(II)	100 mg L^{-1}	719.42	–	4		

As(V) from contaminated water with an excellent removal capacity of 73.2 mg g^{-1}. Risk of secondary pollution that may occur from the utilization of toxic organic reagents and structural modification can be avoided in direct epitaxial strategy which is environmentally friendly, time saving, and most importantly an economic process (Huo et al. 2019).

Karimi and his coworkers reported a novel and green strategy to obtain a reasonably designed MMOF nanocomposite, Fe_3O_4-$NHSO_3H$@HKUST-1, by forming chemical bonds between Fe_3O_4-$NHSO_3H$ MNPs and the surface of HKUST-1 MOF structures (Fig. 21). Fe_3O_4-$NHSO_3H$@HKUST-1 composite was utilized as an adsorbent for removal of Pb(II) from contaminated water with a maximum adsorption capacity 384.6 mg g^{-1} at 298 K temperature. The adsorption mechanism was ascribed to the coordination Pb(II) with –NH_2 group present on the surface of Fe_3O_4-$NHSO_3H$@HKUST-1 adsorbent. For regeneration of the adsorbent, desorption of Pb(II) ions from the magnetic sorbent was done by using 10 mL of 0.1 M HCl solution as eluent followed by ultrasonication for 5 min. The magnetic sorbent was reused up to four adsorption–desorption cycles with > 90% removal efficiency (Karimi et al. 2019).

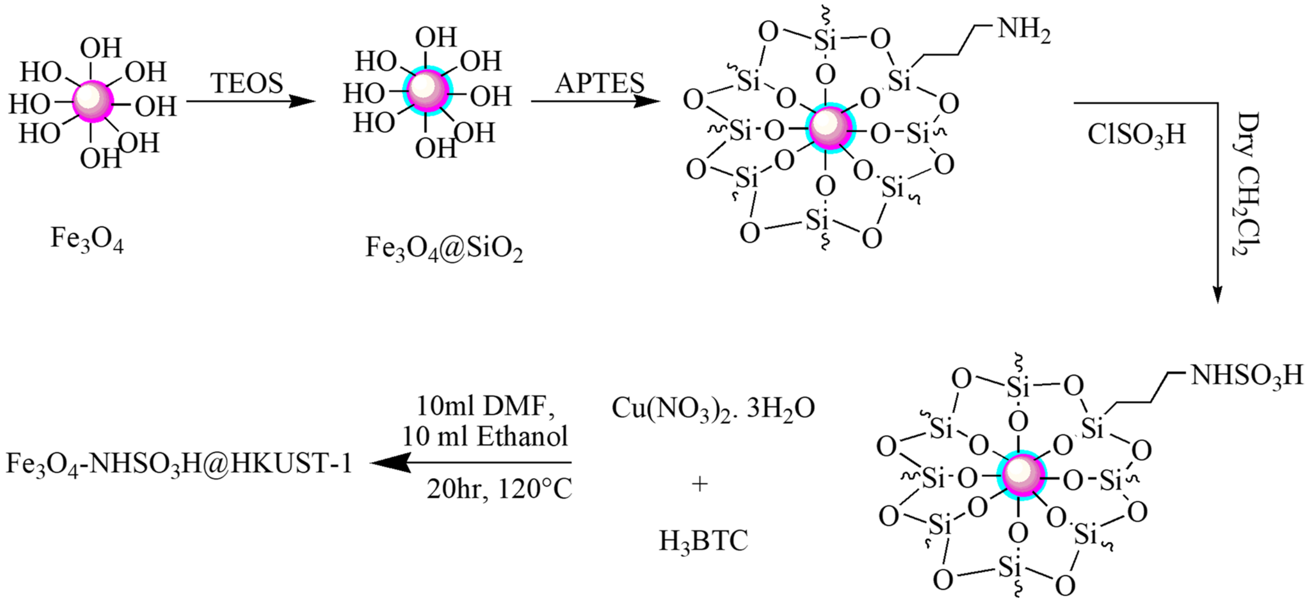


Fig. 21 Synthesis of Fe_3O_4-$NHSO_3H$@HKUST-1 composite for removal of Pb(II)

Li et al. fabricated a CTAB-functionalized magnetic MOF@MOF composite, Fe_3O_4@UiO-66@UiO-67/CTAB, by employing a facile solvothermal strategy and utilized it for the removal of Cr(VI) ion from aqueous media with a maximum removal capacity of 932.1 mg g^{-1}. Other co-existing ions such as Na^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} affected the adsorption of Cr(VI) ion occupying the adsorption sites on the adsorbent. Adsorption was observed to increase rapidly during the initial 120 min and then eventually slowed down and attained equilibrium at a contact time of 240 min. Adsorption-coupled reduction was ascribed to the adsorption mechanism of Cr(VI) on Fe_3O_4@UiO-66@UiO-67/CTAB. Adsorption of Cr(VI) on the sorbent was facilitated by electrostatic interactions between Cr(VI) ions and positively charged groups (CTA^+) on the CTAB-modified surface and other forces, e.g., H-bonding force and van der Waals forces. Simultaneously, CTAB on the modified surface acted as electron donor to provide electrons for the reduction of Cr(VI) to lesser toxic Cr(III). CTAB itself get oxidized to CTA^+ which strengthen the adsorption of Cr(VI). The spent Fe_3O_4@UiO-66@UiO-67/CTAB was collected with external magnet and immersed in a NaOH solution for desorption and regeneration of the adsorbent. Regenerated Fe_3O_4@UiO-66@UiO-67/CTAB was used for subsequent removal of Cr(VI), and removal efficiency of 90.14% was maintained with maximum adsorption capacity of 112.68 mg g^{-1} even after five adsorption-regeneration cycles (Li et al. 2020).

An approach to remove radioactive Cs(I) from contaminated water was demonstrated by Feng and his coworkers by utilizing novel MMOF composites UiO-66/Fe_3O_4 and UiO-66/Fe_3O_4/GO synthesized via one-step strategy. Maximum adsorption capacity of 57.29 and 62.07 mg g^{-1} with UiO-66/Fe_3O_4 and UiO-66/Fe_3O_4 /GO, respectively, for Cs^+ was ascribed to the size compatibility of the nanosized cavities of the adsorbent. The adsorption process was observed to be best fitted to the pseudo-second-order kinetic model and Langmuir adsorption isotherm model which was indicated by their higher correlation coefficient value suggesting single-layered, uniform adsorption. Cs^+ adsorption by UiO-66, UiO-66/Fe_3O_4, and UiO-66/Fe_3O_4/GO was well fitted to pseudo-second-order kinetic model demonstrating chemisorption. Thermodynamic data suggested interactions between ion and solid. Co-existing ions like Na^+ and K^+ adversely affected the adsorption of Cs^+ ion on the adsorbents. This was attributed to the chemical interactions of Na^+ and K^+ ions with the -OH groups on MNPs and –COOH groups on GO. Desorption was carried out with 0.1 M HCl as desorption agent, and regeneration was done with 0.1 M NaOH as regeneration agent. Adsorption capacity of UiO-66/Fe_3O_4/GO decreased significantly after three adsorption-regeneration cycles, but it was still higher than that of UiO-66 and UiO-66/Fe_3O_4 (Feng et al. 2019).

Trivalent arsenic As(III) and antimony Sb(III) exhibit high toxicity and mobile properties. A novel core–shell MMOF composite, Fe_3O_4@TA@UiO-66, was fabricated by Qi and his coworkers via in situ generation of UiO-66 shell around the polyphenol tannic acid (TA)-modified Fe_3O_4 magnetic core (Fe_3O_4@TA) for rapid removal of As(III) and Sb(III). Easily accessible and biodegradable polyphenol tannic acid modification of the MNPs as the hydrophilic surface not only prevented the aggregation of the magnetic cores but also increased dispersion stability along with additional active sites for adsorption, improving the removal of As(III) and Sb(III) ions from contaminated aqueous solution. Connection between UiO-66 MOFs and Fe_3O_4 magnetic core was facilitated by TA, and also, it improved the adsorption capacity via hydrogen bonding as well as inner-sphere complexation between the adsorbed species and magnetic surface. XPS and FTIR data for Fe_3O_4@TA@UiO-66 before and after adsorption process suggested that the adsorption of As(III) and Sb(III) was facilitated via Zr-O-As and Zr-O-Sb complexation. The Langmuir model was well fitted to the adsorption of As(III) and Sb(III) with suggesting monolayer adsorption process for both As(III) and Sb(III) (co-existing ions including SO_4^{2-}, PO_4^{3--}, CO_3^{2-}, and SiO_3^{2-} were observed to have no significant adverse effect on the arsenic and antimony uptake over a wide pH range, Qi et al. 2019).

A simple modification strategy for the fabrication of a core–shell MMOF composite, Fe_3O_4@ZIF-8, with higher water stability, large surface area (606.91 m^2/g) and plenteous surface functional groups (-OH, -COOH, -NH, -C = N, N–O, and Zn–O), and abundant pores, was demonstrated by Wu and his group (Wu et al. 2019). In the first step, the surface of pre-synthesized Fe_3O_4 MNPs was negatively charged by treating them with anionic polyelectrolyte, followed by subsequent growth of ZIF-8 thin layer structures around the Fe_3O_4 MNPs to obtain magnetic core–shell Fe_3O_4@ZIF-8 microspheres. The composite was utilized for the removal of hexavalent actinide and trivalent lanthanide with maximum adsorption capacity of 539.7 mg g^{-1} for U(VI) and 255.6 mg g^{-1} for Eu(III) from radionuclide-contaminated water body (Fig. 22). The highest selective separation ability (199.9 m_{equiv}/g) of the magnetic adsorbent towards U(VI) confirmed excellent selective removal of U(VI) in presence of other co-existing radioactive nuclides. Sufficient pores on Fe_3O_4@ZIF-8 surface provided plenteous active sites available for rapid adsorption of U(VI) in intra-particle diffusion layer. Functional groups such as hydroxyl groups (-OH), nitrogen groups (-NH- and C = N-), oxygen groups (Zn–O and N–O), and carboxyl functional groups (-COOH) on the surface participated in adsorption via surface complexation reactions. Rapid capture of U(VI) was further facilitated by electrostatic attraction. Moreover, core–shell Fe_3O_4@

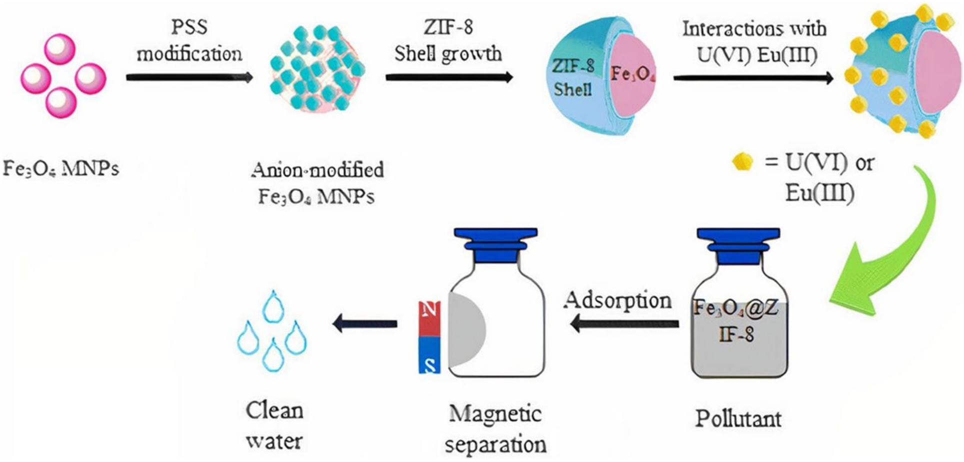


Fig. 22 Schematic representation for synthesis of magnetic core–shell Fe_3O_4@ZIF-8 microspheres and separation of pollutants from solutions under external magnetic field

ZIF-8 also improved the U(VI) adsorption capability. More impressively, 3 M HNO_3 solution was used for regeneration of Fe_3O_4@ZIF-8 and adsorptive property remained unaffected after at least five adsorption–desorption cycles, demonstrating their amazing stability and recyclability.

Mahmoodi et al. reported a novel bio-based MMOF composite (ZIF-67@Fe_3O_4@ESM) by growing and stabilizing ZIF-67 structures on support bed of magnetic egg-shell membrane Fe_3O_4@ESM. The magnetic material exhibited high surface area of 1263 m^2g^{-1} and was demonstrated as an excellent sorbent for Cu(II) removal with maximum removal capacity of 344 mg g^{-1}. Obtained equilibrium data was finely fitted to the Langmuir adsorption isotherm model indicating monolayer adsorption on uniform adsorbent surface. Adsorption kinetics followed was pseudo-second-order model and the adsorption mechanism involved in the insertion of Cu(II) ion into the ZIF-67@Fe_3O_4@ESM composite. Spent adsorbent was regenerated by using 5 mM HCl acid solution as eluent and ultrasonic aid. Adsorption efficiency of ZIF-67@Fe_3O_4@ESM slightly decreased after fifth cycles (93%) however showed excellent stability. Significant reduction of adsorption efficiency (%) in the sixth regeneration process was attributed to imperfect desorption of Cu(II) ion from the adsorbent and their occupation in the active sites (Mahmoodi et al. 2019a, b).

Recently, a microwave-assisted green chemical strategy was employed by Mahmoud and his group to anchor –NH_2 functional 3-aminopropyltrimethoxysilane onto the mesopores of nFe_3O_4@MIL-88A(Fe) frameworks resulting in an amino-functionalized MMOF composite, Fe_3O_4@MIL-88A(Fe)/APTMS. The amino-functionalized MMOF composite was found to have potential application as a recyclable adsorbent for rapid removal of Pb(II), Cd(II), and Cr(VI) with maximum removal capacities of 532.66, 693.0, and 1092.22 mg g^{-1}, respectively. The amino groups on Fe_3O_4@MIL-88A(Fe)/APTMS improved its adsorption capacity by enhancing the binding properties with the targeted metal ions. Kinetics study satisfied pseudo-second-order model indicating a chemisorption process. Surface of Fe_3O_4@MIL-88A(Fe)/APTMS exhibited negative and positive charges at $pH > 4$ and $pH < 4$, respectively. The adsorption mechanisms of nFe3O4@MIL-88A(Fe)/APTMS with the cationic species (lead and cadmium ions) were attributed to the formation of coordinate bond at $pH > 4$ or ion-pair attraction forces in case of anionic species (chromium (VI)) adsorption at $pH < 4$. Regeneration of the spent adsorbent was performed using 0.M HCl solution. The magnetic composite was demonstrated as a highly efficient and regenerable adsorbent which was found to exhibit almost all the initial characteristics even after 5 cycles (Mahmoud et al. 2020).

Goyal et al. reported a novel hydrothermal process for the synthesis of polyacrylic acid capped Fe_3O_4 nanoparticles-Cu-MOF hybrid (i-MOF) possessing an ideal surface area for an absorbent material. i-MOF was developed for rapid and selective removal of lead ions Pb(II) via an ion exchange process even when exposed simultaneously with naturally abundant co-existing cations (Na(I), Ca(II), and Mg(II)), with high removal efficiency (93%) and very high adsorption capacity of 610 mg g^{-1}. Adsorption kinetics and isotherm were well fitted pseudo-second-order kinetics process and Langmuir model, respectively, demonstrating chemisorption of Pb(II) ions by i-MOF. SEM–EDX elemental mapping, XRD pattern, XPS spectra, and ICP-OES data suggested the leaching of Cu(II) from the MOF, indicating the formation of coordination bond between Pb(II) and the residual oxygen of i-MOF during the removal process. Adsorption process was ascribed by an ion exchange mechanism in which extraction of Pb(II) and release of Cu(II) from the i-MOF were concomitant. Coordination of Pb(II) to the carboxylates group of organic linkers on i-MOF was further confirmed by XRD pattern in which peaks for $Pb(CO_3)$, $Pb_3(CO_3)O_2$, and $Pb_5O(OH)2(CO3)_3$ were observed (Goyal et al. 2020).

Keykhaee et al. reported a novel semispherical bio-magnetic MOF composite (Fe_3O_4-Car-MOF) by constructing

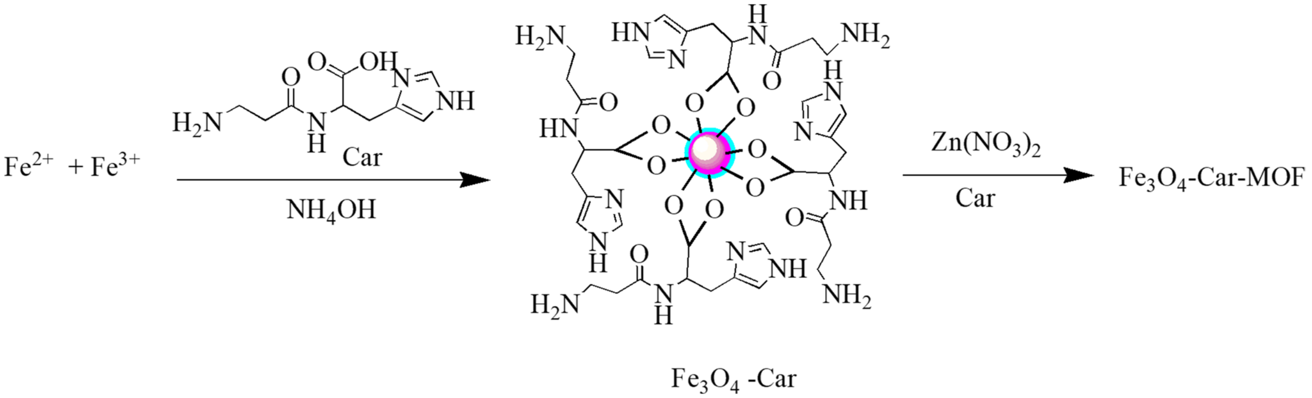


Fig. 23 Synthesis of Fe_3O_4-Car-MOF composite for removal of arsenic

carnosine MOF on carnosine-coated Fe_3O_4 MNPs (Fig. 23). The carnosine-based MMOF composite was demonstrated as an adsorbent for effective removal of As from contaminated aqueous solution with a maximum monolayer adsorption capacity 94.33 mg g^{-1} at an optimum pH 8.5 at room temperature. The adsorption isotherm and kinetic study data were best fitted to the Freundlich isotherm model. The saturation magnetization values (33 emu/g for Fe_3O_4-Car and 28 for emu/g Fe_3O_4-Car-MOF) were determined by VSM study, and a significant drop in magnetization value of Fe_3O_4-Car-MOF was attributed to the non-magnetic behavior of zinc and carnosine. To investigate reusability, the adsorbent was magnetically separated from the solution and FTIR analysis was carried out for fresh Fe_3O_4-Car-MOF and spent adsorbent. After four cycles, no significant changes in the essential functional groups on the composite were observed suggesting the stability and reusability of the adsorbent (Keykhaee et al. 2020).

Recently, Zhou and his coworkers prepared a newly designed magnetic core-double shell composite with Fe_3O_4 MNPs as the magnetic core, a Zr-based MOF (UiO-66) as the inner shell, and polypyrrole (Ppy) as the outer shell to obtain magnetic UiO-66@Ppy composite for enhanced elimination of highly toxic Cr(VI) from aqueous solution. A maximum adsorption capacity of 259.1 mg g^{-1} for the removal of Cr(VI) was obtained at pH value 2. Co-existing cations including Cu(II), Zn(II), and Cd(II) and anions including Cl^-, SO_4^{2-}, and NO_3^- were found to have no significant adverse effect on the adsorption process. Under acidic conditions, N atoms in Ppy chains on the magnetic UiO-66@Ppy get protonated generating positive charge on the adsorbent. Meanwhile, Cr(VI) existing in anionic form as $HCrO_4^-$ get immobilized on the cationic surface of the adsorbent. Diffusion of anion and the efficiency of anion exchange was facilitated by large surface area of the sorbent, UiO66@Ppy. Moreover, the electron for the reduction of Cr(VI) to Cr(III) was provided by electron-rich amino groups on polypyrrole. Besides, immobilization of generated hard acid Cr(III) on the surface of UiO-66@Ppy was attributed to the chelation of Cr(III) with oxygen-containing or nitrogen-containing groups which was supported by hard-soft acid–base theory. Desorption and regeneration were done by using 0.1 M NaOH as an eluent. After regeneration, adsorption capacity of magnetic UiO66@Ppy was found to be 85.7 mg/g even after four adsorption–desorption cycles, which was better as compared to most traditional adsorbents. Excellent stability of the adsorbent was established by XRD and FT-IR analysis, which showed no significant changes in functional groups of magnetic UiO-66@Ppy and crystal structures before and after adsorption process. Moreover, leakage of Fe ions and Zr ions was not observed in the pH range 4.0–8.0, suggesting the chemical stability of magnetic UiO-66@Ppy. However, at pH 2, 0.0209 mg/L Zr ions and 0.2409 mg/L Fe were detected in the solution but it did not give rise to any secondary pollution (Zhou et al. 2021).

Wang and his group modified UiO-66-NH_2 with $Ni_{0.6}Fe_{2.4}O_4$ MNPs and polyethyleneimine (PEI) to obtain a green and environment friendly magnetic Zr-based MOF composite, $Ni_{0.6}Fe_{2.4}O_4$-UiO-66-NH_2-PEI. The PEI-impregnated MMOF composite exhibited high thermal stability along with sufficient magnetic properties that allowed efficient solid–liquid separation. $Ni_{0.6}Fe_{2.4}O_4$-UiO-66-NH_2-PEI composite had maximum adsorption capacities of 428.6 mg g^{-1} for Cr(VI) at pH 3 and 273.2 mg g^{-1} for Pb(II) at pH 4 in acidic aqueous solution. Adsorption mechanism of Pb(II) was attributed to the chelation of metal ion with amine/imine functional groups, whereas adsorption of Cr(VI) was originated from electrostatic interaction, chelation, and redox reaction. Experimental (XPS, FTIR) and theoretical (DFT) studies suggested the adsorption of lead via chelation between Pb(II) and the imine/amine functional groups of $Ni_{0.6}Fe_{2.4}O_4$-UiO-66-NH_2-PEI. Cr(VI) adsorption was attributed to electrostatic interactions, reduction, and chelation between chromium and $Ni_{0.6}Fe_{2.4}O_4$-UiO-66-NH_2-PEI.

Selective sorption for both Pb(II) and Cr(VI) was achieved with $Ni_{0.6}Fe_{2.4}O_4$-UiO-66-NH_2-PEI in the presence of other competing ions and also good binding capacities (92.3% for Pb(II) and 99.8% for Cr(VI)) were retained even after end 5th recycle. Stability of the sorbent was further supported by leaching experiment. For Pb adsorption test under pH 1.0, 0.8 mg/L iron and 0.9 mg/ L nickel were found to be leached out to the solution, while for Cr adsorption test, 0.39 iron and mg/L and 0.7 mg/L nickel were detected in the solution. Leaching of iron and nickel decreased with increasing solution pH, and at pH value 3.0, negligible leaching of both metals was observed, suggesting good chemical stability of $Ni_{0.6}Fe_{2.4}O_4$-UiO-66-NH_2-PEI in acid solutions (pH > 3.0) (Wang et al. 2021a).

In another approach, Nasiri and his coworkers demonstrated a MMOF composite containing NH_2-MIL53 (Al) framework structures and cysteine-functionalized Fe_3O_4 MNPs. The magnetic sorbent material had great potential for Pb(II) removal from wastewater with a maximum adsorption capacity of 361.53 mg g^{-1}. Ion exchange and complex formation mechanisms were ascribed to the adsorption lead on the sorbent. In acidic conditions, H^+ ions compete with Pb^{2+} ions thereby protonating the functional groups. Protonation of active sites reduced the adsorption capacity of the sorbent. With increase in pH value of the solution, the competition between Pb^{2+} and H^+ decreased resulting in more lead absorption on the surface of the composite. At higher pH, adsorption was found to be increased which was attributed to the deprotonation of functional groups that facilitated complex formation between the lead and functional groups. Desorption of adsorbed metal ions from the sorbent was performed with 5 mL 0.1 M acetic acid solution for 20 min of contact time. After three cycles, lead adsorption decreased from 83 to 51% and percentage of desorption was 71% which was attributed to the permanent trapping of some lead ions on the sorbent which is a challenge for the future researchers to modify the recovery process (Nasiri et al. 2021).

Zhu et al. reported a novel biochar-supported magnetic sorbent material (represented as BSMU) containing Fe_3O_4 MNPs and UIO-66-2COOH framework structures. BSMU was utilized for efficient removal of Sb(III) with maximum adsorption capacity of 56.49 mg g^{-1} under alkaline condition (pH value 9.1). Higher adsorption density was achieved with low dose of the adsorbent, experiencing no significant adverse effect of other co-existing ions including Cl^-, SO_4^{2-}, PO_4^{3-}, and NO_3^- during the removal process. Kinetic and adsorption isotherm study data suggested pseudo-second-order kinetics and Sb(III) was absorbed onto BSMU surface via chemical interaction. Adsorption mechanism was ascribed to the chemical interactions between Sb(III) and carboxyl, hydroxyl, and amine functional groups on BSMU surface. After reaching sorption equilibrium, no significant change in sorption capacity was observed indicating easy release of antimony to aqueous environment again (Zhu et al. 2021).

Chen et al. designed a novel thermally stable MMOF composite, finely tuned by plenteous amine groups (mag-MOF-NH_2), and demonstrated it as an excellently thermostable sorbent for the removal of U(VI) from polluted water with a maximum adsorption capacity of 80 mg g^{-1}. Adsorption mechanism was attributed to surface complexation and chemical interactions between the N-containing groups on the adsorbent and the targeted ion which was established by XPS data. Other competing ions including Ca(II) and Mg(II) were found to exhibit passive impact on the adsorption process. Decrease in U(VI) adsorption percentage from 90.37% at the first cycle to 88.57% at the fifth cycle demonstrated excellent regeneration of Mag-MOF-NH_2 composite with tremendous potential in the practical application. The average adsorption percentage was found to be 98.43%, indicating enormous potential of Mag-MOF-NH_2 in the practical application for remediation of U(VI)-contaminated wastewater (Chen et al. 2021).

Omer and his group reported a core-dual shell MMOF composite bead (Fe_3O_4/ZIF-67@AmCs) by decorating ZIF-67 frameworks with Fe_3O_4 MNPs and finally embedding it into aminated chitosan matrix (AmCs). Fe_3O_4/ZIF-67@AmCs composite beads were demonstrated as an outstanding adsorbent for the removal of Cr(VI) with a maximum removal capacity 119.05 mg g^{-1} at temperature 25 °C. High adsorption capacity was attributed to the synergetic effect between Fe_3O_4, AmCs, and ZIF-67. Hypothetical adsorption mechanism involving three steps was provided for the adsorption of Cr(VI) onto Fe_3O_4/ZIF-67@AmCs composite beads. At first, protonation of amino groups on the surface of Fe3O4/ZIF-67@AmCs3 composite beads occurred under acidic condition. Subsequently, positive charge was generated on the surface of the adsorbent facilitating a strong electrostatic interaction between anionic Cr(VI) and positively charged beads. Secondly, reduction of adsorbed Cr(VI) to Cr(III) is by electron-donner groups such as NH_2 and OH on the surface of the beads. The third step was involved in the formation of coordinate–covalent bond between Cr(III) and Fe_3O_4/ZIF-67@AmCs composite beads. Coexisting cations (Na^+, K^+, and Ca^{2+}) and anions (Cl^-, NO_3^-, and SO_4^{2-}) were found to compete with Cr(VI) anions for the active sites thereby significantly decreasing adsorption capacity. Furthermore, after each adsorption, the spent magnetic Fe_3O_4/ZIF-67@AmCs composite beads were magnetically separated from the solution and soaked into 50 mL mixture of methanol/NaCl solution followed by stirred for 2 h to achieve complete leaching of Cr(VI) ions from the adsorbent. Removal efficiency of the adsorbent exceeded 60% even after the seventh cycle with a maximum adsorption capacity 73.05 mg/g demonstrating excellent recycling property of the synthesized magnetic Fe_3O_4/ZIF-67@AmCs beads (Omer et al. 2021).

A core–shell MMOF composite, Fe_3O_4@ZIF-8, with high stability and high specific surface area (724.7 $m^2\ g^{-1}$) was designed by Jiang et al. for effective removal of Cu(II) and Pb(II) from contaminated water with maximum adsorption capacities 301.33 mg g^{-1} and 719.42 mg g^{-1}, respectively. Fe_3O_4@ZIF-8 composite showed fast adsorption kinetics and adsorption process was well described by the Langmuir adsorption isotherm model. In acidic aqueous solution, Fe_3O_4@ZIF-8 is stable similar to the pristine ZIF-8. Uptake capacity of Fe_3O_4@ZIF-8 did not change over pH range 3.0–6.0 suggesting the adsorption driven by coordination reaction or other adsorption rather than electrostatic interactions. Further, FTIR, XPS, and ICP-OES analysis confirmed that the adsorption occurred via coordination of Cu^{2+} and Pb^{2+} ions with the imino groups of 2-methylimidazole on ZIF-8 shell of Fe_3O_4@ZIF-8 as well as ion exchange between Zn^{2+} of the sorbent and analyte ions. 30 mL 0.025 M solution of EDTA-2Na was used as eluent at 250 rpm for 10 h at 50 °C for desorption of the adsorbed metal ions from a solution of 100 mg L^{-1} on 10 mg of adsorbent. Regenerated adsorbent was reused up to four adsorption–desorption cycles, and it displayed a high removal efficiency for both Pb^{2+} and Cu^{2+} ions suggesting good reusability of the sorbent (Jiang et al. 2021).

Desorption and pre-concentration of metal ions

Desorption of the adsorbed metal ions into a new solution and pre-concentration of that are major concerns in industrial perspectives. Moreover, regeneration of the spent adsorbent for long-time application is important from "green chemistry" as well as industrial point of view. For pre-concentration of the metal ions in a new solution and regeneration of the spent sorbent again for their application, proper selection of eluting solution is very important for the desorption process. Regarding the desorption of metal ions from the MMOF adsorbents, the type, volume, and concentration of the desorbing solvent (eluent) are the major parameters that should be thoroughly examined and optimized as their wrong choice may collapse the framework structure by leaching either the central metal ion of the framework or the magnetic part. Usually effective elution of metal ions can be achieved with acidic solutions of sulfuric, nitric, or hydrochloric acid as eluent. As H^+ ions compete for the active binding sites of the adsorbent, desorption can be attributed to the presence of H^+ ions that weakens the interaction between the MMOF adsorbents and metal ion (adsorbates) analytes (Sohrabi et al. 2013). However, decomposition of most MMOF adsorbents may take place in acidic conditions. Other reagents that can be employed as eluent for the elution of metal ions without decomposing MMOF material are NaCl, NaOH in thiourea, EDTA, NaOH in EDTA, etc. Other parameters that have significant impact on pre-concentration are pH of sample, dosage of adsorbent, stirring speed, and time. For quantitative desorption of the adsorbed analytes, enough elution time should be provided (Manousi et al. 2019).

It is worth to mention here that Mousavi and his group recently reported a novel MMOF composite, MIL-101(Cr)/Fe_3O_4@SiO_2@2-ATP, by fabricating MIL-101(Cr) with SiO_2-coated and 2-aminothiophenol (2-ATP)-functionalized Fe_3O_4 MNPs. The MIL-101(Cr)/Fe_3O_4@SiO_2@2-ATP composite was successfully utilized for pre-concentration/separation of trace Ag(I) ion from aqueous solution with a maximum adsorption capacity 103 mg $g^{-1}$and very low limit of detection 0.05 ng mL^{-1} (Fig. 24). For Ag(I) uptake, 21 mg of the adsorbent, MIL-101(Cr)/Fe_3O_4@SiO_2@2-ATP, was added to the analyte sample keeping pH of sample fixed at 6.2 and the suspension was stirred for 13 min for successful adsorption. Then, the solution was magnetically isolated from the adsorbent and the Ag(I) uptake percentage was determined by FAAS quantification (Mousavi et al. 2021).

Among different acidic solutions (1 mol L^{-1} sulfuric acid, nitric acid, and hydrochloric acid), nitric acid was found to be the best desorbing solution with which the highest recovery of silver ions from MIL-101(Cr)/Fe_3O_4@SiO_2@2-ATP composite was observed. pH of sample, volume and concentration of eluent, uptake time, and dosage of MIL-101(Cr)/Fe_3O_4@SiO_2@2-ATP were found to have significant impact on the pre-concentration of Ag(I) ions and were optimized. For the desorption and pre-concentration of Ag(I) ions, the adsorbent was suspended in 0.56 M, 1.7 mL solution of nitric acid and the suspension was stirred for 16 min. The supernatant was introduced into FAAS to determine its silver content after the separation of the adsorbent from the extraction medium. To check the durability of MIL-101(Cr)/Fe_3O_4@SiO_2@2-ATP sorbent, decrease in the recovery of Ag(I) ions in several consecutive uptake–elution cycles under the optimum condition was studied. Effective uptake and elution of Ag(I) ions by MIL-101(Cr)/Fe_3O_4@SiO_2@2-ATP sorbent up to 6 uptake-elution cycles suggested the sufficient stability of the sorbent.

Tadjarodi et al. reported a solvothermal strategy to synthesize MMOF nanocomposite from HKUST-1 (MOF-199) and chelator-modified 4-(5)-imidazoledithiocarboxylic acid-functionalized magnetite (Fe3O4@DTIM) with excellent surface area of 654 $m^2\ g^{-1}$ for separation and pre-concentration of Hg(II). The MMOF sorbent was characterized by SEM, XRD, IR spectroscopy, elemental analysis, and BET analysis. The sorption capacity was found to be 254 mg g^{-1} with low limit of detection (LOD) 10 ng L^{-1}.

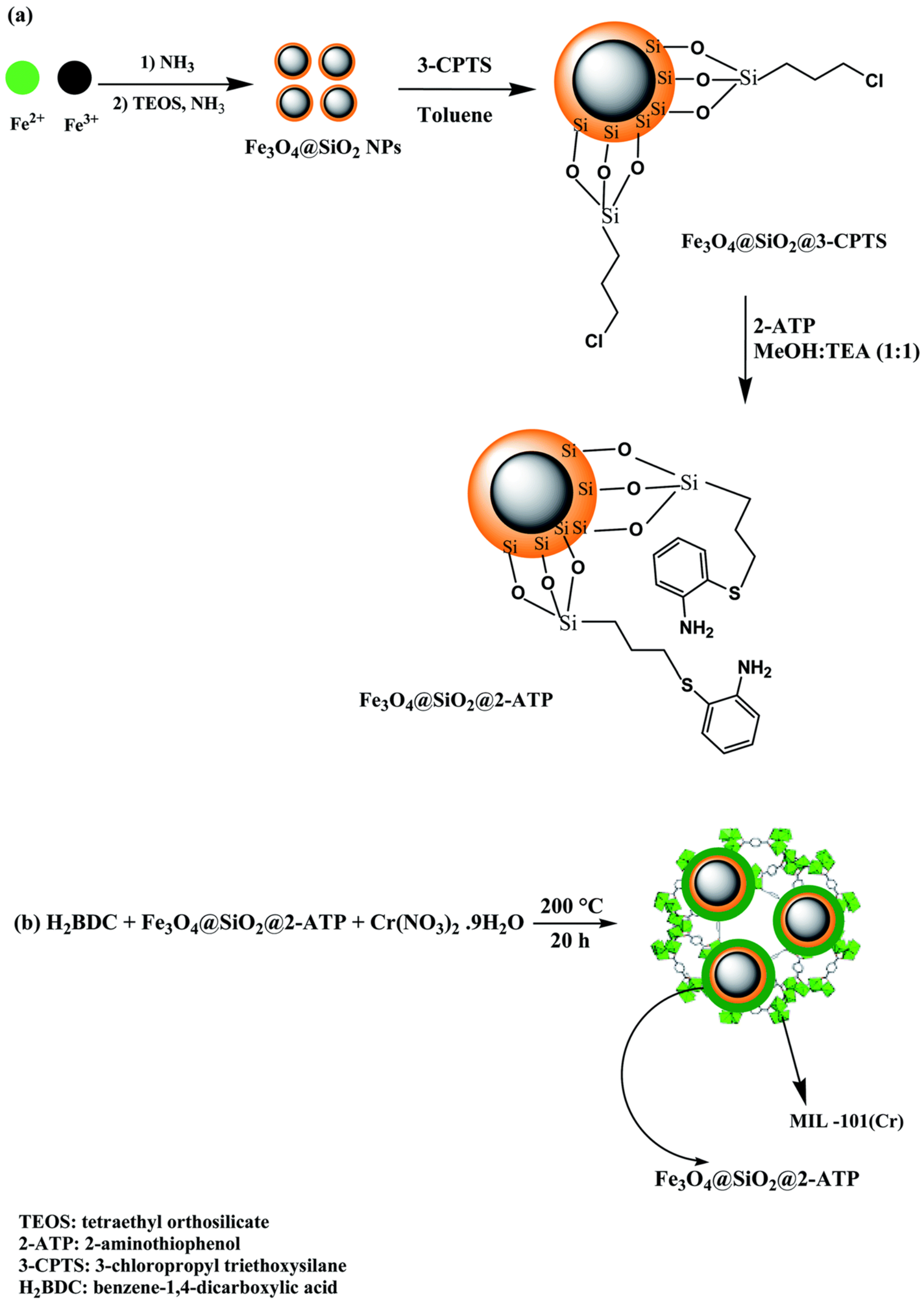


Fig. 24 A scheme for the synthesis of **a** $Fe_3O_4@SiO_2@2$-ATP nanoparticles and **b** MIL-101(Cr)/$Fe_3O_4@SiO_2@2$-ATP nanocomposite. Reproduced from Reference Mousavi et al. 2021 with permission from The Royal Society of Chemistry

For elution of adsorbed Hg(II) ions, 3.5 mL solution (1.1 M) of thiourea as an eluent was added to the MMOF sorbent and the solution was shaken. This magnetic sorbent was recovered by using a strong magnet, and the amount of eluted Hg(II) ions present in the clear solution was determined by Cold Vapor Atomic Adsorption Spectroscopy (CVAAS). The stability and reusability of MIL-101(Cr)/$Fe_3O_4@SiO_2@2$-ATP sorbent were investigated by studying the changes that occurred in the recovery of Hg(II) ions through several sorption-elution steps under optimum condition, and the recovered MMOF composite showed no significant changes after 12 adsorption–desorption cycles showing excellent stability (Tadjarodi and Abbaszadeh 2016).

Future perspective and conclusion

In summary, the combination of magnetic nanoparticles and metal–organic frameworks results in the MMOF composites, a promising material that has been effectively used in pollutant remediation by magnetic solid phase extraction. The magnetic recyclability after its use is one of the major advantages of MMOF composites in environmental remediation processes. Compared to other conventional sorbent materials, MMOFs have both the advantages of porous materials (i.e., strong adsorption, large specific surface areas, high stabilities, and designable structures) and those of MNPs (i.e., easy to use, environmental friendliness, and easy and fast recycling).

Careful assessment of organic linkers, metal precursors, and magnetic component makes it possible to tailor the structure, morphology, porosity, and functionality of MMOF composites to meet their essential applications. Pore size of MMOF composites can be controlled by varying the size/chain length of organic linkers. Adsorption of heavy metal ions can be enhanced by converting the bulk MMOF composites into variable morphologies. Moreover, performance of MMOF composites can be improved by hybridizing them with additives or other material such as graphene oxides (GO), membranes, aerogels/hydrogels, microbeads, and nanofiber/textiles (Lin et al. 2020; Zhang et al. 2018; Wang et al. 2021b; Sun et al. 2021; Lin et al. 2020; Abdelhamid 2022).

The theoretical basis for the use of MMOF composites is lacking, and there are still many problems that are needed to be resolved. Although the composites have auspicious properties for various environmental applications, the commercialization remains a challenge due to the lack of water stability and the lack of robustness to the harsh conditions (Dhaka et al. 2019). MMOF composites are convincible to moisture due to weak coordination between the organic linker and metal center. As a consequence, structural collapse, decrease in mechanical strength, and substantial decrease in adsorption capacity of some MMOFs take place due to adsorption of significant amount of water upon exposure to moisture (Tan et al. 2015). Therefore, fabrication of a water-stable MMOF adsorbent is required. For specific targets, the structural design and functionalization of MMOFs need further exploration, especially for analysis of changes induced in crystal structures, functional groups, and adsorption performance. For their practical application as adsorbents, there is insufficient data on MMOF conditions, such as the temperature, pH, selection of MOFs, risk factor types, quantities, and stirring speed. To date, most MMOFs are employed for rapid pretreatment of environmental samples containing risk factors and are limited to the laboratory rather than commercial or industrial use. Therefore, basic theoretical research and development is still needed for extraction of risk factors from authentic samples.

It is worthwhile to mention that effective implementation of MMOF composites in water remediation technologies can be done by fixing the challenges associated with the industrial scale manufacturing of MMOF composites which is prohibiting the composites from practical applications. Researchers should focus on some challenges and opportunities associated with MMOF composites to meet the practical application. Some of them are listed and summarized as follows.

Industrial-scale production

To meet the practical application of MMOF composites in wastewater remediation technologies, cost estimate for industrial-scale production should be well considered (Kim et al. 2016). Several synthetic processes reported by the researchers need complex synthetic conditions such as high temperature and pressure, expensive and toxic precursors, and sophisticated equipment. Another critical cost-driving parameter associated with large-scale production of MMOF composites is the utilization of expensive as well as toxic organic solvents. To overcome this challenge associated with industrial-scale manufacturing of the material, two new approaches can be adapted which are involved in the reduced usage of organic solvents.

Solvent-free synthesis

Avoiding any kind of solvent in synthetic steps is "one step towards cost-effective production." MMOF composites can be effectively synthesized in solvent-free conditions with an excellent yield (Afshariazar and Morsali 2022). Recently, Li et al. have demonstrated the synthesis of magnetic metal-organic framework composites (MFCs) under solvent-free condition, driven by magnetic induction heat which was effectively utilized for CO_2 capture (Li et al. 2019).

Aqueous synthesis

Distilled water can be used instead of toxic and expensive organic solvents in which both the metal salts and organic linkers can be dissolved. One-pot synthesis in a precipitation reactor can be carried out under reflux to get considerable yields. Aqueous synthesis of Mg_2(dobdc) and Ni_2(dobdc) has been reported with considerable yields (more than 90%) (Garzon-Tovar et al. 2015; Cadot et al. 2014).

Liquid-assisted grinding (LAG)

It is a large-scale synthetic process for the preparation of co-precipitates in the presence of a minimum amount of solvent. The activation energy required for the reaction is surpassed by the sufficient mechanical energy delivered by the LAG mill.

Synthesis of MOFs, e.g., HKUST-1, has been successfully demonstrated by employing this technique (Friscic et al. 2010).

Furthermore, expensive equipment can be avoided in the synthetic steps (Dhankhar and Nagaraja 2016). Recently, a cost-effective ultrasound-assisted technique for the synthesis of Cu-I MOF composite was reported by Merlin and his group which was demonstrated as an electrode material for super capacitor application (Merlin et al. 2018).

Designing greener processes

Environmental impact and safety is a major concern for the researchers while considering industrial-scale manufacturing. Greener synthetic approaches are indeed related to the cost of bulk production. Green approaches for the synthesis of magnetic MOF adsorbents can be aided by the following.

Choosing safer linkers

Traditionally used linkers for the synthesis of MOFs such as imidazoles and carboxylic acids in their protonated forms are associated with the formation of toxic byproducts (HNO_3, H_2SO_4, etc.) upon solvothermal synthesis. Evaluating the byproducts formed during the synthetic process is necessary in terms of sustainability of MMOF composites. To avoid the formation of hazardous mineral acids, sodium salts of linkers can be used (Sanchez-Sanchez et al. 2015). Constructing MMOF composites by utilizing some natural and greener substrates can drastically reduce the environmental hazards as well as cost estimates (Jalali et al. 2022). Toxicological impacts can further be reduced by the application of some non-toxic biocompatible (i.e., biomass derived or biomolecules) linkers such as amino acids (Sahiner et al. 2020), polysaccharides (Musarurwa and Tavengwa 2022; Rathod et al. 2019), β/γ-cyclodextrin (Yang et al. 2020a, b, c; Kim et al. 2019), fumaric acid, and muconic acid (Butova et al. 2022; Alam et al. 2022; Liu et al. 2022c). By combining this new class of MOFs (Bio-MOFs) with magnetic components, a new class of MMOF composites can be designed and utilized for wastewater remediation technology which is remaining unexplored till now (Liu et al. 2022a, b, c).

Choosing safer metal salts

For large-scale synthetic processes, choice of metal salts should be well considered as they have significant impact on cost estimate and environment. Several reported synthetic routes exhibit the application of metal chlorides and metal nitrates which are related to corrosion and toxicity, respectively. Metal salts of acetates and sulfates are good alternatives of them yet challenges related to hydrolysis (in case of acetate) and poor solubility (in case of sulfates). Readily available and non-toxic oxides and hydroxides of metal can be a better green alternative. However, alternative synthetic approaches are mandated due to the challenges related to their poor solubility. The toxicity of central metal of MMOF composite should be assessed concerning its disposal. Risks related to the disposal can be reduced and mitigated by the use of alkaline earth metals such as calcium and magnesium over transition metals. However, toxicity data have suggested the use of Ca, Mg, Ti, Mn, Fe, and Zr (Leyva et al. 2022; Thangadurai et al. 2022) metal precursors for safer and greener synthesis. More toxicological testing needs to be considered for better understanding of ecological toxicity, biological fate, and lifecycle of MMOF composites.

Choosing safer magnetic components

Introduction of MNPs into MOFs itself is a green strategy as it offers easy separation and great recyclability which is a major concern of "green chemistry." Biogenic routes should be developed for the synthesis of MNPs (Rui et al. 2021). Several greener biogenic methods have been reported for the eco-friendly synthesis of the MNPs which eliminates the use of toxic substances to restore the environmental sustainability. Inactivated plant tissues, leaf extracts, and other parts of living plants contain various kinds of reducing agents including reductases, hydrogenases, citric acid, ascorbic acids, and flavonoids that provide an environment-friendly route for the synthesis of MNPs (Khalilzadeh et al. 2020). Hence, it is worthwhile to investigate more biological approaches for the synthesis of MNPs to achieve maximum advantages of the component.

Choosing safer solvents

Selection of solvent for synthetic protocols has a large impact on industrial scale-production. Solvothermal synthesis involved in the use of organic solvents, e.g., DMF and DMSO, in large quantities is unattractive owing to their expense and environmental toxicity. Greener alternatives such as solvent-free synthetic route and water-based hydrothermal route can be adapted over solvothermal route (Li et al. 2019; Morsali and Afshariazar 2022). These alternatives are however related to some drawbacks such as low yield due to the insolubility of the precursors. Therefore, more rigorous improvements are required in hydrothermal processes for green and scalable production to alleviate the cost and environmental impact of MMOF synthesis (Howarth et al. 2021). Use of "near-critical high-temperature water" which acts as a non-polar solvent at critical point (374°C, 220 bar) can extend the scope of hydrothermal route as well as enhance the thermal and chemical stability of MMOFs at elevated synthetic condition. Thermochemical and mechanochemical processes should be focused to improve solvent-free synthesis of MMOF composites (Singh et al. 2017). The use of ionic liquid can be a good alternative solvent as they fix the challenges related to poor solubility of the precursors and can be recycled readily. Recently, a bioderived solvent synthesized via olefin metathesis using renewable feedstocks, e.g., plant oils, was explored as a green solvent by Howarth and his group for the synthesis of a family of structurally diverse MOFs (Howarth et al. 2021).

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Data availability All data collected and reviewed are included in this article and properly referenced.

Declarations

Ethics approval We certify that the manuscript titled "Overview on Recent Advances of Magnetic Metal–Organic Framework (MMOF) Composites in Removal of Heavy Metals from Aqueous System" (hereinafter referred to as "the Paper") is entirely our original work, and it does not infringe the copyright of any third party. The submission of the Paper to Environmental Science and Pollution Research implies that the paper has not been published previously. This work is not under consideration for publication elsewhere. Its publication is approved by all authors and, if accepted, it will not be published elsewhere in the same form, either in English or in any other language, without the written consent of the Publisher. Copyrights for articles published in Environmental Science and Pollution Research are retained by the authors, with first publication rights granted to Environmental Science and Pollution Research.

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