



Metal-organic frameworks on 3D interconnected macroporous sponge foams for large-scale water decontamination: A mini review

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ABSTRACT

Water pollution caused by global population growth, urban expansion and industrialization development is one of the urgent issues that need to be addressed in the 21st century. Up to now, it was challenging for metal-organic frameworks (MOFs) to be used in the actual water treatment due to that the powder MOFs suffered from difficult reuse, poor water stability and easy corrosion. It is an effective strategy to immobilize MOFs powder onto porous sponge foam carriers for accomplishing large flux, facile recycling, easy processing water treatment setups. In this review article, the fabrication approaches and applications of different MOFs/sponge composites were highlighted, in which the fluorescence detection of pollutants, adsorption and separation of pollutants, catalytic reduction and oxidation of pollutants were included. Finally, the future challenges and opportunities of MOF/sponge for water treatment are proposed, aiming to provide in-depth guidance for the future design and manufacture of the immobilized MOFs onto sponge foams.

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1. Introduction

Up to now, metal-organic frameworks (MOFs) were widely adopted to detect and remove different pollutants including heavy metals [1–4], radioactive substances [5], emerging pollutants [6–11], oil [12,13], nutrient substances [14,15], bacteria [16,17], alga [18] or volatile organic compounds (VOCs) [19] from the polluted water or air via adsorption and advanced oxidation/reduction processes due to their advantages of exceptionally large specific surface area, structural flexibility and high affinity for pollutant [20]. In the practical applications, MOFs in the form of powder suffered from being shattered into fine ones resulting from hydraulic shear force and water corrosions, leading to separation and recovery difficulties and secondary pollution of the water environment [21]. However, it was difficult to process the pure MOFs into stand-alone monoliths due to their insolubility and non-plasticity [22]. It was essential to immobilize MOFs onto some substrates like cotton fibers [23,24], metal foams [21], Al₂O₃ sheet [25–27], sponge foams [28,29] and others [30,31].

Our group once immobilized MIL-88A(Fe) onto cotton fibers to accomplish effective adsorption toward As(III), As(V), arsenic acid and roxarsone in batch and continuous experiments [24]. After-

ward, we adopted the as-prepared MIL-88A(Fe)/cotton fibers (MC) to achieve long-term operation for the decomposition of oxytetracycline, tetracycline, and chlortetracycline via the photoactivated sulfate radical-advanced oxidation process (SR-AOP) [23]. Zhu *et al.* constructed prGO@cHKUST-1 composite membrane with the modification of dopamine and orientated growth of cubic HKUST-1 (cHKUST-1) to reject organic dye and purify oil/water emulsion [32]. Zhang *et al.* fabricated the sandwich-like CdTe QDs/ZIF-8 fluorescent composite films through facile layer-by-layer strategy to realize selective luminescence response toward hydrogen peroxide and folic acid [33].

From this point, it was feasible to immobilize MOFs onto available substrates for both facile recycling and the boosted performance. Some cheap foams like melamine foam and polyurethane foam were preferred as ideal substrates, due to their interconnected macroporous framework, outstanding mechanical and elastic characteristics [28,34,35]. To immobilize MOFs onto sponge foam with or without the assistance of adhesives can accomplish the following three purposes: (1) forming macro-porosity for the rapid passage of large-scale influent wastewater, (2) easy recycling and high stability for long-term duration under harsh conditions, and (3) facile processing different devices for real water treatment. As well, to immobilize microporous MOFs onto macroporous sponge foams can construct hierarchical macro-meso-microporous composites [36], in which the mesopores and/or micropores in the

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Table 1
Some selected works concerning the MOFs/sponge foams for water purification.

Sponge foams	MOFs	Preparation method	Applications	Ref.
Melamine sponge	Zr-MSA	Dipping-drying method	The Zr-MSA/melamine sponge TLMSM presented high adsorption capacity (~954.7 mg/g) and high selectivity ($K_d > 5.0 \times 10^7$ mL/g) toward Hg(II).	[39]
Melamine sponge	ZIF-L	Dip-coating method	The optimized MS-ZIF ₁₀ /melamine sponge displayed high adsorption capacity toward Pb(II) (624.8 mg/g) and Cu(II) (588.6 mg/g) from water.	[4]
Melamine sponge	NH ₂ -MIL-101(Fe/Ce)	Dipping-drying method	The NH ₂ -MIL-101(Fe/Ce)/melamine sponge exhibited high adsorption capacity (253.66 mg/g) toward phosphate from water.	[15]
Melamine foam	Cd-MOF	<i>In situ</i> one-pot solvothermal approach	The as-obtained Cd-MOF/melamine foam demonstrated outstanding adsorption performance toward nitrofurazone (NFZ, 47.75 mg/g), nitrofurantoin (NFT, 59.97 mg/g), 2,4,6-trinitrophenol (TNP, 456.16 mg/g) and Cr ₂ O ₇ ²⁻ (255.37 mg/g).	[45]
Melamine foam	UiO-66-X (X = NH ₂ , OH, Br and NO ₂)	<i>In situ</i> one-pot solvothermal approach	The as-prepared UiO-66-OH@MF-3 exhibited high adsorption efficiency (95.5% ± 1.2% with the initial concentration of 1.0 g/L) toward microplastics and could maintain long-term experiments.	[46]
Melamine sponge	MIL-101(Cr)	One-step infiltration method	The as-obtained MIL-101(Cr)/chitosan-modified sponge could remove six trace triazine herbicides (Atraton, Desmetryn, Prometon, Ametryn, Prometryn and Dimethametryn) <i>via</i> strong adsorption interactions in a vortex-assisted solid-phase extraction.	[5]
Polyurethane sponge	Ce-MOF	One-step simple immerse method	The absorption capacity of Ce-MOF/polyurethane sponge for oils/solvents (engine oil, colza oil, castor oil, dichloromethane, acetone, <i>n</i> -hexane) was in the range of 15.0–44.9 g/g.	[50]
Polyurethane sponge	Dy-MOF	Impregnation method	The Dy-MOF/polyurethane sponge owned excellent oil absorption properties for oils/solvents (castor oil, colza oil, energy oil, dichloromethane, <i>n</i> -hexane, ethyl acetate, ethylene glycol, toluene, acetone, and isopropyl) in the range of 14–49 g/g.	[12]
Melamine sponge	Tetradecylphosphonic acid modified UiO-66 (P-UiO-66)	Dipping-drying method	The absorption capacity of P-UiO-66/MS for oils/solvents (engine oil, colza oil, castor oil, dichloromethane, acetone, <i>n</i> -hexane) was in the range of 18–43 g/g.	[13]
Melamine sponge	MIL-101-Fe-NH ₂	<i>In situ</i> one-pot solvothermal approach	The MIL-101-Fe-NH ₂ /MS exhibited effective degradation for tetracycline hydrochloride with 77.24% in 30 min at subacidic environment.	[60]
Polyurethane sponge	MIL-88A(Fe)	Dipping-drying method	MIL-88A(Fe)@sponge (0.2 g/L) exhibited superior photocatalytic Cr(VI) reduction performance with 100% within 6.0 min and 3.0 min with the presence of tartaric acid (TA) under UV light and real solar light irradiation, respectively.	[28]
Melamine foam	Mercapto-functionalized Zr-MOF (Zr-MOF-SH)	<i>In situ</i> hydrothermal method	The Zr-MOF-SH/melamine foam displayed superior absorption capacity toward dichloromethane (113 g/g) and adsorption capacity of Hg ²⁺ (412.5 mg/g).	[37]
Melamine sponge	MIL-53(Fe)-MOFiths	Dip-coating method	MOFiths/melamine sponge displayed versatile and superior performances like H ₂ O ₂ activation for 100% MB degradation or catalytic ozonation for 100% <i>p</i> -nitrophenol (4-NP) destruction within 10 min, adsorptive elimination toward cationic heavy metals like Pb ²⁺ (422 mg/g), Cd ²⁺ (222 mg/g) and Cu ²⁺ (105 mg/g).	[29]
Melamine sponge	Octadecyl-phosphonic acid modified UiO-66 (OPA-UiO-66)	<i>In situ</i> one-pot solvothermal approach	Besides oil/water separation (120 g/g for chloroform absorption), the as-obtained OPA-UiO-66@melamine sponge (4 mg) could catalytically degrade 94.8% <i>p</i> -nitrophenyl hexanoate (<i>p</i> -NPH) with the initial concentration of 5 mmol/L <i>via</i> enzyme-like process within 120 min.	[9]
Melamine foam	luminescent Zr-MOF	<i>In situ</i> hydrothermal method	Zr-LMOF/melamine foam was used to sensing detect and adsorb different mycotoxins, and the overall removal efficiencies were more than 75%.	[74]

MOFs framework and the macropores of foams can offer adequate active sites and rapid mass transfer, respectively [34]. Up to now, some works concerning MOFs immobilized onto sponge foams for water purification were reported (Table 1), which indeed demonstrated the above-mentioned advantages [37–39]. In this mini review paper, the representative works were selected to highlight the advances in this field, providing insight and critical comments on the future developments for the combination of MOFs and sponge foams.

2. Application of MOFs/sponge composites for water decontamination

2.1. Adsorptive removal toward pollutants

Over the past decade, the adsorption technique has been regarded as an effective method for treating wastewater owing to the excellent properties of environment-friendly, easy operation and low cost [39–41]. It was well known that functional MOFs were optimal adsorbents for pollutants removal due to various types of interactions like electrostatic interactions, hydrophobic interactions, π - π interactions, hydrogen bonding and complexation can be formed between MOFs and pollutants [42–44]. The combina-

tion of foams with 3D structure and MOFs could be expected for boosting the adsorption performance [39].

As depicted in Fig. 1, the thiol-laced metal-organic framework (TLM) Zr-MSA was immobilized on the melamine sponge (MS) by the facile dipping-drying method to formed the MOF-based sponge monolith (TLMSM) [39]. Significantly, the TLMSM presented high adsorption capacity (~954.7 mg/g) and high selectivity ($K_d > 5.0 \times 10^7$ mL/g) toward Hg(II), which was 3–5 orders of magnitude higher than other “soft” metal cations (Figs. 1b and c). Significantly, a resembled fixed-bed reactor filled with the TLMSM was used to adsorb Hg(II) continuously, and it can effectively purify ~16.8 L wastewater with the Hg(II) concentration of ~500 μ g/L before the breakthrough point of 2 μ g/L (Figs. 1d and e). Moreover, EXAFS combined with DFT calculations revealed that the single-layer -S-Hg-Cl and double-layer -S-Hg-O-Hg-Cl and -S-Hg-O-Hg-OH formed in Hg(II) adsorption process (Fig. 1f). This work presents an applicable approach to construct a point-of-use (POU) device with MOF-based sponge monolith to treat the heavy metal wastewater.

A Cd-MOF [Cd(L)_{0.5}(bpe)_{0.5}(H₂O)]_x(solv) obtained from solvothermal reaction displayed sensitive and recyclable sensing detection toward antibiotics like nitrofurazone (NFZ) and nitrofurantoin (NFT), explosive like 2,4,6-trinitrophenol (TNP)

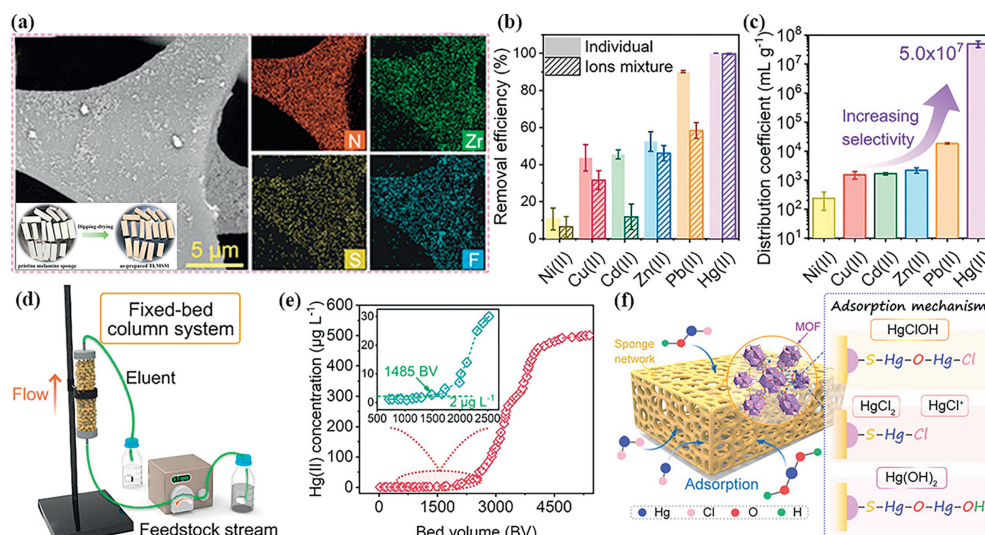


Fig. 1. (a) The SEM and EDS-mapping of TLMSM (Inset: Photographs of pristine MS, and the as-prepared TLMSM). (b) Removal efficiencies of various cations over TLMSM under different conditions. (c) Distribution coefficients of different cations. (d) Diagram of the fixed-bed column reactor. (e) Breakthrough curve of Hg(II) adsorption by the fixed-bed reactor filled with TLMSM. (f) The mechanism of Hg(II) selective adsorption by TLMSM. Reproduced with permission [39]. Copyright 2022, American Chemical Society.

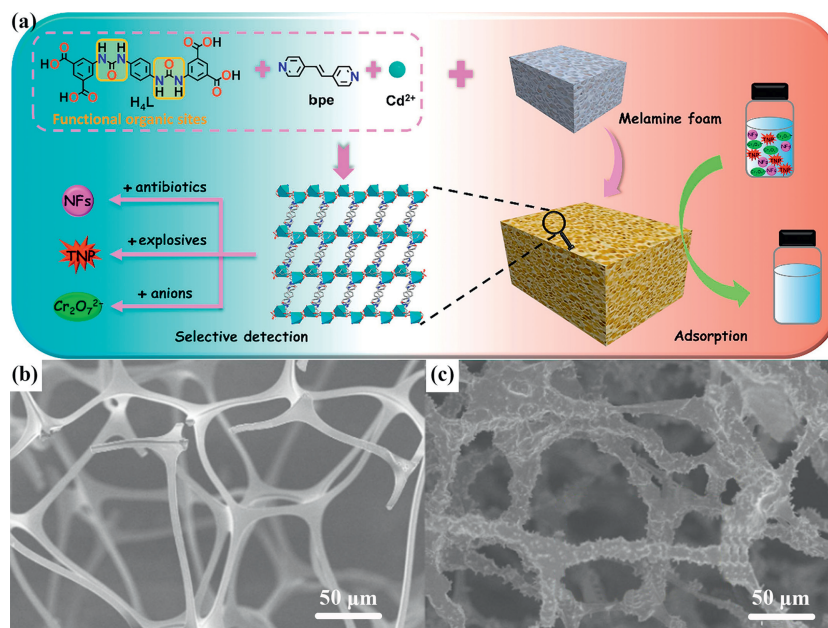


Fig. 2. (a) The scheme of the synthesis, sensing and adsorption performance of the Cd-MOF and Cd-MOF/MF. The SEM images of (b) pristine melamine foam and (c) Cd-MOF/melamine foam. Reproduced with permission [45]. Copyright 2022, Elsevier.

along with Cr₂O₇²⁻ anions following the mechanism of obvious luminescence quenching effect and red-shift of maximum emission [45] (Fig. 2). The as-prepared powder Cd-MOF exhibited poor adsorption activity toward NFZ (16.78 mg/g), NFT (16.36 mg/g), TNP (14.92 mg/g), and Cr₂O₇²⁻ (71.87 mg/g) within up to 7 d, suffering from its limited pore size (0.618 × 0.260 nm) and large sizes of NFZ (0.934 × 0.225 nm), NFT (0.891 × 0.352 nm), TNP (0.558 × 0.490 nm), and Cr₂O₇²⁻ (> 0.26 nm). The Cd-MOF was immobilized onto melamine foam (MF) to obtain Cd-MOF/MF via simple one-pot solvothermal approach. The as-obtained Cd-MOF/MF demonstrated outstanding adsorption performance toward NFZ (47.75 mg/g), NFT (59.97 mg/g), TNP (456.16 mg/g) and Cr₂O₇²⁻ (255.37 mg/g) benefiting from the urea functional groups as accessible active adsorption sites in Cd-MOF and the 3D interconnected macroporous structure of melamine foam. This work provided

a feasible method to design and synthesize new MOFs with multifunction.

For the purpose of microplastics removal, various UiO-66(Zr) derivatives like UiO-66, UiO-66-NH₂, UiO-66-OH, UiO-66-Br, and UiO-66-NO₂ were immobilized on melamine foam with different loading contents to fabricate UiO-66-x@MF-n via acetone-assisted method [46]. The positively charged UiO-66-x@MF-n displayed good affinity to different microplastics like poly(vinylidene fluoride) (PVDF, -18.9 ± 2.3 mV), polystyrene (PS, -7.5 ± 1.2 mV) and polymethylmethacrylate (PMMA, -10.5 ± 2.7 mV), in which the optimal UiO-66-OH@MF-3 (25.4 wt% MOF loading) can achieve best microplastics removal efficiencies (Fig. 3). In this work, it was deemed that the good affinity between the as-prepared UiO-66/MF and microplastics could be attributed to the following factors: (1) The 3D interconnected macroporous structure of melamine

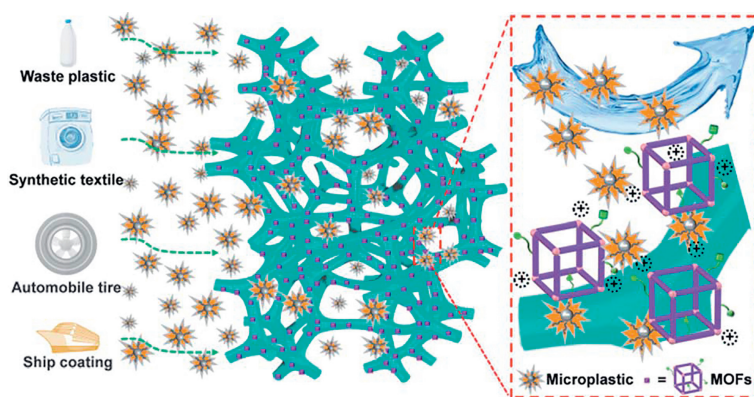


Fig. 3. The schematic illustration of MOF/melamine foam for different microplastics removal. Reproduced with permission [46]. Copyright 2020, Royal Society of Chemistry.

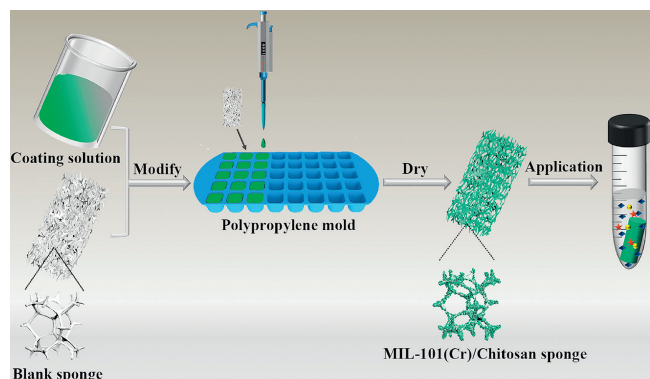


Fig. 4. The schematic illustration of MIL-101(Cr)/CS-sponge columns fabrication. Reproduced with permission [5]. Copyright 2021, Elsevier.

foam can guarantee the rapid passage of the treated influent and the adequate interaction with the microplastics. (2) The positively charged UiO-66 on the skeleton of melamine foam yielded strong electrostatic affinity with the negatively charged MPs. (3) The functional groups like $-NH_2$, $-OH$, $-Br$ and $-NO_2$ in the UiO-66-X could form hydrogen bonding and van der Waals interactions with the targeted microplastics. The findings in this work provided a new clue to remove the emerging microplastics from the water body with the versatile MOFs. Besides melamine sponge or foam, polyurethane foam (PUF) was also adopted as an available substrate to immobilize MOFs like UiO-66- $(COOH)_2$ for the purpose of removal toward different organic dyes like rhodamine B (RhB), methylene blue (MB), and congo red (CR) [47]. It was believed that the electrostatic interactions, hydrogen bonding interaction as well as Lewis acid-base interactions between the as-prepared UiO-66- $(COOH)_2$ /PUF membrane and targeted organic dyes.

Considering that chitosan (CS) displays good hydrophilicity and possesses large amount of active adsorption sites, it was adopted as adhesive to fabricate MIL-101(Cr) onto melamine column for the purpose of obtaining MIL-101(Cr)/CS-modified sponge column (Fig. 4) [5]. The as-obtained MIL-101(Cr)/CS-modified sponge column could achieve concentration of six trace triazine herbicides via strong adsorption interactions. This work was aimed to conduct solid-phase extraction (SPE) coupled with HPLC-MS/MS to detect triazine herbicides. However, it can induce us to immobilize MOFs onto foams with the aid of the adhesive materials like chitosan for the improved adsorption activity.

2.2. Separative removal toward pollutants

Recently, different hydrophobic functional materials were developed to solve the threat from the oil spills, in which func-

tional MOFs were preferred to be selected as alternative materials. To fully exploit of potentials of MOFs for separating oil from water, some attempts were put to fabricate typical MOFs like ZIF-8 [48], ZIF-67 [49] and UiO-66- NH_2 [38] onto different sponges. He and coworkers proposed that the UiO-66-NH-C18 with long alkyl chain was synthesized via the amidation reaction between $-NH_2$ groups in UiO-66- NH_2 and octadecanoyl chloride [38]. The as-obtained UiO-66-NH-C18 was fabricated onto the MS to produce superhydrophobic UiO-66-NH-C18@sponge by the facile dip coating method with the aid of polydimethylsiloxane (Fig. 5). The UiO-66-NH-C18@sponge displayed superior oil/water separation ability toward different oils and organic solvents like diesel oil (45 g/g), *n*-hexane (32.3 g/g), decane (ca. 45 g/g), toluene (45 g/g), dimethylformamide (ca. 47 g/g), acetone (45 g/g), ethyl acetate (45 g/g), and dichloromethane (66.1 g/g). Meng *et al.* found that superhydrophobic Ce-MOF/polyurethane sponge could purify the water-in-oil emulsions [50]. It was deemed that both the hydrophobic modification of MOFs and the subsequent MOFs coating on sponge foam are prospective approaches to construct superhydrophobic materials for oily wastewater treatment.

2.3. Catalytic oxidation and reduction for pollutants removal

Recently, MOFs were widely adopted as advanced oxidation processes (AOPs) or advanced reduction processes (ARPs) catalysts to degrade the emerging organic pollutants [51,52]. Among various MOFs, Fe-MOFs attracted increasing attentions in the AOPs for water treatment due to their abundant Fe-O clusters, the cycle of Fe^{3+}/Fe^{2+} and unsaturated Fe active sites [53,54], which could display outstanding catalytic removal activities toward organic and/or inorganic contaminants via the photocatalysis, (photo)-Fenton, sulfate radical-advanced oxidation processes (SR-AOPs), ozone catalysis or their combined processes [55]. Especially, some updated research revealed that some Fe-MOFs can be produced from industrial chemicals and even industrial wastes, achieving high-throughput and low-cost production [56–59].

Considering that MIL-101-Fe- NH_2 as Fenton catalyst possessed the characteristics like large surface area, satisfied stability, as well as the effective electron transfer between 2-aminoterephthalates and Fe-O clusters, Li and coworkers loaded MIL-101-Fe- NH_2 onto MS with the help of binding agent dopamine to guarantee the uniform distribution of MIL-101-Fe- NH_2 particles onto the skeleton of the MS (Fig. 6) [60]. The active species like HO^\bullet , $O_2^{\bullet-}$ and 1O_2 formed from the as-prepared MS@MIL-101-Fe- NH_2 accomplished good Fenton-like catalytic degradation toward tetracycline hydrochloride under weakly acidic condition, taking advantages of both hierarchical pore structure for rapid mass transfer and uniform distribution mode of MIL-101-Fe- NH_2 particles for exposing more active sites. The accelerated reaction rate, longer cycle

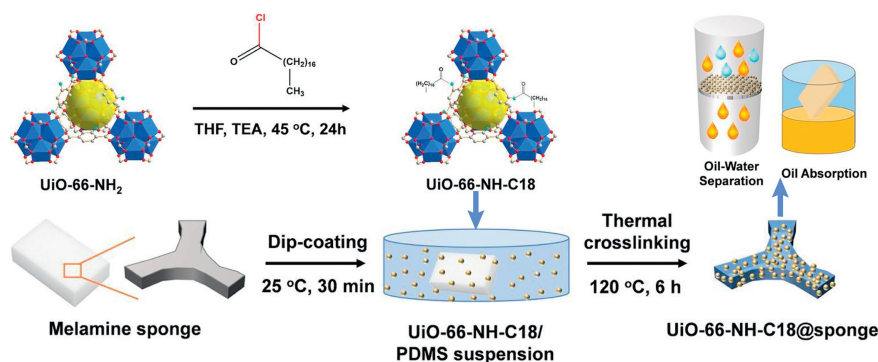


Fig. 5. The illustration of the fabrication and application of UiO-66-NH-C18 and UiO-66-NH-C18@sponge. Reproduced with permission [38]. Copyright 2020, Elsevier.

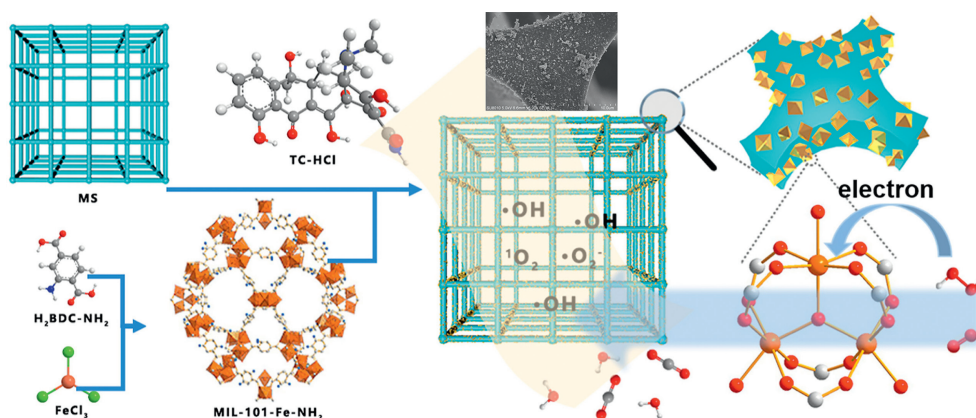


Fig. 6. The fabrication of MS@MIL-101-Fe-NH₂ and the mechanism of photocatalytic tetracycline hydrochloride degradation over MS@MIL-101-Fe-NH₂. Reproduced with permission [60]. Copyright 2022, Elsevier.

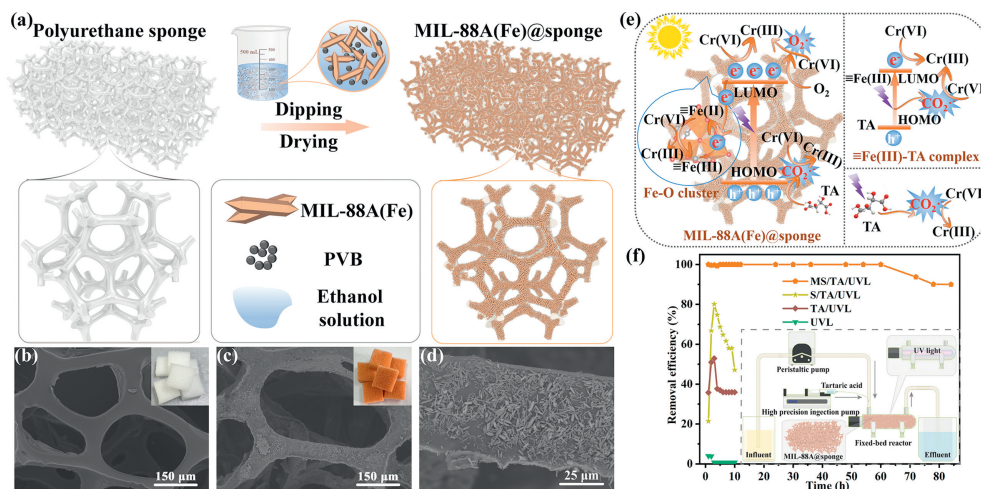


Fig. 7. (a) The fabrication of MIL-88A(Fe)@sponge. The SEM images of (b) bare polyurethane sponge and (c, d) MIL-88A(Fe)@sponge. (e) The mechanism of photocatalytic Cr(VI) reduction over MIL-88A(Fe)@sponge. (f) The removal efficiency of Cr(VI) reduction continuously under different conditions. Reproduced with permission [28]. Copyright 2023, Elsevier.

duration, facile recycling and less leaching metal ion could achieve the as-prepared bulk composite for potential practical application.

Our group developed an easy-to-use approach to coat the MIL-88A(Fe) onto the 3D macroporous polyurethane (PU) sponge with the assistance of polyvinyl butyral (PVB) to construct MIL-88A(Fe)@sponge (Fig. 7a) [28]. It was observed that the rod-like MIL-88A(Fe) particles with size of 2–6 μm were uniformly distributed onto the skeleton of the PU sponge (Figs. 7b–d). The as-prepared MIL-88A(Fe)@sponge exhibited superior photocatalytic Cr(VI) reduction performance with the presence of tartaric acid (TA) under UV light and real solar light, in which the photo-yielded

electrons, $\text{O}_2^{\cdot-}$ and $\text{CO}_2^{\cdot-}$ participated in the transformation from Cr(VI) to Cr(III) (Fig. 7e). A fixed-bed reactor was constructed with MIL-88A(Fe)@sponge as catalyst to achieve continuous 100% Cr(VI) reduction up to 60 h (Fig. 7f). The aforementioned results indicate the feasibility of MIL-88A(Fe) immobilization onto PU sponge for long-term operation in water decontamination.

2.4. Multifunctional applications

In general, wastewater contains multiple pollutants like organics, oils and even heavy metals [61–65]. It was necessary

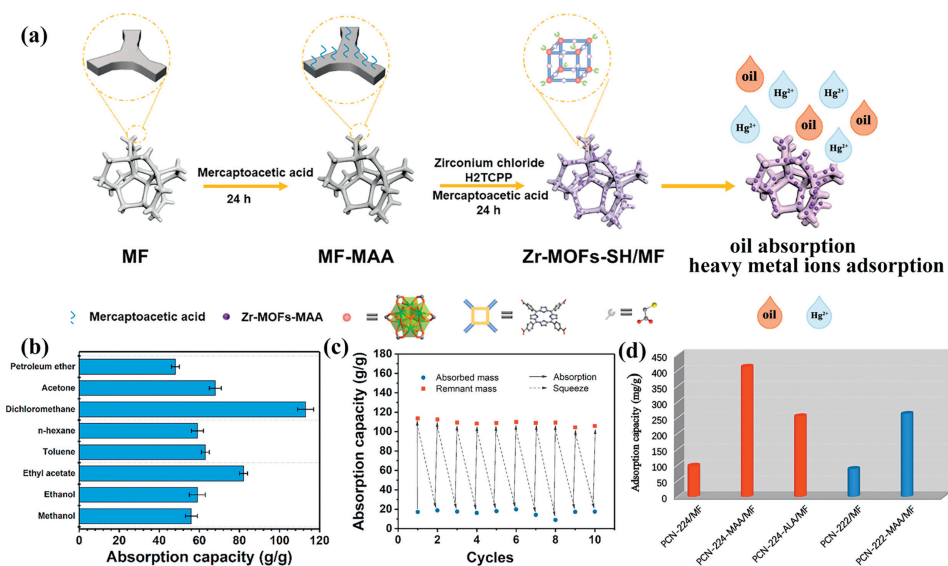


Fig. 8. (a) The illustration of the Zr-MOFs-SH/MF preparation process. (b) The adsorption capacities of PCN-224-MAA/MF toward various oils. (c) The reuse of the as-prepared PCN-224-MAA/MF for dichloromethane adsorption, in which the adsorbed dichloromethane was desorbed by direct squeezing. (d) Hg²⁺ adsorption capacity of the different composites. Reproduced with permission [37]. Copyright 2020, American Chemical Society.

to develop multi-purpose functional materials for simultaneous elimination toward the co-existing pollutants. For the purpose of removing the heavy metals and oils in the wastewater discharged from oil production and electroplating process, Huang and coworkers fabricated series Zr-MOFs like PCN-222 and PCN-224 on melamine foam to obtain PCN-222-MAA/MF, PCN-224-MAA/MF, and PCN-224-ALA/MF adopting mercaptoacetic acid (MAA) or α -lipoic acid (ALA) as the modulator (Fig. 8a) [37]. The MAA or ALA pretreated onto the skeleton of MF via the physical adsorption can react with the Zr ions to construct MAA or ALA-modified Zr-oxo clusters, which were further linked by meso-tetra(4-carboxyphenyl)porphine (TCPP) to form PCN-222-MAA/MF, PCN-224-MAA/MF, and PCN-224-ALA/MF. Among the as-prepared composites, PCN-224-MAA/MF exhibited good absorption capacities toward different selected organics from 48 g/g to 113.6 g/g (Fig. 8b). The initial and the 10th cycle absorption capacities of PCN-224-MAA/MF toward dichloromethane were 113.6 g/g and 105.8 g/g (Fig. 8c), demonstrating outstanding reusability after direct squeezing. The PCN-224-MAA/MF, PCN-224-ALA/MF, and PCN-

222-MAA/MF displayed superior adsorption capacities toward Hg²⁺ up to 412.5, 255.5, and 263.1 mg/g (Fig. 8d), which resulted from the strong affinity between the Hg²⁺ and S in mercapto groups attached on MAA or ALA. As well, the interaction between Hg²⁺ and S contributed to the selective adsorption toward Hg²⁺ in the simulated wastewater containing various metal ions like Hg²⁺, Cd²⁺, Co²⁺, Cr³⁺, Mn²⁺, Ni²⁺, and Pb²⁺. Finally, the PCN-224-MAA/MF was used as effective adsorbent and absorbent to simultaneously remove the Hg²⁺ and chloroform in the Hg²⁺/chloroform matrix, in which the increasing proportion of chloroform led to the enhanced Hg²⁺ removal efficiency. This finding demonstrated that it was a facile approach to construct dual-functional material for multiple pollutants elimination.

Yu and coworkers developed a two-step method to prepare the ultra-stable MOFs-based monoliths (MOFiths), in which the as-prepared dimethylformamide (DMF) slurry containing different selected MOFs (MIL-53(Fe), MIL-88A(Fe), UiO-66 and CuBTC) particles and PVDF was impregnated into the voids inside MS via facile squeezing treatment (Fig. 9) [29]. The as-prepared MOFiths could

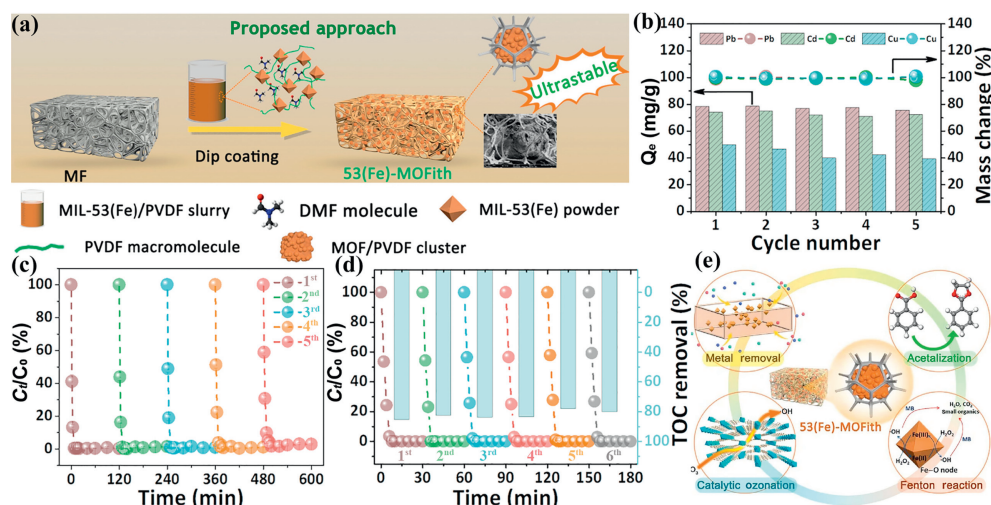


Fig. 9. (a) The preparation of MIL-53(Fe)-MOFith. The cyclic tests of (b) heavy metal adsorption, (c) Fenton-like MB oxidation, and (d) 4-NP ozonation over MIL-53(Fe)-MOFith. (e) Multiple-functional applications illustration as a representative of the various as-prepared MOFiths. Reproduced with permission [29]. Copyright 2022, Springer.

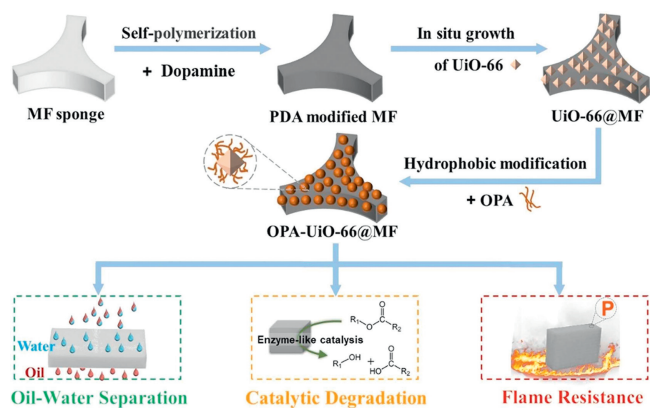


Fig. 10. The schematic fabrication and applications of the as-prepared OPA-UiO-66@MF sponge. Reproduced with permission [9]. Copyright 2022, Elsevier.

withstand the solvent erosions as well as different mechanical treatments like extruding, stirring, centrifugation, and even ultrasonication. The 53(Fe)-MOFith₂₀, a selected as-prepared MOFiths, displayed versatile and superior performances like H₂O₂ activation for MB degradation, catalytic ozonation for *p*-nitrophenol (4-NP) destruction, adsorptive elimination toward cationic heavy metals like Pb²⁺, Cd²⁺ and Cu²⁺, along with catalytic acetalization toward benzaldehyde (Figs. 9b–e). Importantly, the efficient MB degradation via H₂O₂ activation and effective 4-NP degradation via O₃ catalysis over 53(Fe)-MOFith₂₀ could be accomplished for long operation time, resulting from the rapid mass transfer and easily available active sites.

The polymer oil adsorbents and the oils are combustible, which were potentially dangerous during the oil spills collection from the water surface. To void the potential flame, Wang and coworkers developed a multifunctional OPA-UiO-66@melamine sponge (OPA-UiO-66@MS) with the aid of polydopamine (PDA) as adhesive for the purpose of effective oil/water separation, in which the phosphorus element in octadecyl-phosphonic acid (OPA) contributed to the superior flame resistance characteristic of OPA-UiO-66@MS (Fig. 10) [9]. Besides oil/water separation, the as-obtained OPA-UiO-66@MS could catalytically degrade *p*-nitrophenyl hexanoate (*p*-NPH) via enzyme-like process, resulting from the catalytic active sites in UiO-66.

The luminescent MOFs have attracted increasing attentions due to that they can accomplish the sensing detection toward explosives [66,67], heavy metal ions [68,69], emerging pollutants [8,9,26], anions [70,71] and viruses [72]. It was feasible and facile approaches to design and synthesize the MOFs with both adsorption and luminescent sensing detection activity [73], in which the luminescence activity can provide obvious signal to determine the adsorption saturation or complete desorption of the MOF adsorbents. Fu and coworkers immobilized the luminescent Zr-MOF onto melamine foam (Zr-LMOF/MF) for sensing detection and removal toward different mycotoxins [74]. As depicted in Fig. 11,

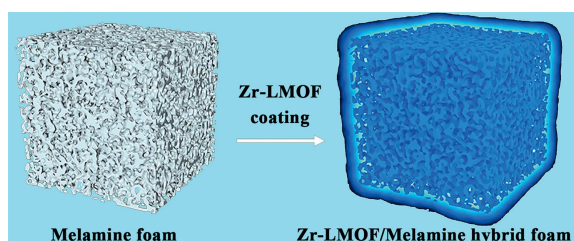


Fig. 11. The fabrication of the fluorescent Zr-LMOF/melamine sponge foam. Reproduced with permission [74]. Copyright 2021, Elsevier.

the as-prepared Zr-LMOF/MF was sensitive to mycotoxins via fluorescence quenching with the mechanism of the electron transfer from the LUMO of MOF to LUMO of mycotoxins. In addition, the stronger analyte-sensor interactions and higher order of π - π interactions accelerate the electron transfer and produce larger extent of quenching effect on sensitive detection, in which the fluorescence quenching signals can be observed even by the naked eyes. Besides sensing detection, the Zr-LMOF/MF could effectively concentrate the various toxins like aflatoxin B1, aflatoxin B2, aflatoxin G1, aflatoxin G2, aflatoxin M1 and ochratoxin A. This work provided a dual-functional material to detect and remove hazardous matters for food safety and water treatment. It was worth noting that this work might be further improved by simultaneously detecting and removing mycotoxins, in which the detecting via fluorescence quenching might qualitatively indicate the adsorption amount toward targeted pollutants.

3. Conclusion and outlooks

From the advances of MOF/sponge foam composites for water remediation, it was concluded that immobilizing MOFs onto different sponge foams can really increase the duration and practicality of the emerging MOFs materials. The macro-porosity and the elastic property of melamine or polyurethane sponge guaranteed the high throughput flow of the treated wastewater and facile process of water treatment devices. The selected MOFs loaded onto the sponge foam could realize individual or multiple functions like sensing detection, adsorptive removal and catalytic oxidation/reduction toward different organic and inorganic pollutants, which can overcome the intrinsic disadvantages of powder MOFs like fragility, erosion, dissociation. Judged from the current status of MOFs and immobilized MOFs onto some substrates for water purification, it was one of the future and prosperous strategies to apply MOFs for water treatment and purification.

However, there was a long way to utilize MOFs/sponge foam composites for practical applications. Some efforts should be devoted in the future. Firstly, it was essential to develop suitable techniques for high throughput and low-cost MOFs, which was the first and vital step for the large-scale production of MOF/sponge composites. Up to now, some reports revealed that mechanical chemistry, slow evaporation, microwave, ultrasound, electro-deposition were superior to the hydrothermal and solvothermal techniques. As to the late four techniques, it was difficult to separate the as-obtained MOFs from the mother solution, which can be put more efforts to solve. Secondly, it was hardly to find the large-scale production methods to obtain massive MOF/sponge products for real applications. In the future, some auto-devices should be developed to continuously immobilize MOFs onto sponges with or without the assistance of adhesives. Also, the *in-situ* production from the precursors of MOFs and/or sponge foams should be tried and tested, which might further enhance the stability and duration of the functional MOFs in the composites. Thirdly, considering the specific characteristics of safe water treatment, it was important to develop various bio-MOFs free of biological toxicity. Last but not least, it was essential to develop suitable wastewater setups to pack the as-prepared MOF/sponge, which can fully fulfill the role of versatile MOFs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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