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ANALYTICAL CHEMISTRY IN ENVIRONMENTAL MONITORING AND CHEMISTRY STUDIES

On the use of metal-organic frameworks for the extraction of organic compounds from environmental samples

Natalia Manousi[1] · **George A. Zachariadis**[1] · **Eleni A. Deliyanni**[2]

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Abstract

The determination of trace metals and organic contaminants in environmental samples, such as water, air, soil, and sediment, is until today a challenging process for the analytical chemistry. Metal-organic frameworks (MOFs) are novel porous nanomaterials that are composed of metal ions and an organic connector. These materials are gaining more and more attention due to their superior characteristics, such as high surface area, tunable pore size, mechanical and thermal stability, luminosity, and charge transfer ability between metals and ligands. Among the various applications of MOFs are gas storage, separation, catalysis, and drug delivery. Recently, MOFs have been successfully introduced in the field of sample preparation for analytical chemistry and they have been used for sample pretreatment of various matrices. This review focuses on the applications of MOFs as novel adsorbents for the extraction of organic compounds from environmental samples.

Keywords Metal-organic frameworks · MOF · Sample preparation · Environmental samples · Water · Soil · HPLC · GC

Introduction

In the recent years, a lot of progress has been made in the field of sample preparation. Novel extraction techniques, such as solid-phase microextraction (SPME), stir bar sorptive extraction (SBSE), dispersive solid-phase extraction (d-SPE), magnetic solid-phase extraction (MSPE), fabric phase extraction (FPSE), and liquid-phase microextraction (LPME), have been developed and successfully applied in the analysis of complex matrices (Anthemidis and Mitani 2013; Filippou et al. 2017; Karageorgou et al. 2016; Karageorgou and Samanidou 2011; Manousi and Zachariadis 2019; Nazyropoulou and Samanidou 2015). Compared to the well-established sample preparation techniques, including solid-phase extraction (SPE) and liquid-liquid extraction (LLE), the novel microextraction techniques require less time and steps, decrease the consumption of organic solvents, and can be more easily automated (Manousi et al. 2017).

Furthermore, novel sorbents, such as molecular imprinted polymers (MIPS), single-wall and multi-wall carbon nanotubes, graphene oxide (GO), carbon-based nanomaterials, and metal-organic frameworks (MOFs), have been developed in order to improve the efficiency of the sample preparation process. These materials can be easily synthesized and coupled with various sample preparation techniques offering multiple benefits (Bitas and Samanidou 2018; Manousi et al. 2017; Samanidou 2012; Su et al. 2014).

Metal-organic frameworks became popular in 1995, when Yaghi and Li reported the hydrothermal synthesis of a MOF material that contained large rectangular channels (Yaghi and Li 1995). Since then, a lot of progress has been made regarding the synthesis and the applications of MOFs. These materials are characterized by a flexible structure, high surface areas (up to 14,600 $m^2\ g^{-1}$), and tunable pore size (Fahra et al. 2012). Among their interesting properties are their mechanical and thermal stability, luminosity, and ability for charge transfer between the metal and the organic ligand. Therefore, metal-organic frameworks have a wide field of possible applications including catalysis, gas storage, drug delivery, separation, fuel cells, and supercapacitors (Furukawa et al. 2013; Ibrahim et al. 2017; Li et al. 2018;

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✉ Natalia Manousi
nmanousi@chem.auth.gr

[1] Laboratory of Analytical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

[2] Laboratory of Chemical and Environmental Technology, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

Mueller et al. 2006). In the field of analytical chemistry, MOFs have been widely used both as sorbents in sample preparation and as novel stationary phases for analyte separation (Rocío-Bautista et al. 2019; Yu et al. 2013; Yusuf et al. 2014).

In order to design MOFs with high extraction efficiency, careful selection of the metal center and the organic linkers is required, since their coordination is responsible for generating a particular topology with specific characteristics of pore size and window. Regarding the selection of the metal ion, low-toxicity metal ions are preferable. Among the existing metal salts, metal oxides and hydroxides are preferred since water is the only potential by-product. However, their solubility, reactivity, and cost should be also considered. As for the organic linker, low-cost carboxylic acids, such as terephthalic acid, are preferred. Considering the synthetic procedure, mild conditions and decreased use of organic solvents are necessary to comply with the principles of green chemistry. Intermediates and by-products that can be produced should additionally be carefully considered. Enhancement of the extraction efficiency can be achieved through functionalization or modification of the desired MOF, the formation of nanocomposites based on efficient frameworks for the targeted application, or by grafting the active MOF phase on specific substances. (Manousi et al. 2018; Rocío-Bautista et al. 2019).

The main limitation of MOFs is their low stability in aqueous solutions. When used in sample preparation, MOFs must be stable both under adsorption and under desorption conditions to provide good reproducibility and reusability of the sorbent. MOFs such as the zirconium-based UiO (University of Oslo) and MIL-53(Fe) (Material Institut Lavoisier) sorbents exhibit satisfactory stability in aqueous solutions. However, various MOFs such as HKUST-1 (Hong Kong University of Science and Technology) are not stable in water. To overcome this drawback, functionalization of MOFs has been proposed. Other approaches to enhance the stability of the MOFs are by changing/modifying the metal ions (Manousi et al. 2019; Giannakoudakis et al. 2016, 2017a, b).

Environmental samples, such as water, air, soil, and sediment, are considered complex and demanding matrices. Determination of emerging contaminants including pesticides, drugs, and industrial by-products as well as trace metals and metalloids remains until today a challenging process (Rubio and Pérez-Bendito 2009). Gas chromatography-mass spectrometry (GC-MS) and high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) are the workhorses in analytical organic chemistry, while flame atomic absorption spectrometry (FAAS), inductively induced plasma-optical emission spectrometry (ICP-OES), and inductively plasma-mass spectrometry are the most famous techniques for the determination of metals and metalloids (Bester 2008). Current trends regarding the handling of environmental samples include the development of alternative phases and geometries for sorptive extraction as well as the development of novel solvents and configurations (Rubio and Pérez-Bendito 2009). Recently, MOF materials have been successfully utilized for the analysis of environmental samples providing numerous advantages. As for the implementation of MOFs for sample preparation, these materials were used as coatings for SPME or SBSE techniques, as such for d-SPE technique or after magnetization for MSPE technique.

Various review papers have discussed the applications of MOFs in the analytical chemistry (Hashemi et al. 2017; Manousi et al. 2018; Rocío-Bautista et al. 2019; Wang et al. 2017a; Yu et al. 2013; Yusuf et al. 2014; Manousi et al. 2019). Herein, we aim to discuss the use of metal-organic frameworks in the analysis of environmental samples. The applications of MOFs are presented based on the extraction technique with which they were coupled, since sample preparation is a critical step in the analysis of environmental samples. The advantages and disadvantages of MOFs as sorbents for the extraction of organic pollutants, as well as a comparison with other well-established sorbents, are also discussed. Application of different subfamilies of metal-organic frameworks, such as zeolite imidazole frameworks (ZIFs), metal-organic nanotubes (MONTs), and metal azolate frameworks (MAFs), will also be presented (Zhang et al. 2016; Liu et al. 2019; She et al. 2015).

Extraction of organic compounds from environmental samples

Metal-organic frameworks have been successfully coupled with many sample preparation techniques including SPE, SPME, MSPE, d-SPE, SBSE, etc. Figure 1 shows the coupling of MOFs with the different analytical techniques for the extraction of organic compounds from environmental samples

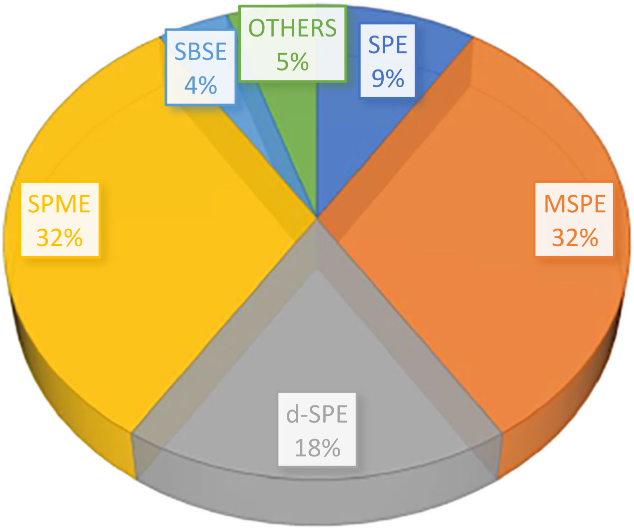

Fig. 1 Analytical techniques coupled with MOFs for the extraction of organic pollutants from environmental samples

prior to instrumental analysis. The π–π interactions of the aromatic rings of the analytes with the aromatic molecules of the organic ligand, as well as the π-complexation of the electron-rich analytes to the Lewis acid sites in the pores of the metal-organic frameworks are the predominant mechanisms of the analytes' extraction from sample matrices.

Solid-phase extraction

Solid-phase extraction is a well-established technique for sample preparation. Application of cartridges is the most popular commercially available SPE configuration and various sorbents including general purpose sorbents (e.g., C8, C18, and silica-based sorbents), class-specific sorbents, and analyte-specific sorbents are widely used (Faraji et al. 2019). MOFs have been recently employed as SPE sorbents providing many benefits in the sample preparation process.

Li et al. (2014a) synthesized MIL-101(Cr) and used it for the SPE of triazine herbicides prior to their detection with direct analysis in real-time mass spectrometry (DART-MS). Triazine herbicides have been used both for selective pre- and postemergence weed control (e.g., for corn, barley) and for nonagricultural uses (e.g., railways and roadside verges). The MOF material was prepared by mixing chromium nitrate nonahydrate and terephthalic acid in hydrofluoric acid in a Teflon autoclave which was heated at 220 °C for 8 h. Accordingly, the sorbent was added to the sample in a glass vial and the mixture was shaken. The solution was filtered and the MIL-101(Cr) sorbent that was contained in the syringe filter was treated with isopropanol to elute the herbicides. With the novel sorbent, the limit of detection (LOD) ranged from 0.1 to 0.2 ng mL^{-1} and extraction recovery was higher than 85%. The method was successfully applied for the analysis of lake water samples.

Dai et al. (2016) used MIL-101(Cr) as a SPE sorbent for the determination of sulfonamides (SAs) in environmental water samples prior to ultrahigh-pressure liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) analysis. The sorbent was suspended in methanol and packed into a cartridge with a polypropylene frit at its bottom. The developed method was successfully used for the extraction and analysis of SAs in different water samples. With the MOF sorbent, low LOD values (0.03–0.08 ng mL^{-1}) and satisfactory recoveries (83.5–107.3%) were achieved.

MIL-101(Cr) has been also used as a micro-solid-phase extraction (μ-SPE) sorbent for the efficient enrichment of five organochlorine pesticides from water samples prior to GC-MS analysis. Under optimum conditions, LODs were 0.0025–0.016 ng mL^{-1} and recoveries were 87.6–98.6%. The proposed device was found to be reusable for up to 20 times (Huang and Lee 2015). The same MOF material has been implemented for the in-syringe SPE of polycyclic aromatic hydrocarbons (PAHs) from environmental water samples prior to their detection by GC-MS. The sorbent was slurry-packed inside the nozzle of disposable syringe between an upper and a lower filter. The extraction procedure was optimized in terms of eluent type and volume number of elution cycles, as well as the volume and pH value of the loaded sample solution. The method was implemented for on-site sampling providing low LODs (0.2–1.9 ng L^{-1}), while recovery values ranged between 84.4 and 104.5% (Zhang et al. 2018c).

Tan and Lee (2019) used MIL-101(Cr) for ultrasound-assisted emulsification microextraction (USAEME) of polar estrogens from water samples prior to UHPLC-MS/MS analysis. Due to their polarity, the analytes are unable to pass through the polypropylene membrane that is usually used in μ-SPE. Therefore, 1-octanol was used in this work in USAEME in order to extract and pre-concentrate the steroids in order to facilitate the transfer to the MIL-101(Cr) sorbent that was retained by the membrane in the subsequent μ-SPE step. Limits of detection were down to 0.95–23 ng L^{-1} and recoveries ranged between 85.4 and 120.8%.

In the same year, Nurerk et al. (2019) et al. used MIL-101(Cr) as adsorbent for the extraction of multiclass organic UV filters (benzophenone-derivatives, salicylates, cinnamates and others) from water samples prior to their determination by gas chromatography tandem mass spectrometry (GC-MS/MS). In this case, a miniaturized on-column SPE containing the adsorbent was manufactured. The novel methodology provided low LODs (1.0 to 11.7 ng L^{-1}), satisfactory recoveries (82–105%), and good repeatability for organic UV filters from different chemical groups. The same sorbent has been also applied for the porous membrane-protected μ-SPE coupled with GC-MS for the analysis of six phthalate esters from drinking water samples. Compared to activated carbon and MIL-100(Fe), the chosen sorbent exhibited various advantages (Wang et al. 2015a). Figure 2 shows the synthetic procedure and the application of MIL-100(Fe) for the determination of organic UV-filters.

MOF-5 has been evaluated for its application as a SPE sorbent for the extraction of PAHs from water samples. Synthesis of the nanosized MOF-5 was performed by mixing zinc acetate dihydrate with terephthalic acid in N,N-dimethylformamide (DMF) at room temperature. To fabricate the cartridges, the MOF material was dispersed in acetonitrile and packed into a polypropylene tube within 2 polypropylene frites. The novel technique was used for the extraction of PAHs from water samples prior to high-pressure liquid chromatography-fluorescence detection (HPLC-FLD) determination. Although MOF-5 is unstable in water, it was found that the derived material is a good sorbent due to efficient π–π interactions. Recoveries obtained with the developed method extraction ranged from 80.2 to 120.2% and LODs were 0.4–4 ng L^{-1} (Yang et al. 2013b).

UiO-66 (University of Oslo-66) zirconium (Zr)1,4-dicarboxybenzene metal-organic framework has been also

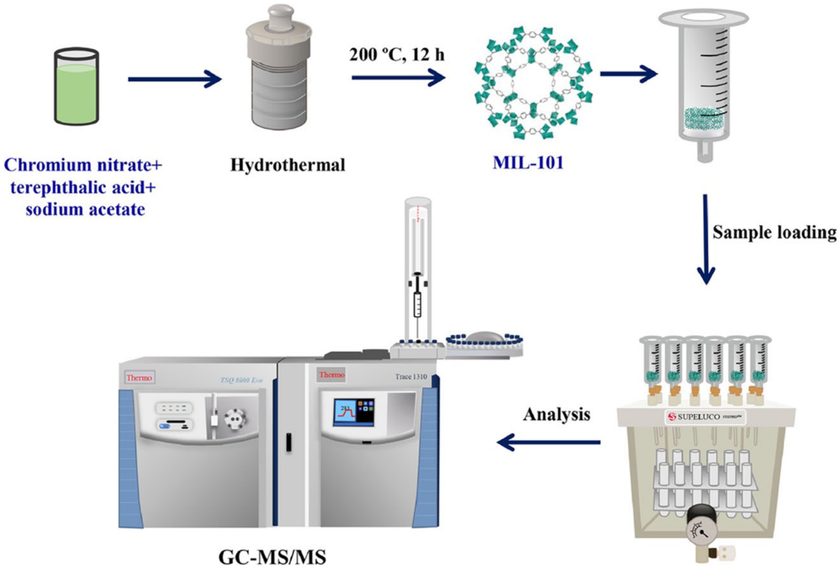

Fig. 2 Preparation and application of MIL-101(Fe) for the determination of UV-filters. Reprinted from (Nurerk et al. 2019) Nurerk et al., Solid-phase extraction based on MIL-101 adsorbent followed by gas chromatography tandem mass spectrometry for the analysis of multiclass organic UV filters in water, Page 3, Copyright (2019), with permission from Elsevier

evaluated as sorbent for porous membrane-protected μ-SPE of androgens and progestogens from environmental water samples coupled prior to HPLC-MS/MS analysis. Other MOFs that were evaluated in the study were MIL-101(Cr), MIL-100(Fe), and MIL-53(Al), however, UiO-66(Zr) showed the highest extraction efficiency among the four sorbents. The developed eco-friendly pretreatment method provided good recovery values (80.5–102.4%), low LODs (2–10 ng L^{-1}), and low consumption of organic solvents, as well as satisfactory selectivity, sensitivity, and accuracy (Gao et al. 2019).

In conclusion, MOFs can be successfully used as SPE sorbents providing good extraction recoveries. Compared with commercial SPE cartridges including C8, C18, and hydrophilic-lipophilic-balanced sorbents, MOFs in most cases exhibited higher extraction recoveries. This can be attributed to the strong π–π and hydrophobic interactions between MOFs and organic pollutants, since for the conventional C18 sorbent, extraction is mainly based on hydrophobic interactions.

Magnetic solid-phase extraction

Magnetic solid-phase extraction is a procedure based on the use of a magnetic adsorbent which is added to a solution or suspension containing the target analyte. After adsorption of the analyte, separation of the sorbent from the solution is achieved by using external magnetic field. Subsequently, elution of the analyte is performed and the magnetic field is once again used to remove the sorbent from the eluent prior to its analysis (Šafaříková and Šafařík 1999). Figure 3 describes the stages of MSPE procedure.

The applications of MOFs for the MSPE of organic compounds from environmental samples are summarized in Table 1.

Magnetic MIL-101 (Fe_3O_4@MIL-101) has been employed for the MSPE of phthalate esters from water and plasma samples prior to their determination by GC-MS. The sorbent was prepared with the hydrothermal approach and it was added to the sample. A strong Nd-Fe-B magnet was used to separate the magnetic sorbent at adsorption and desorption steps (Dargahi et al. 2017). The same magnetic MOF has been employed for the magnetic solid-phase extraction and preconcentration of estrogens in environmental water samples after functionalization with amine groups. Compared to carbon coated MIL-101 and carboxylic functionalized Fe_3O_4@MIL-101, the herein used Fe_3O_4-NH_2@MIL-101 material showed higher extraction efficiency and was finally chosen (Huang et al. 2016).

MOF-199 has been synthesized and used for the MSPE of neonicotinoid insecticides prior to HPLC-MS/MS analysis. For this purpose, Fe_3O_4 nanoparticles were prepared with the chemical co-precipitation method and they were mixed with copper acetate monohydrate and trimesic acid. The novel sorbent was successfully applied for the analysis of environmental water samples (Cao et al. 2016).

MOF-177 was synthesized by mixing zinc nitrate hexahydrate and trimesic acid in N,N-diethylformamide (DEF) and used for the MSPE of phenols in environmental water samples after functionalization with Fe_3O_4@SiO_2. For the extraction, Fe_3O_4@SiO_2 and MOF-177 were placed in a 25-mL glass vial, it was washed with water, and then sample solution was added. The developed method showed great adsorption ability and selectivity towards phenols (Wang et al. 2014).

In 2013, Hu et al. synthesized Fe_3O_4@MOF-5 via chemical bonding assembly and used as sorbent to extract polar and non-polar analytes from environmental, food, and plant samples. The sorbent was used for the MSPE of PAHs prior to GC-MS detection and MSPE of gibberellic acid prior to LC-MS/MS analysis and exhibited superior enrichment capacity for all the examined analytes (Hu et al. 2013a).

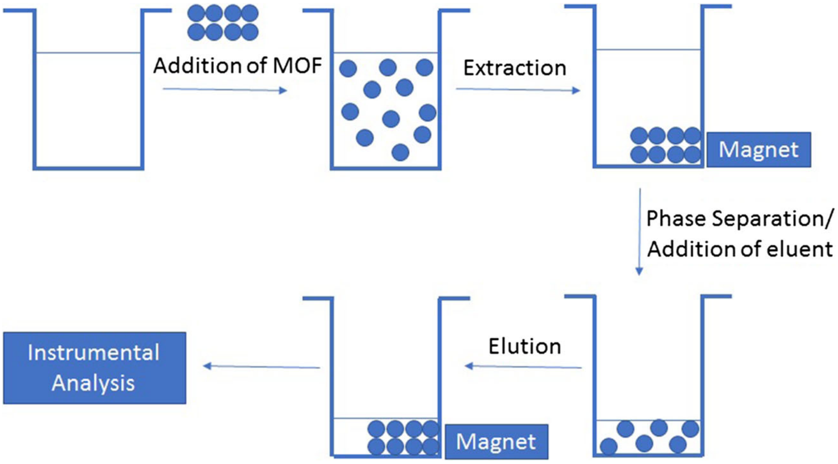

Fig. 3 MSPE procedure with metal-organic frameworks

In 2016, Ma et al. used MIL-101 for MSPE of pyrazole/pyrrole pesticides in environmental water samples prior to HPLC-PDA analysis. The hydrothermal method was used for the synthesis of amino-functionalized Fe_3O_4 nanoparticles, while the solvothermal approach was employed for the synthesis of magnetic MOF-5. The developed method can be characterized as convenient, fast, cheap, effective, and eco-friendly (Ma et al. 2016a). In 2018, the same working group used a magnetic MOF-5 for the MSPE of heterocyclic pesticides in reservoir and river water samples prior to HPLC-PDA analysis. The developed method exhibited high adsorption capacity and it simplified the sample preparation procedure due to its magnetic properties (Ma et al. 2018).

Fungicides have been extracted from water samples with the use of magnetic iron(III)-based framework composites. In this case, four different modified MOF materials were evaluated, including MIL-101@Fe_3O_4-COOH, MIL-101-NH_2@Fe_3O_4-COOH, MIL-53@Fe_3O_4-COOH, and MIL-53-NH_2@Fe_3O_4-COOH. Among the examined materials, MIL-101-NH_2@Fe_3O_4-COOH showed the highest extraction efficiency and was finally chosen for the MSPE of the target analytes (Huang et al. 2018a).

Wang and Deng (2015) synthesized a zirconium-based magnetic MOFs (magG@PDA@Zr-MOF) and used it as sorbent for the MSPE of bisphenols from water followed by HPLC-UV analysis. For the synthesis of the material, magnetic graphene was initially prepared with the solvothermal method. Accordingly, magG@PDA was prepared with the self-polymerization of dopamine at room temperature. Subsequently, the synthesized magG@PDA was dispersed in DMF followed by the addition of zirconium chloride and terephthalic acid. The mixture was heated at 140 °C for 20 min and the obtained magG@PDA@Zr-MOFs were washed and dried. The novel material showed large surface area, homogeneous pore size, satisfactory magnetic properties, and good hydrophilicity.

Zhou et al. (2017a) developed a new magnetic nanomaterial nanoscale zero valent iron-functionalized MIL-101 by co-precipitation method. The developed material was used for the MSPE of polycyclic aromatic hydrocarbons from environmental water samples prior to HPLC-UV analysis. The novel material exhibited good adsorption ability towards PAHs. The same working group developed a zerovalent iron nanoscale material modified with MOF-5 which was implemented for the MSPE of N- and S-containing polycyclic aromatic hydrocarbons from water samples prior to their determination by HPLC (Zhou et al. 2017).

In 2016, Du et al. (2016) synthesized MIL-100(Fe) magnetic microspheres and used them for the MSPE of trace PAHs from water samples prior to HPLC-FLD analysis. It was found that the microspheres were stable enough for 150 extraction–desorption cycles. Magnetic Fe_3O_4@MIL-100 core–shell magnetic microspheres have been also employed for the MSPE of polychlorinated biphenyls from environmental water samples (Chen et al. 2013). An aptamer-functionalized zirconium 2-amino-benzenedicarboxylate MOF (UiO-66-NH_2) material has been also employed for the determination of polychlorinated biphenyls. The MOF material was employed for the MSPE of the analytes from soil samples prior to their determination by GC-MS (Lin et al. 2016).

Alkylphenols were extracted from environmental water samples by a thermo-responsive polymer PNIPAM tethered MOF core–shell magnetic microspheres. For this purpose, Fe_3O_4@SiO_2 nanoparticles were initially synthesized and used for the functionalization UiO-66-NH_2. Due to the presence of the amino groups of the ligand, it was able to couple with the polymer and to give the desired Fe_3O_4@SiO_2@UiO-66-NH_2-PNIPAM. The novel MOF material was successfully used as a MSPE sorbent for the sample preparation of spring, pond, river, and drinking water sample prior to HPLC-MS/MS analysis (Jia et al. 2016a).

Nasrollahpour and Moradi (2018) synthesized a magnetic modified MIL-100(Fe) metal-organic framework (Fe_3O_4@MIL-100(Fe)) and used it for the vortex-assisted MSPE of triazine herbicides from environmental water and

Table 1 Applications of MOFs for the MSPE of organic compounds from environmental samples

Analyte	MOF	Matrix	Detection	Recovery (%)	LOD (ng mL^{-1})	Reference
Phthalate Esters	Fe_3O_4@MIL-101	Water and plasma	GC-MS	85.1–106.7	0.15	(Dargahi et al. 2017)
Estrogens	Fe_3O_4-NH_2@MIL-101	Water	HPLC-UV	80.6–99.6	0.06–0.22	(Huang et al. 2016)
Neonicotinoid insecticides	Fe_3O_4-MOF-199	Water	HPLC-MS/MS	88.0–107.0	0.3–1.5	(Cao et al. 2016)
Phenols	Fe_3O_4@SiO_2-MOF-177	Water	GC-MS	83.3–108.7	0.0168–0.2083	(Wang et al. 2014)
PAHs	Fe_3O_4@MOF-5	Soil	GC-MS	76.2–112.0	0.91×10^{-3}–1.96×10^{-3}	(Hu et al. 2013a)
Gibberellic acid	Fe_3O_4@MOF-5	Soil	HPLC-MS/MS	71.8–127.4	0.006–0.08	(Hu et al. 2013a)
Pyrazole/pyrrole pesticides	Fe_3O_4@MIL-101	Water	HPLC-PDA	> 81.0	0.3–1.5	(Ma et al. 2016a)
Heterocyclic pesticides	Fe3O4@MOF-5	Water	HPLC-PDA	80.20–108.33	$0.04–0.11 \times 10^{-6}$	(Ma et al. 2018)
Fungicides	MIL-101-NH2@Fe3O4-COOH	Water	HPLC-UV	71.1–99.1	0.04–0.4	(Huang et al. 2018a)
Bisphenols	magG@PDA@Zr-MOF	Water	HPLC-UV	64.8–92.7	0.1–1	(Wang and Deng 2015)
PAHs	Nanoscale zero valent iron-functionalized MIL-101	Water	HPLC-UV	85.7–97.3	0.064	(Zhou et al. 2017a)
S- and N-PAHs	Fe@MOF-5	Water	HPLC-UV	92.6 and 97.3	25×10^{-3}–33×10^{-3}	(Zhou et al. 2017)
PAHs	Magnetic MIL-100(Fe) microspheres	Water	HPLC-FLD	81.4–126.9	0.032–2.11	(Du et al. 2016)
Polychlorinated biphenyls	Fe_3O_4@MIL-100	Water	GC-MS/MS	80.0–111.7	1.07×10^{-3}–1.57×10^{-3}	(Chen et al. 2013)
Polychlorinated biphenyls	Fe_3O_4@PDA@UiO-66-NH_2	Water	GC-MS	89.2–95.2	0.010–0.015	(Lin et al. 2016)
Alkylphenols	Fe_3O_4@SiO_2@UiO-66-PNIPAM	Water	HPLC-MS/MS	78.7–104.3	1.5×10^{-3}	(Jia et al. 2016a)
Triazine herbicides	Fe_3O_4@MIL-100(Fe)	Water and vegetables	HPLC-PDA	97.6–101.5	2.0–5.3	(Nasrollahpour and Moradi 2018)
Sulfonylurea herbicides	Magnetic MIL-101(Fe) functionalized with polydopamine	Water and vegetables	HPLC-PDA	87.1–108.9	0.12–0.34	(Deng et al. 2018)
Pyrethroid insecticides	Fe_3O_4-NH_2@MIL-101(Cr)	Water	GC-ECD	75.4–108.0	0.005–0.009	(He et al. 2018)
Organochlorine pesticides	Fe_3O_4-NH_2@MIL-101(Cr)	Soil	GC-ECD	71.2–102.4	0.15–0.28 ng g^{-1}	(He et al. 2019)
Sex Hormones	MIL-53 derived carbon	Water and urine	HPLC-UV	94.6–98.7	0.005–0.01	(Ma et al. 2016)
Phenols and anilines	MIL-53(Fe)	Water	HPLC-PDA	39.5–93.3	0.03–0.2	(Jalilian et al. 2019)
Benzenoid-containing insecticides	Magnetic Cu-MOFs embedded within GO nanocomposites	Water and fruits	HPLC-UV	81.2–113.1	0.30–1.58	(Wang et al. 2018)
Caffeic acid	Fe_3O_4@SiO_2@Ti-MOF	Plant extracts, water	HPLC-UV	99.76	0.016–0.021	(Moradi et al. 2019)
Nitrophenols	Fe_3O_4@PDA@ZrMOF	Particulate matter	MALDI-TOF MS	97.4–102.1	25×10^{3}–28×10^{3}	(Li et al. 2019)
Fluoroquinolones	Fe_3O_4@Cys@MIL125-NH_2	Water	UHPLC-UV	83.8–109.4	0.05–0.2	(Lian et al. 2018)
Blood lipid regulators	nano-Fe_3O_4@MOF	Water	HPLC-MS/MS	70–112	4–99	(Peña-Méndez et al. 2020)
Benzophenones	MOF-1210(Zr/Cu)	Soil	HPLC-UV	87.6–113.8	0.01–0.02	(Li et al. 2019a)

vegetable samples. The novel material exhibited high adsorption capacity as well as fast sorption and elution kinetics. The same year, Deng et al. (2018) synthesized a magnetic composite of MIL-101(Fe) functionalized with polydopamine through a simple one-pot solvothermal method and used it for the MSPE of sulfonylurea herbicides from both environmental water and vegetable samples. The analytes were further separated and detected by a high-pressure liquid chromatography-photodiode array detection (HPLC-PDA) system. He et al. (2018) synthesized an amino-functionalized magnetic metal-organic framework Fe_3O_4-NH_2@MIL-101(Cr) through the solvothermal method and used it for the MSPE of pyrethroid insecticides prior to gas chromatography-electron capture detector (GC-ECD) detection. The sorbent was used for the sample pretreatment of environmental water. The same sorbent was later successfully employed for the microwave-assisted MSPE of organochlorine pesticides in soil samples prior to their determination by GC-ECD (He et al. 2019).

Ma et al. (2016) synthesized MIL-53 by mixing terephthalic acid and ferric chloride hexahydrate in DMF at 150 °C for 2 h. The material was treated at 700 °C for 6 h and the obtained magnetic porous carbon was used for the MSPE of sex hormones from water and human urine. A nanosized magnetic MIL-53(Fe) metal-organic framework was also employed for the dispersive coextraction of phenols and anilines prior to their quantitation by HPLC-PDA. The novel method was optimized by response surface methodology and was successfully applied for the analysis of river, rain, and hookah water samples (Jalilian et al. 2019).

Magnetic copper 1,3,5-benzenetricarboxylate MOFs embedded within graphene oxide nanocomposites have been also employed to enhance the preconcentration of benzenoid-containing insecticides from water and fruit samples prior to their determination with HPLC-UV. The nanocomposite was functionalized with silica-coated magnetic nanoparticles (Fe_3O_4@SiO_2) and it was found that the chemical bonding between Fe_3O_4 and SiO_2, GO, and Cu-MOFs resulted in high chemical stability and great adsorption ability (Wang et al. 2018).

A titanium 5-aminoisophthalate MOF functionalized with silica-coated magnetic nanoparticles (Fe_3O_4@SiO_2) was employed as a magnetic nanocomposite sorbent for the trace analysis of caffeic acid in the medical extracts of plants and water samples prior to its determination with HPLC-UV (Moradi et al. 2019). A zirconium-based MOF modified with polydopamine-coated magnetic nanoparticles (Fe_3O_4@PDA@ZrMOF) was synthesized and employed for the MSPE of nitrophenols prior to negative ion mode of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). The material showed good stability and low background interferences, while the adsorbed analytes could be directly spotted for MALDI analysis without elution step (Li et al. 2019). A titanium-based MOF functionalized magnetic microspheres (Fe_3O_4@Cys@MIL125-NH_2) were used for the MSPE of fluoroquinolones from water samples (Lian et al. 2018). A nano-iron benzene-1,3,5-tricarboxylate MOF modified with magnetic nanoparticles (nano-Fe_3O_4@MOF) was used for the MSPE of blood lipid regulators from water prior to UHPLC-MS/MS analysis (Peña-Méndez et al. 2020). Metal-organic framework-1210(Zr/Cu) modified magnetic nanoparticles was used for the MSPE of benzophenones from soil samples prior to their HPLC-UV determination (Li et al. 2019a).

In conclusion, good extraction recoveries and enrichment factors were reported with the use of MOFs for the MSPE of organic pollutants from environmental matrices. Moreover, due to the easy separation step (with the use of an external magnetic field), the resulted sample preparation techniques were considered simple and rapid.

Dispersive solid-phase extraction

Dispersive solid-phase extraction is an alternative approach to SPE in which the adsorbent is added and dispersed into the sample matrix. Dispersion enhances the efficiency of the SPE technique and it can be achieved with mechanical stirring, ultrasonic radiation, vortex assistance, or addition of chemicals. Centrifugation or filtration are commonly used for phase separation (Chisvert et al. 2019). Table 2 summarizes the applications of MOFs for the d-SPE of organic compounds from environmental samples.

Rocío-Bautista et al. (2015) used HKUST-1 for vortex-assisted dispersive micro-solid-phase extraction of parabens from environmental waters, urine, and cosmetic creams prior to their determination by HPLC-PDA. Under the optimum conditions, the samples were mixed with the sorbent and were subjected to vortex mixing for 5 min. Accordingly, the supernatant was discarded using a Pasteur pipette. Elution was performed by addition of methanol and vortex mixing. After filtration, the eluent was dried and reconstituted in the mobile phase. In this work, MOF-5 and MIL-53(Al) were also evaluated.

The same working group evaluated the application of HKUST-1, MOF-5(Zn), MIL-53(Al), UiO-64, and MOF-74(Zn) on dispersive miniaturized solid-phase extraction method (D-μSPE) for the determination of pollutants of different nature (PAHs, hormones, drugs, disinfectants) from tap and wastewater. The analytes had different chemical characteristics, such as hydrophobicity, polarity, and/or aromaticity. It was found that there are difficulties in predicting the adsorption of an analyte in a specific MOF material. Among the evaluated MOF materials, MIL-53(Al) showed the best adsorption characteristics and was finally chosen (Rocío-Bautista et al. 2018).

MIL-53 has been also used for the preconcentration of phenolic compounds of various aqueous samples (waste, river, sea, lake, drinking, treated and tap water samples) prior to HPLC-PDA analysis. The material was functionalized with amine groups and used for the d-SPE of eight United States Environmental Protection Agency’s priority phenols (Boontongto et al. 2018). The same MOF has been

Table 2 Applications of MOFs for the d-SPE of organic compounds from environmental samples

Analyte	MOF	Matrix	Detection	Recovery (%)	LOD (ng mL^{-1})	Reference
Parabens	HKUST-1	Water, urine and cosmetic creams	HPLC-PDA	80.3	0.1	(Rocío-Bautista et al. 2015)
PAHs, hormones, drugs, disinfectants	MIL-53(Al)	Water	HPLC-PDA and HPLC-MS	On average 109 (HPLC-PDA) and 105 (HPLC-MS)	Down to 0.040 (HPLC-PDA) and 0.013 (HPLC-MS)	(Rocío-Bautista et al. 2018)
Phenolic compounds	MIL-53(Al)	Water	HPLC-PDA	72.3–111.4	4–13.3	(Boontongto et al. 2018).
Estrogens and glucocorticoids	MIL-53(Al)	Water and urine	UHPLC-MS/MS	80.6–98.4	0.0015–1.0	(Gao et al. 2018)
PBDEs	Cd-based MOF	Water	GC-MS/MS	82.5–104.6	0.08×10^{-3}–0.15×10^{-3}	(Su et al. 2015)
Plasticizer Compounds	Zn(II)-based MOF	Water	GC-FID	88–110	0.2–0.7	(Tahmasebi et al. 2016)
Endocrine disruptors	MIL-101	Water	GC-MS	70.7–119	0.006–0.023	(Huang and Lee 2015a)
Phenoxycarboxylic acids	MIL-101	Water	UHPLC-MS/MS	95.3–105.5	0.18×10^{-3}–0.88×10^{-3}	(Ji et al. 2019)
Thiols	MOF-5	Water	HPLC-FLD	86.6–98.5	17.1 pmol L^{-1}	(Lv et al. 2016)
Nitrophenols	UiO-66	Wastewater	HPLC-UV	91–106	0.5	(Salimi et al. 2018)
Neonicotinoid insecticides	UiO-66	Water	HPLC-MS/MS	73.7–119.0	0.02–0.4	(Cao et al. 2018)
Nitrobenzenes	UiO-66-NH2	Water	HPLC-PDA	85.2–104.5	0.72 to 1.90	(Dou et al. 2019)
Organophosphorus pesticides	Zn(II)-based MOF	Water, fruit juice	GC-FID	91.9–99.5	0.03–0.21	(Amiri et al. 2019)
Pesticides	Zn(II) benzenetricarboxylate	Industrial wastewater, domestic sewage, and tap water	HPLC-UV	88.6–116.1	0.20–1.60	(Wang et al. 2017)
Nitro-polycyclic aromatic hydrocarbons	In(III) sulfide@MIL-125(Ti)	Water	GC-MS	71.3–112.2	2.9×10^{-3} 83.0×10^{-3}	(Jia et al. 2018)
PAHs	IL-MIL-100(Fe)	Water, vegetables, fruit juices	GC-FID	97.0–103.5	2.0×10^{-3} –5.5×10^{-3}	(Nasrollahpour et al. 2017)
PAHs	JUC-48	Water	HPLC-PDA	85.8–109.55	0.068–50	(Xia et al. 2018)
PAHs	MOF@Graphene	Water	GC-FID	91.9–99.5	3.0×10^{-3}–10×10^{-3}	(Amiri et al. 2019a)

successfully employed for the d-SPE of estrogens and glucocorticoids from water and urine samples prior to UHPLC-MS/MS determination (Gao et al. 2018). Su et al. (2015) designed and used a cadmium(II)-based MOF for the d-SPE of polybrominated diphenyl ethers (PBDEs) from environmental water sample prior to their detection by GC-MS/MS. The MOF material was synthesized by mixing cadmium nitrate hexahydrate, [5-(1-carboxyethoxy) isophthalic acid and 4,4′-bipyridine. Tahmasebi et al. (2016) developed a Zn(II)-based metal-organic framework and used it as an efficient d-SPE sorbent for preconcentration of plasticizer compounds. The MOF was employed for the sample preparation of water samples prior to analysis by gas chromatography-flame ionization detector (GC-FID).

The metal-organic framework MIL-101 has been employed for d-SPE of endocrine disruptors from water samples after surface modification. After the extraction process, the mixture was centrifuged and the extracts were dried and derivatized with N-methyl-N-(trimethylsilyl)trifluoroacetamide and analyzed by GC-MS (Huang and Lee 2015a). MIL-101 has been successfully applied for the d-SPE of phenoxy carboxylic acids from environmental water samples prior to UHPLC-MS/MS analysis (Ji et al. 2019).

In 2016, Lv et al. (2016) used MOF-5 for the d-SPE of thiols after their reaction with carbazole-9-ethyl-2-maleimidefrom wastewater samples prior to their HPLC-fluorescence detection (HPLC-FLD) analysis. The HPLC-FLD method showed high selectivity and low limits of detection.

Recently, Salimi et al. (2018) synthesized and used a UiO-66 after functionalization with amino group for the d-SPE of selected nitrophenols prior to HPLC-UV analysis. In this case, centrifugation was chosen for the phase separation and the method was successfully applied for the analysis of environmental water samples. UiO-66 has been also used for the d-SPE of neonicotinoid insecticides in water samples prior to HPLC-MS/MS analysis (Cao et al. 2018). In this case, the sorbent was found to be reusable for at least 10 times. Amino group–functionalized UiO-66 (UiO-66-NH_2) has been employed for the d-SPE of nitrobenzenes from water samples (Dou et al. 2019). After 5 cycles of adsorption and desorption, no significant loss of extraction efficiency was observed.

A zinc-based metal-organic framework with histamine as an organic linker was used for the dispersive solid-phase extraction of organophosphorus pesticides in water and fruit juice samples prior to GC-FID detection (Amiri et al. 2019a). The MOF was prepared with the solvothermal approach by mixing zinc chloride and histamine dihydrochloride in an autoclave at 100 °C for 48 h. The developed method showed good selectivity and sensitivity and reusability (up to 8 times). Figure 4 shows the steps of the sample preparation procedure.

In 2017, Wang et al. synthesized a Zn(II) benzenetricarboxylate metal-organic framework with chrysanthemum-like structure. The novel sorbent was used for the extraction of pesticides from industrial wastewater, domestic sewage, and tap water prior to HPLC-UV analysis (Wang et al. 2017).

Jia et al. (2018) synthesized a core–shell In(III) sulfide@MIL-125(Ti) nanocomposite through a solvothermal method and used it as an adsorbent for the d-SPE of nitropolycyclic aromatic hydrocarbons. The material was prepared by adding indium nitrate and carbon disulfide together with thioacetamide and heating at 150 °C for 12 h in an autoclave. The novel sorbent was successfully used for the sample preparation of water samples prior to GC-MS analysis and it was found to be reusable for 50 times.

Nasrollahpour et al. (2017) used an ionic liquid-modified MOF (IL-MIL-100(Fe)) for the vortex-assisted d-SPE of PAHs prior to their measurement by GC-FID. For this purpose, the initially synthesized MIL-100(Fe) nanoparticles were treated with 1-butyl-3-methylimidazolium chloride at room temperature for 15 h under stirring. The sorbent was successfully employed for the sample preparation of environmental water, vegetables, and fruit juices.

A cadmium biphenyl-4,4′-dicarboxylate MOF (JUC-48) has been also employed for the d-SPE of PAHs from environmental water samples. The analytes were further separated and detected by HPLC-PDA. It was observed that there was a negative relationship between extraction capacity and molecule size (Xia et al. 2018). Hybrid nanocomposites prepared from MOF-199(Cu) and graphene or fullerene have been evaluated as adsorbents for the d-SPE of PAHs. The MOF-graphene nanocomposite showed the highest adsorption affinity and durability and was employed for the sample preparation of water samples prior to GC-FID detection (Amiri et al. 2019).

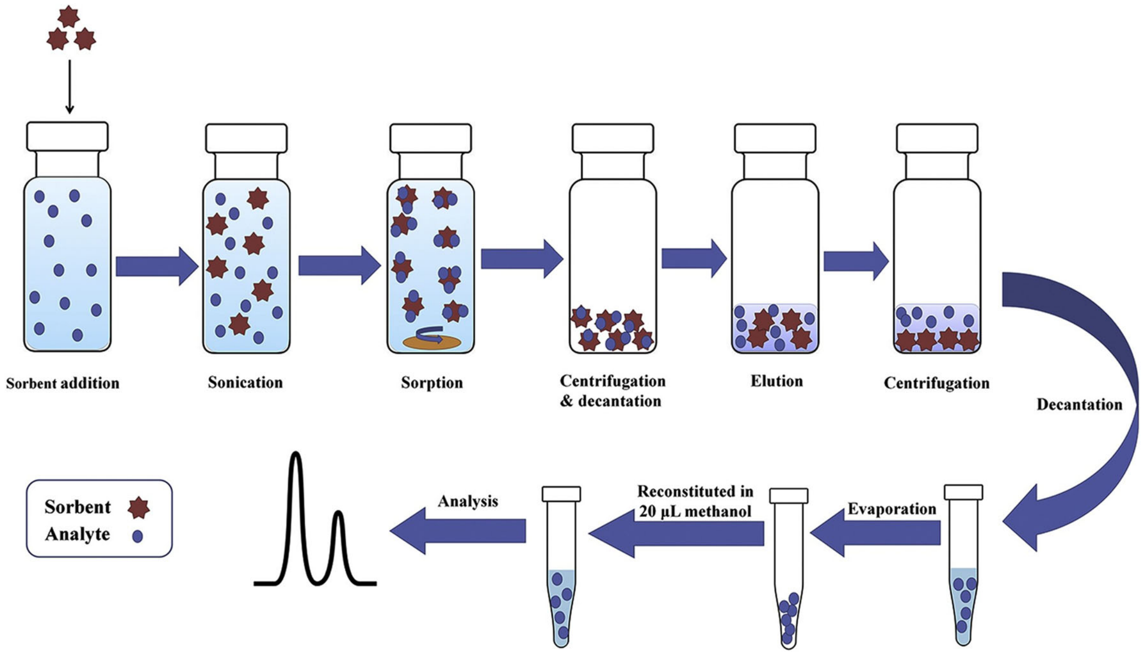

Fig. 4 Steps of the d-SPE of organophosphorus pesticides with zinc-based MOF. Reprinted from (Amiri et al. 2019a), Vol 1597, Amiri et al., Synthesis of a zinc-based metal-organic framework with histamine as an organic linker for the dispersive solid-phase extraction of organophosphorus pesticides in water and fruit juice samples, Page 40, Copyright (2019), with permission from Elsevier

In conclusion, MOFs have been employed for the d-SPE of a wide variety of organic compounds from environmental matrices providing extraction recoveries higher than 70.7%. However, only a few of the examined MOFs were found to be reusable after adsorption and desorption of the target analytes. In particular, UiO-66 and amino-functionalized UiO-66 were found to be reusable for at least 10 and 5 times, respectively, due to the good stability of UiO-66 in aqueous solutions. Moreover, a core–shell In(III) sulfide@MIL-125(Ti) nanocomposite exhibited excellent reusability (at least 50 times). Regarding the other MOFs that were used in d-SPE technique, no reusability data were provided, which is a limitation of these developed sorbents.

Solid-phase micro extraction

Since the development of the SPME by Janusz Pawliszyn in 1989, a lot of research has been done in terms of developing novel coating materials to fabricate efficient and robust SPME fibers. Various MOF materials have been used to develop novel SPME fibers, showing many advantages. Physical deposition, sol–gel technique, chemical bonding, and electrochemical deposition are the most popular techniques that are employed for the fabrication of coated fibers (Ghaemi et al. 2014). Table 3 summarizes the applications of MOFs for the SPME of organic compounds from environmental samples.

Cui et al. (2009) developed an in situ hydrothermal growth of MOF 199 films on stainless steel fibers for SPME of gaseous benzene homologs prior to GC-FID detection. A stainless steel wire was etched with hydrofluoric acid and dipped in an autoclave in which a solution of copper nitrate trihydrate in water and a solution of trimesic acid in ethanol were added. The autoclave was heated at 120 °C for 8 h. After drying, the fiber was used to extract the benzene homologs from air samples. Compared to the commercial polydimethylsiloxane (PDMS) and polydimethylsiloxane/divinylbenzene (PDMS/DVB), the novel MOF 199 fibers showed excellent performance.

Shang et al. (2014) used a SPME fiber coated with UiO-66 for the preconcentration of polar phenols from water samples. For the fabrication of the SPME fiber, a physical adhesion method was chosen, using epoxy resin glue. The novel SPME fiber showed good thermal stability and chemical stability in acidic and alkali solutions and was successfully used for the preconcentration of phenols prior to their determination by GC-FID.

Two years later, the same MOF material was used as fiber coating for the SPME of PAHs from water and soil samples prior to GC-MS analysis. In that case, the MOF-coated fiber was prepared with an in situ solvothermal synthesis procedure. It was found that the chemical bonding can dramatically improve the stability and lifetime of the SPME fibers (Gao et al. 2016).

Zhang et al. (2018a) developed a Ni-Zn MOF-C_3N_4 nanoflowers for solid-phase microextraction of PAHs from water and soil samples. For this purpose, MOF-5 was synthesized and doped with Ni ions in order to trigger the formation of crystal structure and to increase the metal active sites. Afterwards, hydrophobic carbon nitride was introduced through chemical bonds with nickel. The SPME fiber was synthesized by using the in situ solvothermal approach, showing good moisture and acid stability. The novel fiber was used for the preconcentration of PAHs from water and soil samples by SPME-GC-MS analysis.

Zhang et al. (2014) manufactured a PDMS/MIL-101-coated fiber via through sol–gel technique and used it for the preconcentration of PAHs prior to GC-MS analysis. For this purpose, a stainless steel wire was treated with hydrofluoric acid. A sol-solution of the MOF material, methyltrimethoxysilane, dichloroethane, OH-PDMS, and 95% TFA/water was prepared, and the wire was dipped into it for 1 min. The coated wire was dried at 60 °C and the coating procedure was repeated thrice. HKUST-1 metal-organic framework has been also employed as coating material to manufacture SPME fibers for the extraction of PAHs from environmental water analysis (Sun et al. 2019).

Wang et al. (2015) fabricated MOF-177-coated stainless steel SPME fibers by an adhesive method and used them for the enrichment of polychlorinated biphenyls and poly cyclic aromatic hydrocarbons from environmental water samples. For this purpose, silicone sealant diluted with n-hexane was used. The developed fiber showed good stability and long lifetime. The same working group employed the MOF-177-coated SPME fibers for the HS-SPME of phenols from environmental water samples prior to their separation and determination with GC-MS. Compared to the commercial PDMS, PDMS/DVB, and polyacrylate (PA) coatings, the MOF-177 showed higher extraction efficiency (Wang and Lei 2017).

In 2014, Wu et al. synthesized MIL-88B, with nanosized bipyramidal cages and large surface area, and used it for SPME of polychlorinated biphenyls (PCBs) prior to their determination by GC-MS. For the fabrication of the SPME fiber, a stainless steel wire was treated with aqua regia and the coating was prepared with an in situ hydrothermal method by mixing iron chloride hexahydrate and terephthalic acid with methanol and sodium hydroxide in a Teflon-lined bomb in which the wire was adjusted. The developed method was successfully applied for the analysis of water and soil samples (Wu et al. 2014).

Zheng et al. (2014) fabricated an IRMOF-3@ILs/PDMS-coated SPME fiber for the extraction of PAHs from environmental water samples prior to GC-MS analysis. The IRMOF-3 coating was protected with ionic liquids (ILs) and PDMS in order to create a novel material with superior humidity and thermal resistance. Zinc nitrate hexahydrate and 2-aminoterephthalic acid were used to synthesize the MOF

Table 3 Applications of MOFs for the SPME of organic compounds from environmental samples

Analyte	MOF	Matrix	Detection	Recovery (%)	LOD (ng L^{-1})	Reference
Gaseous benzene homologs	MOF 199	Indoor air	GC-FID	87–106	8.3–23.3	(Cui et al. 2009)
Polar phenols	UiO-66	Water	GC-FID	80–115	110–1230	(Shang et al. 2014)
PAHS	UiO-66	Water	GC-MS	83.8–116.7	0.28–0.60	(Gao et al. 2016)
PAHs	Ni-Zn MOF-C_3N_4	Water, soil	GC-MS	82.9–109.2	0.1–3.0	(Zhang et al. 2018a)
PAHs	MIL-101	Water	GC-MS	78.2–110.3	> 4.0	(Zhang et al. 2014)
PAHs	HKUST-1	Water	GC-MS	80.8–114.1	0.12–9.9	(Sun et al. 2019)
PAHs and polychlorinated biphenyls	MOF-177	Water	GC-MS	81.8–113	0.69–4.42	(Wang et al. 2015)
Phenols	MOF-177	Water	GC-MS	84.5–98.6	15–43	(Wang and Lei 2017)
Polychlorinated biphenyls	MOF-88	Water, soil	GC-MS	79.7–103.2	0.45–1.32	(Wu et al. 2014).
PAHs	IRMOF-3@ILs/PDMS	Water	GC-MS	78.2–114	12.0–15.4	(Zheng et al. 2014)
BTEX	Cd(II)-MOF	Water	GC-MS	82.61–102.06	1–10	(Li et al. 2014b)
BTEX	MIL-101	Water	GC-MS	80.0–113	0.32–1.7	(Xie et al. 2015)
PAHs	MIL-101	Water	GC-MS	84.8–106	0.12–2.1	(Xie et al. 2015)
VACs	MIL-101	Water	GC-MS	76.4–116.1	1–5	(Zang et al. 2015)
Nitrobenzenes	UiO-67	Water	GC-MS	74.0–102	5–10	(Zang et al. 2016)
PAHs	Al-MOF	Water, soil	GC-MS	72.4–108.0	5.0–20 (30–90 ng g^{-1} for soil)	(Zhang et al. 2015b)
PAHs	MIL-53(Al)	Water	GC-MS/MS	75.7–125.8	0.10–0.73	(Chen et al. 2012)
PAHs	Bio-MOF-1	Water	GC-FID	80–115	20–5570	(Huo et al. 2016)
PAHs, OCPs	Bio-MOF-10	Water	GC-FID	79.8–110.8	0.23–2.3	(Liu et al. 2015a)
Nitrated PAHs	Zr-based porphyrinic MOF	Water, atmospheric particulate matter, soil	GC-MS	81.2–113	0.10–20	(Li et al. 2017)
Polychlorinated biphenyls	PDA-MIL-53(Fe)	Soil	GC-MS	92.4–97.1.	50–90 pg g^{-1}	(Lv et al. 2017).
OCBs	MIL-53(Al)	Water	GC-MS	77.4–117	0.051–0.97	(Xie et al. 2017)
SMs	MIL-53(Al)	Water	GC-MS	80.3–115	0.025–0.83	(Xie et al. 2017)
PAHs	Ytterbium-based MOF	Water, soil	GC-MS	69.3–114.4	0.07–1.67	(Li et al. 2015)
BTEX	Tri-metal MOF	Water	GC-MS	80.8–119.5	0.13–0.88	(Liu et al. 2017b)
Trihalomethanes and halonitromethanes	MIL-96	Water	GC-MS	81.0–109.9	3–11	(Zhang et al. 2018b)
Odorous organic contaminants	MOF-74-C	Water	GC-MS	90.1–107.3	0.01–100	(Wei et al. 2019)
Penicillins	MIL-101(Cr)–Polymeric Monolith	Water	CEC-UV	63–96.2	1.2–4.5	(Lin et al. 2014)
Phenol compounds	MOF-5/periodic mesoporous silica	Water	GC-MS	Not available	0.01–3.12	(Abolghasemi et al. 2015)

Table 3 (continued)

Analyte	MOF	Matrix	Detection	Recovery (%)	LOD (ng L^{-1})	Reference
PAHs	MON-MOF	Water, smoked meat	GC-MS/MS	71.2–109.7	0.03–0.30	(Jia et al. 2016)
PAHs	Cu 1,4--benzenedicarboxylate MOF	Water	GC-MS	81.7–116	0.11–2.10	(Wei et al. 2017)
Chlorobenzenes	MOF/PANI	Water	GC-MS	92–98	0.2	(Bagheri et al. 2016)
Organochlorine pesticides	MOF-199/GO	Water, soil	GC-ECD	> 72.2	2.3–6.9	(Zhang et al. 2013)

material and the chemical bonding method was employed to fabricate the SPME fibers. The coated fibers were dipped in 1-buty-3-methylimidazolium-based ionic liquids to age thermally and were immersed in silicone sealant and PDMS for further protection.

Li et al. (2014b) manufactured quartz SPME fibers coated with a cadmium-based MOF material with 4-amino-3,5-bis(4-pyridyl-3-phenyl)-1,2,4-triazole ligand. The Cd(II)-MOF thin films were grown in situ on a quartz fiber that was primarily treated with hydrofluoric acid and then with a mixture of hydrogen peroxide and sulfuric acid in order to generate a hydroxylated surface. Subsequently, the fiber was aminated by immersing an EtOH solution of 3-aminopropyl-triethoxysilane and the fiber was carboxylated after treatment with an EtOH solution of succinic anhydride. Finally, the fiber was dipped into a solution of dichloromethane, methanol, and cadmium perchlorate at room temperature for 10 h. Compared to the commercial PDMS and PDMS/DVB fibers, the novel fibers showed higher extraction efficiency.

Xie et al. (2015) manufactured MIL-101(Cr)-coated SPME fibers and used them for the extraction of benzene, toluene, ethyl-benzene and xylenes (BTEX), and PAHs from environmental water samples prior to their determination by GC-MS. Silicon sealant diluted with toluene was used for the coating of MOF onto the surface of a stainless steel wire. The novel fiber was found to be very stable, while it provided high extraction efficiency. Figure 5 shows the scanning emission spectroscopy (SEM) images of the coated SPME fibers at × 500 (a), × 1500 (b), × 3000 (c), and × 8000 (d) magnification. MIL-101-coated fibers have been also employed for the SPME of seven volatile aromatic compounds (VACs) from tap and lake water samples prior to their determination with GC-MS. In this case, the fibers were prepared by the sol–gel technique by mixing the MOF material with dichloromethane, methyltrimethoxysilane, and hydroxy-terminated polydimethylsiloxane. Compared to the commercial PDMS and PA fibers, the developed fibers exhibited higher extraction efficiency (Zang et al. 2015).

The same working group used the sol–gel coating technique for the preparation of a UiO-67-coated SPME fibers onto stainless steel wires. The obtained fiber coating had a rough, porous, and wrinkled structure. The novel fibers were successfully employed for the determination of five nitrobenzenes from water samples prior to GC-MS detection, providing good extraction efficiency and thermal efficiency (Zang et al. 2016). The sol–gel coating technique was also employed to created SPME fibers coated with nanoporous carbon derived from an aluminum-based MOF synthesized from aluminum chloride hexahydrate and 2-aminoterephthalic acid. The SPME fibers were successfully applied for the extraction of PAHs from water and soil samples prior to their determination by GC-MS. High mechanical and thermal stability was observed and the material could be used at least 160 times (Zhang et al. 2015b).

Different MIL-53(Al, Cr, Fe) fibers have been evaluated as coating materials for the solid-phase microextraction of 16 PAHs from water samples prior to their determination by GC-MS/MS. Etched stainless steel wires were coated with the different MOFs by the adhesive method and with the assistance of epoxy resin glue. The highest extraction efficiency was observed with the MIL-53(Al) fiber, which was chosen for further optimization of the whole SPME process (Chen et al. 2012).

Huo et al. (2016) used a dual-ligand MOF (bio-MOF-1) film that was in situ hydrothermally grown on stainless steel fiber for the SPME of PAHs from environmental water samples. Bio-MOFs can be MOFs containing biomolecule or MOFs that have direct application across medicine and biology (Giliopoulos et al. 2020). For the fabrication of the SPME fiber, adenine, 4,4′-biphenyl dicarboxylic acid, zinc acetate dihydrate, nitric acid DMF, and water were added into a Teflon vial in which a hydrofluoric acid-etched stainless steel wire was immersed. Subsequently, the mixture was heated at 130 °C for 24 h. The novel fibers were successfully applied for the SPME of PAHs from river and wastewater prior to their separation and determination by GC-FID.

Liu et al. (2015a) reported the successful utilization of the stepwise ligand exchange approach for the improvement of adsorption ability of a series of bio-MOF 100–102 for the fabrication of coated SPME fibers. For this purpose, bio-MOF-101 was synthesized with the solvothermal approach

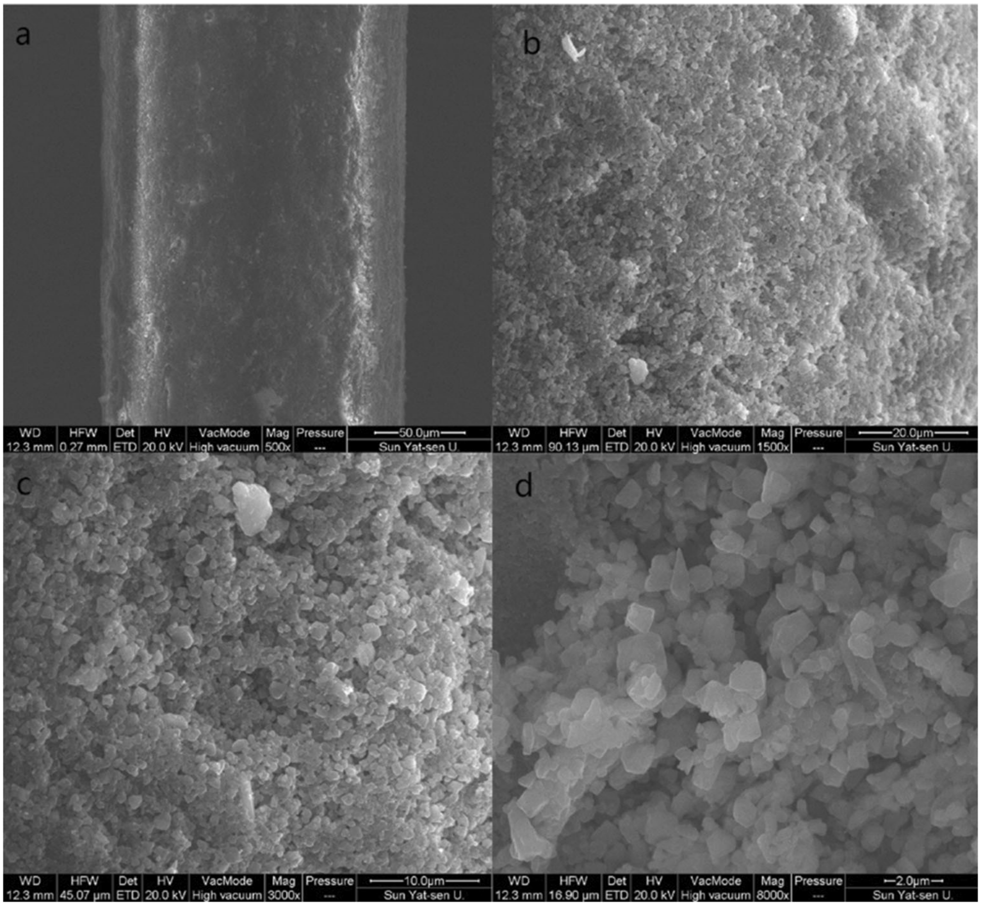

Fig. 5 SEM images of the coated MIL-101(Cr) SPME fibers at × 500 (**a**), × 1500 (**b**), × 3000 (**c**), and × 8000 (**d**) magnification. Reprinted from (Xie et al. 2015), Vol 853, Xie et al., Preparation and characterization of metal-organic framework MIL-101(Cr)-coated solid-phase microextraction fiber, Page 306, Copyright (2015), with permission from Elsevier

by mixing zinc acetate, adenine, and 2,6-naphthalene dicarboxylic acid in DMF. With the ligand exchange approach, bio-MOF-100 and bio-MOF-102 were synthesized with 4,4′-biphenyldicarboxylic acid and 4,4′-azobenzenedicarboxylic acid ligands, respectively. Silicone sealant diluted in o-xylene was used to prepare the SPME fibers. The fibers were used to extract PAHs and organochlorine pesticides (OCPs) from environmental water. Bio-MOF-102 showed the best extraction efficiency, which was directly relevant to their pore volumes of the examined MOFs.

The in situ hydrothermal approach was used to fabricate zirconium-based porphyrinic metal-organic framework coating onto the surface of stainless steel fibers. The coated fibers were successfully employed for the SPME of nitrated PAHs from environmental water, atmospheric particulate matter, and soil samples prior to GC-MS analysis (Li et al. 2017).

In 2017, Lv et al. used a poly-dopamine-based MOF coating (PDA-MIL-53(Fe)) for the ultrasound-assisted SPME of polychlorinated biphenyls from soil samples prior to their determination by GC-MS. MIL-53(Fe) is thermally stable; however, a modification is required in order to enhance its water stability and to manufacture coated SPME fibers. Polydopamine was used for the modification since it is an environmentally friendly material able to adsorb PCBs. The novel fiber could be used for at least 50 times, providing good stability (Lv et al. 2017). The same year, Xie et al. fabricated an amine-functionalized MIL-53(Al)-coated stainless steel fiber for the SPME of synthetic musks and OCPs from water samples. The fibers were also prepared with the adhesive approach using a multi-functional silicone sealant and exhibited higher extraction efficiencies compared to the commercial PDMS, PDMS/DVB, and PA coatings while showing good thermal and chemical stability (Xie et al. 2017).

An ytterbium-based MOF has been also employed for the preconcentration of PAHs from environmental samples. The novel material was grown in situ at the surface of a stainless steel SPME fiber. For this purpose, hydrochloric acid was used to harshen the surface of the fiber. Subsequently, the fiber was placed in a Teflon-bomb containing ytterbium nitrate, 2,2′-bipyridine, and 5-aminoisophthalic acid in water and the mixture was heated at 160 °C for 72 h (Li et al. 2015).

Liu et al. synthesized a tri-metal centered MOF and used it as coating for SPME fibers. For the optimization of the coating, different proportions of Ga, Al, and In atoms in the MOF were evaluated. The coating was prepared by the adhesive approach using a silicon sealant. For this purpose, the sealant was diluted in toluene and a washed stainless steel wire was dipped into the solution. After wiping the excess of the adhesive media, the wire was rotated into the MOF material. Finally, the fiber was cured at 150 °C for 30 min. The novel fibers were successfully fabricated for the determination of BTEX from environmental water samples and showed better extraction efficiency than the commercially available PDMS coated fibers (Liu et al. 2017b).

A MIL-96-coated fiber was fabricated for the SPME of trihalomethanes and halonitromethanes from water samples. MIL-96 was initially synthesized by mixing aluminum nitrate nonahydrate and 1,3,5-benzenetricarboxylic acid with water in an autoclave and heating at 200 °C for 24 h. Accordingly, a stainless steel wire was etched with hydrofluoric acid, immersed into silicone glue, and finally dipped into the MOF material. The novel fibers were compared with commercially available CAR/PDMS and DVB/CAR/PDMS fiber and resulted in higher peak areas for the examined analytes. Furthermore, the MIL-96 material helped to overcome thermal desorption of the analytes (Zhang et al. 2018b).

Odorous organic contaminants have been extracted from environmental water with coated MOF-74-C. The MOF material was synthesized from nickel nitrate hexahydrate and dihydroxyterephthalic acid and was subsequently treated with furfuryl alcohol. The novel material was ideal for the extraction of small molecules (Wei et al. 2019).

A novel hybrid MIL-101(Cr)-polymeric monolith-coated fiber has been also employed for the extraction of penicillins prior to their determination by capillary electrochromatography (CEC) coupled with UV detector. In this case, the coating was prepared by using ethylene dimethacrylate (EDMA), butyl methacrylate (BMA), and an imidazolium-based IL as porogenic solvent followed by microwave-assisted polymerization with the addition of 25% the sorbent. The novel sorbent was successfully used for the analysis of water samples (Lin et al. 2014).

Another example of a hybrid material that has been evaluated as a novel coating for SPME fibers was reported by the research group of Abolghasemi. In this case, a MOF-5 material was confined in periodic mesoporous silica in order to enhance the hydrostability of the sorbent. The fibers were successfully employed for the preconcentration of phenolic compounds from water samples prior to GC-MS analysis (Abolghasemi et al. 2015).

In order to improve the water stability of MOFs, Jia et al. used microporous organic network (MON) for coating MOFs (MIL-101 and MOF-5) through a Sonogashira coupling reaction. The hybrid material was used as coating for SPME fibers. High efficiency was observed since the MON coating was able to hinder the competitive moisture adsorption into the MOF material. The moisture resistance and stability of the fiber were significantly improved and the fibers were employed for the extraction of PAHs from wastewater samples and smoked meat samples prior to their determination by GC-MS/MS (Jia et al. 2016).

In 2017, Wei et al. fabricated polymeric composite incorporating metal-organic framework nanosheets to make coated SPME fibers for the extraction of PAHs from water samples. For this purpose, a copper 1,4-benzenedicarboxylate MOF was synthesized and dispersed into chloroform. Subsequently, commercial polyimide resin was added and the resultant suspension was stirred. The novel SPME sample preparation technique resulted in low LODs and LOQs, and wide linear range as well as satisfactory recovery values (Wei et al. 2017).

Bagheri et al. (2016) evaluated the use of metal-organic framework-polyaniline (MOF/PANI) nanocomposite as a fiber coating for SPME of chlorobenzenes from water samples prior to their determination by GC-MS. The coating was electrodeposited onto the surface of stainless steel wires. The MOF material was prepared from a cadmium salt and 2,6-naphthalene dicarboxylic acid in DMF with electropolymerization under a constant deposition potential. The coating was compared to PANI coating and showed superior extraction efficiency. In addition, it was stable at temperature as well as at various chemicals and mechanical factors.

A hybrid MOF-199/graphite oxide coating for SPME fibers was evaluated for the preconcentration of organochlorine pesticides prior to GC-ECD detection. Due to the presence of carboxyl groups in both materials, the desired fiber was fabricated by chemical bonding using 3-amino-propyltriethoxysilane (APTES) as cross-linking agent. The developed method was successfully applied to the analysis of water and soil samples. Compared to MOF-199 fiber and GO-fiber, the hybrid MOF-GO fiber showed great extraction efficiency and thermal stability, while it can be reused for more than 140 times (Zhang et al. 2013).

In conclusion, MOF materials offer another interesting alternative solution to conventional commercially available SPME fibers (e.g., PDMS, PDMS/DVB, PA). Due to the strong π–π interactions between MOFs and organic pollutants, higher extraction efficiencies and selectivity and can be achieved with MOF-coated SPME fibers. Moreover, good chemical and mechanical stability of the fiber has been reported.

Stir bar sorptive extraction

Stir bar sorptive extraction is a sample preparation technique based on a coated bar that is directly introduced in sample and extraction takes place under sample stirring. PDMS was the first coating material that was employed in SBSE (Baltussen et al. 1999). Nowadays, various MOFs have been used for coating SBSE prior to the sample preparation of environmental samples.

Hu et al. (2013) developed a stir bar sorptive phase extraction method using a PDMS/MOF coated stir bar for the determination of estrogens in environmental water samples prior to

HPLC-UV analysis. For this purpose, three different MOF materials, i.e., MOF-5, MOF-199, and IRMOF-3, were evaluated and the PDMS/IRMOF-3 was finally chosen. IRMOF-3 was prepared from 2-amino terephthalic acid and zinc acetate dihydrate. The novel bars were constructed using the sol–gel technique. The method was successfully applied to the sample preparation of water samples and showed satisfactory recovery values (72.2–124.4%) and low LODs (0.15–0.35 ng mL^{-1}). No significant loss of extraction performance was observed after 35 adsorption-desorption cycles.

Xiao et al. (2016) fabricated a PDMS/MIL-101-Cr-NH_2 stir bar and used for the SBSE of organophosphorus pesticides from environmental water samples prior to gas chromatography-flame photometric detection (GC-FPD). The sorbent was synthesized via a direct hydrothermal method and was coated onto the surface of a glass bar with the sol–gel technique. With the proposed sample preparation techniques, LODs ranged between 0.043 and 0.085 ng mL^{-1}, while recoveries were 80.0–115%. The stir bar exhibited good reusability (> 50 times).

Furthermore, a PDMS/AL-MIL-53-NH_2-coated stir bar was used for the SBSE of PAHs prior to their separation and detection by HPLC-FLD. The stir bars were prepared through the sol–gel method and were successfully applied for the sample preparation of environmental water samples. The stir bar was found to be reusable for at least 40 times. LODs were 0.05–2.94 ng mL^{-1} and recoveries were in the range 71.5–122%. (Hu et al. 2014).

A PDMS/MIL-100(Fe)-coated stir bar was also prepared by the sol–gel technique and used for the SBSE of triazines from environmental water samples prior to HPLC-UV determination (Lei et al. 2017). The SBSE method provided high enrichment factors (51.1–102), low LODs (0.021–0.079 ng mL^{-1}), and good recovery values (94–118%). The stir bar was found to be reusable for at least 50 extraction cycles. The cross-section SEM image of the PDMS/MIL-100(Fe) coating and the scanning emission spectroscopy image of PDMS/MIL-100(Fe) coating at 200 magnifications are shown in Fig. 6.

As a result, MOFs can be successfully used as coatings for PDMS-coated stir bars through the sol–gel technique. Recovery values were above 71.5% for a wide variety of organic compounds including estrogens, PAHs, triazines, and organophosphorus pesticides. The developed SBSE bars coated with MOFs exhibited great aqueous and mechanical stability since they were found to be reusable for at least 35–50 times, offering an interesting alternative to the conventional PDMS stir bars.

Other extraction techniques

Gu et al. (2010) synthesized MOF-5 and they used it for in-field sampling and preconcentration in combination with thermal desorption GC-MS for determination of atmospheric formaldehyde. The sorbent was placed in a tube and the air sample was pumped at a flow rate of 100 mL min^{-1} for 10 min. The MOF-5-packed tube could be used for at least 200 times and was successfully applied for the analysis of indoor and outdoor samples.

In 2015, Zhang et al. synthesized three different Ag(I)-organic frameworks and used them as sorbents for the for microextraction of polybrominated diphenyl ethers after their embedment into silica gels. The MOFs were prepared by mixing pyridine-3,5-dicarboxylic acid, silver nitrate, and acetonitrile:water solution with different *v*/*v* ratios. Subsequently, the different MOFs were dispersed in DMF and water and tetraethoxysilane, hydroxy-terminated-PDMS, and trifluoroacetic acid were added to create a sol–gel solution which was then cool and freeze-dried in order to form a silica gel. After optimizing the extraction parameters such as sorbent mass, water volume, temperature, extraction time, and back-extraction, the developed methods were validated and successfully applied for the sample preparation of soils. Detection of the target analytes was performed by GC-micro-cell electron capture detector (μ-ECD) (Zhang et al. 2015).

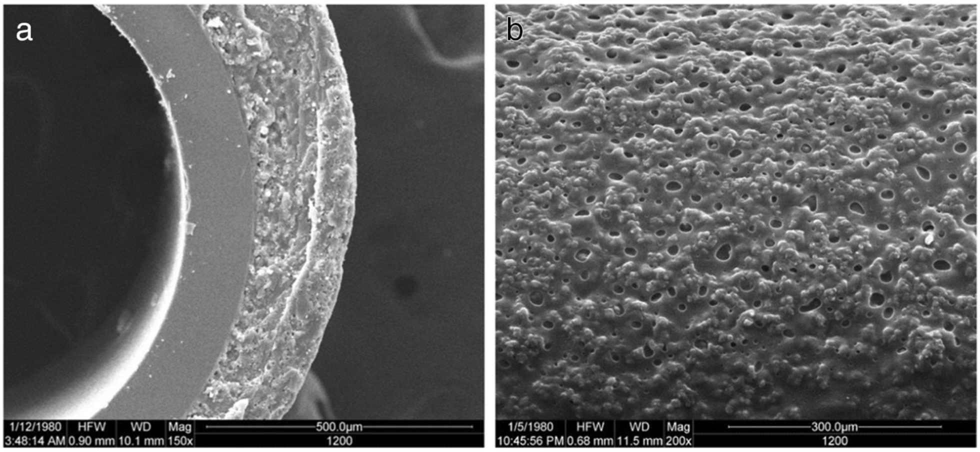

Fig. 6 SEM images of he cross-section of the PDMS/MIL-100(Fe) coating (**a**) and PDMS/MIL-100(Fe) coating at 200 magnifications (**b**). Reprinted from (Lei et al. 2017), Vol 175, Lei et al., Polydimethylsiloxane/MIL-100(Fe) coated stir bar sorptive extraction-high-performance liquid chromatography for the determination of triazines in environmental water samples, Page 162, Copyright (2017), with permission from Elsevier

MIL-53(Al) has been employed for the polymer monolith microextraction (PMME) based on capillary monolithic column of non-steroidal anti-inflammatory drugs from water and urine samples. In order to anchor the MOF sorbent onto the monolith, the capillary was silanized with γ-methacryloxypropyltrimethoxysilane. Accordingly, the capillary was filled with a mixture of butyl methacrylate, ethylene, dimethacrylate, 1-propanol, 1,4-butanediol, azobisisobutyronitrile, and the MIL-53(Al). Finally, polymerization was performed at 60 °C for 12 h. The target analytes were detected by a HPLC-PDA system and the monolith was found stable for 120 extraction cycles. Recovery values were 77.3–104% and LODs were 0.12–0.24 ng mL^{-1} (Liu et al. 2015).

Recently, Chen et al. synthesized a hybrid material by growing a covalent organic framework (COF) in situ on the surface of functionalized metal-organic framework MIL-68. The MOF material was obtained by mixing indium(III) nitrate and 2-aminoterephthalic acid and reacted subsequently with tris(4-formylphenyl)amine and tris(4-aminophenyl)amine to create the final hybrid COF. Accordingly, the nanomaterial was packed into a 200-μL pipette tip with both ends sealed by cotton. The packed column was used for the pipette tip-SPE of sulfonamides from environmental water, milk, and meat samples. For the sample preparation, the adsorbent was preconditioned with acetonitrile and water, the sample was loaded, and elution of the analytes was performed with acetonitrile. Among the benefits of the MOF@COF material were the high water stability, satisfactory recoveries (68.9–103.8%), low LODs (1 ng mL^{-1}), and good reproducibility (Chen et al. 2019).

In the same year, Hashemi et al. investigated the application of a cobalt-based MOF material for the pipette-tip SPE of organic dyes prior to their determination by HPLC-PDA. The MOF material was synthesized by mixing cobalt nitrate and 2,6-dicarboxylic acid in a Teflon reactor at 85 °C for 7 h. The technique was successfully applied for the analysis of seawater samples, providing low LODS (0.09–0.38 ng mL^{-1}), easy handling, and satisfactory recoveries (> 97%) (Hashemi et al. 2019).

Applications of ZIFs, MONTs, MAFs, and MOF-derived carbons in environmental sample preparation

Zeolitic imidazole frameworks (ZIFs) are a new subfamily of metal-organic frameworks that combine the benefits of both zeolites and MOFs. Various ZIFs have been synthesized and used for the sample preparation of environmental samples. Table 4 summarizes the applications of ZIFs, MONTs, MAFs and MOF-derived carbons for the sample preparation of environmental samples.

Zhang et al. (2016) used a zeolitic imidazolate framework (ZIF), for the MSPE of PAHs after its polydopamine-reinforced magnetization. The material was prepared with a solvothermal method, by mixing zinc nitrate hexahydrate and benzimidazole in DMF under sonication, followed by heating at 160 °C in an autoclave. The ZIF-7 material showed high porosity and surface areas, in addition to exceptional thermal and chemical stability. The novel sorbent was used for the sample preparation of air-water environment by GC-MS.

ZIF-7 and ZIF-11 have been also evaluated as SPE sorbents for the extraction of PAHs from environmental water samples with HPLC coupled with fluorescence detection. The two materials had the same organic linker and metal ion Zn^{2+}, but different structure; i.e., ZIF-7 was cubic and ZIF-11 had rhombic dodecahedron structure. ZIF-11 resulted in markedly better extraction efficiencies, low LOD values, and satisfactory extraction recoveries (Hu et al. 2014a).

Another type of ZIF materials, ZIF-8, was used as sorbent was packed in polypropylene membrane to construct a novel μ-SPE device for the sample preparation of aqueous samples for the determination of estrogens prior to analysis by UHPLC-MS-MS (Wang et al. 2013). ZIF-8 has been also used for the determination of phthalate esters in environmental water by SPE prior to HPLC-PDA analysis. The novel sorbent was modified by coating mercaptoacetic acids capped Fe_3O_4 nanoparticles with ZIF-8. For the MSPE procedure, the sorbent was mixed with the sample solution for 8 min under sonication and desorption was achieved with the addition of methanol under sonication for the same time span. The developed method showed great sensitivity, and ease of operational as well as satisfactory recovery and repeatability (Chen et al. 2013a).

ZIF-8 has been also used for the in-tube solid-phase microextraction of PAHs from environmental samples prior to HPLC-FLD analysis. A novel bio-inspired polydopamine method was developed in order to immobilize the material inside the chemical resistance poly-(ether ether ketone) (PEEK) tube for online SPME procedure. For this purpose, a layer of polydopamine was assembled inside the PEEK tube and the ZIF-8 nanoparticles were attracted and anchored onto the inner surface of tube. The novel ZIF-8-polydopamine-PEEK tube showed very good stability and high enhancement factors (Zhang et al. 2015a). Figure 7 shows the preparation of the ZIF-8 modified peek tube.

In 2016, Su et al. developed a core–shell MOF-titanium dioxide nanocomposite and used it as adsorbent in the MSPE of triazole fungicides from environmental water samples. For the synthesis of the sorbent, zinc nitrate hexahydrate and 2-methylimidazole were used and the ZIF-8 MOF was functionalized with $Fe_3O_4@SiO_2$. The obtained $Fe_3O_4@SiO_2@$ZIF-8 microspheres were mixed with tetrabutyl titanate and ethyl alcohol and sonicated. Subsequently, the mixture was heated at 160 °C for 15 h in an autoclave. The synthesized sorbent showed high extraction efficiency towards fungicides (Su et al. 2016).

Table 4 Applications of ZIFs, MONTs, MAFs, and MOF-derived carbons for the sample preparation of environmental samples

Analyte	Sorbent	Matrix	Sample Preparation	Detection	Recovery (%)	LOD (ng L^{-1})	Reference
PAHs	ZIF-7	Air, water	MSPE	GC-MS	> 82	0.71–5.79	(Zhang et al. 2016)
PAHs	ZIF-11	Water	SPE	HPLC-FLD	82.4–112.7	0.8–1.6	(Hu et al. 2014a)
Estrogens	ZIF-8	Water	µ-SPE	UHPLC-MS/MS	85.6–108.2	50–100	(Wang et al. 2013)
Phthalate esters	ZIF-8	Water	MSPE	HPLC-PDA	85.6–103.6	80–240	(Chen et al. 2013a)
PAHs	ZIF-8	Water	In-tube SPME	HPLC-FLD	82.5–98.6	0.5–5	(Zhang et al. 2015a)
Triazole fungicides	ZIF-8	Water	MSPE	HPLC-MS	90.2–104.2	0.19–1.20	(Su et al. 2016)
Triazine herbicides	ZIF-8	Water and gourd	MSPE	HPLC-PDA	80.3–120.6	20	(Jiao et al. 2016)
Endocrine disruptors	ZIF-90	Water	SPME	HPLC-UV	89–104	28.9–196	(Yu and Yan 2013)
Polychlorinated biphenyls	ZIF-90	Water, soil, and vegetable oil	SPME	GC-MS	85.9–105.8	0.0013–0.053	(Zhang et al. 2018)
PAHs	ZIF-8	Water	µ-SPE	GC-MS	98.0–106.5	2–12	(Ge and Lee 2011)
PAHs	ZIF-8	Water	SAEME-VA-µ-SPE	GC-MS	88.9–111	4–11	(Ge and Lee 2012)
PAHs	ZIF-8	Water	d-SPE	HPLC-FLD	66.7–121.2	0.1–1	(Liang et al. 2016)
Acidic drugs	ZIF-8	Water	SAEME-VA-µ-SPE	GC-MS	88.9–115.1	10–40	(Ge and Lee 2012a)
Tetracyclines	ZIF-8	Water and milk	On-line SPE	HPLC-PDA	70.3–107.4	1500–8000	(Yang et al. 2013a)
Tetracyclines	ZIF-8	Water	MSPE	UHPLC-MS	78.3–90.7	122 –143	(Liu et al. 2017)
Triazole Fungicides	ZIF-8	Water	MSPE	GC-MS/MS	83.4–98.3	80–270	(Huang et al. 2018)
Estrogens	ZIF-67	Wastewater	Magnetic dispersive µ-SPE	GC-MS	86–115	2200–3800	(González et al. 2016)
Dichlorodiphenyltrichloroethane and its metabolites	ZIF-8	Water	MSPE	GC-MS/MS	72.6–98.5	1.6–7.2	(Huang et al. 2019)
Sulfonamides, fluoroquinolones, trimethoprim	ZIF-9	Water	Binding gels	HPLC-MS/MS	> 97	1.0–18.0	(Ren et al. 2018)
Polychlorinated biphenyls	MONT	Water	SPME	GC-MS/MS	71.3–104	3.9×10^{-3}–21.7×10^{-3}	(Li et al. 2014)
Polybrominated diphenyl ethers	MONT	Water	d-SPE	GC-MS	80.5–119.2	0.08–0.22	(She et al. 2015)
Polychlorinated biphenyls	Fe_3O_4@Co-MONT	Water	MSPE	GC-MS	71.0–110.1	0.31–0.49	(Li et al. 2016a)
PAHs	MAF-66	Water and food samples	SPME	GC-FID	90–108.5	1–7.5	(Liu et al. 2019)
Chlorophenols	Zn/Co MOF derived carbon	Water	MSPE	HPLC-UV	83–114	0.1–0.2	(Li et al. 2016)
Organochlorine pesticides	Zn/Co MOF derived carbon	Water	MSPE	GC-MS	> 95.0	0.39–0.70×10^{-3}	(Liu et al. 2017a)

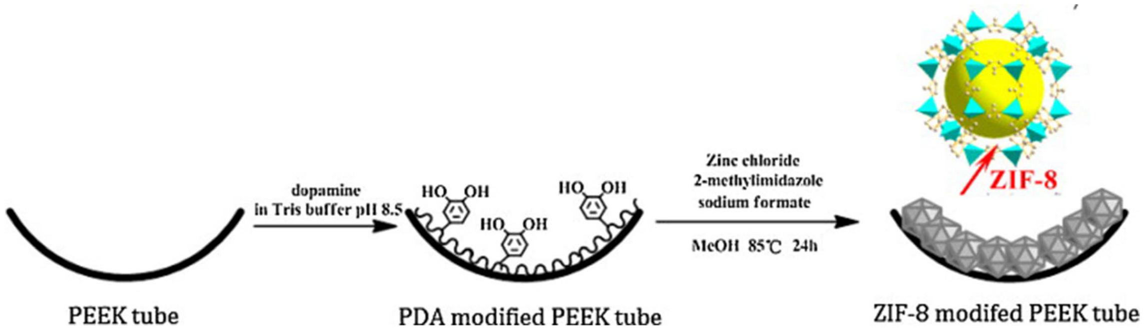

Fig. 7 Preparation of the ZIF-8 modified peek tube. Reprinted from (Zhang et al. 2015a), Vol 1388, Zhang et al., Polydopamine-based immobilization of zeolitic imidazolate framework-8 for in-tube solid-phase microextraction, Page 11, Copyright (2015), with permission from Elsevier

In the same year, Jiao et al. synthesized a Co-doped hierarchically porous carbon from Co/Zn-ZIF-8 and used it as an adsorbent for the MSPE of triazine herbicides from environment water and white gourd samples. The novel material was characterized by micro-, meso-, and macropores and it exhibited excellent adsorption capacity and easy magnetic separation (Jiao et al. 2016).

In 2013, Yu et al. fabricated ZIF-90-coated SPME fibers with covalent bonding and used them for the extraction of endocrine disrupting compounds from water samples. Initially, a silica fiber was heated and the formed hydroxyl groups on the fiber surface reacted with the ethoxy groups of APTES. Finally, the functionalized fiber was placed into a Teflon liner, and the amino groups reacted with the aldehyde groups of imidazolate-2-carboxyaldehyde to form the ZIF-90-coated fiber. The method was successfully applied for the sample preparation of water and soil samples prior to GC-FID analysis (Yu and Yan 2013).

In 2018, Zhang et al. compared various metal-organic frameworks such as ZIF-90 (Zn), MOF-199 (Cu), MIL-101 (Cr), and MOF-5 (Zn) for their effectiveness as coatings for SPME fibers for polychlorinated biphenyls. The most stable MOF among them was found to be ZIF-90 (Zn) and three different fiber preparation methods, i.e., chemical bonding method, adhesive method, and deposition method, were studied. Chemical bonding was proved to result in the most stable fibers and was finally selected. The method was applied to the analysis of water, soil, and vegetable oil (Zhang et al. 2018).

ZIF-8 has been used in the porous membrane-protected micro-solid-phase extraction of PAHs. The method was successfully applied for the GC-MS analysis of environmental water samples (Ge and Lee 2011). The same working group fabricated ZIF-8 for the sonication-assisted emulsification microextraction samples combined with vortex-assisted porous membrane-protected micro-solid-phase extraction (SAEME-VA-µ-SPE) of PAHs from water sample. The method was characterized as timesaving and highly efficient (Ge and Lee 2012). Subsequently, the same approach was implemented for the extraction of acidic drugs from environmental water samples (Ge and Lee 2012a).

PAHs were also extracted from environmental water samples with porous cellulose/ZIF-8 composite microspheres prior to their determination with HPLC-FLD. The sorbent was applied for the d-SPE of spring, river, and lake water samples and the whole methodology was characterized as simple and rapid (Liang et al. 2016).

In 2013, Yang et al. made stainless steel columns packed with ZIF-8 for the online SPE of tetracyclines from water and milk samples prior to HPLC-PDA determination (Yang et al. 2013a). In 2017, Liu et al. synthesized a magnetic modified core–shell ZIF (Fe_3O_4@ZIF-8) and used it for the extraction of tetracycline antibiotics from water samples prior to ultrahigh-pressure liquid chromatography-mass spectrometry (UHPLC-MS) analysis. The MSPE-UHPLC-MS provided lower LODs and higher simplicity (Liu et al. 2017).

A hybrid magnetic multiwalled carbon nanotube@polydopamine/ZIF-8 material has been used for the MSPE of triazole fungicides from environmental water samples. The extracts were analyzed by GC-MS/MS and the novel sorbent showed large total pore volume, and large surface area (Huang et al. 2018).

ZIF-67 was also used for the automated magnetic dispersive micro-SPE of estrogens from wastewater samples. The sorbent was synthesized and carbonized at 800 °C for 3 h and the magnetic-derived carbon was used for the sample preparation prior to derivatization and GC-MS determination (González et al. 2016).

Huang et al. (2019) used an ionic liquid-modified magnetic multiwalled carbon nanotube/ZIF-8 for the MSPE of dichlorodiphenyltrichloroethane and its metabolites from environmental water samples prior to GC-MS/MS analysis.

A ZIF-9-derived porous carbon was employed to create binding gels based on diffusive gradients in thin films for in situ measurement of antibiotics in waters. ZIF-9 was obtained by mixing cobalt nitrate hexahydrate and benzimidazole in DMF and heating at 130 °C for 48 h, while carbonization was performed at 800 °C for 5 h. Sulfonamides, fluoroquinolones, and trimethoprim were included in the study (Ren et al. 2018).

Li et al. (2014) evaluated the application of metal-organic nanotubes (MONTs) as coating materials for SPME fibers.

MONTs combine the excellent properties of MOFs and CNTs, such as a tunable pore size and high surface area, while they exhibit exceptional thermal and chemical stability. Silicone glue was used for the fiber coating. The novel SPME fiber was used for the preconcentration of polychlorinated biphenyls in the environmental samples prior to GC-MS/MS analysis. A porous lead(II)-based MONT was also used as an adsorbent for d-SPE of polybrominated diphenyl ethers from environmental water samples prior to GC-MS analysis. The novel sorbent showed significant potential in the analysis of organic pollutants at trace levels in complex matrices (She et al. 2015). A three-dimensional, echinus-like magnetic Fe_3O_4@cobalt(II)-based metal-organic nanotube yolk-shell microspheres (Fe_3O_4@Co-MONT) has been employed for the MSPE of polychlorinated biphenyls from environmental and biological samples. The novel material was synthesized by mixing 4,4′-biphenyldicarboxylic acid–modified magnetic nanoparticles, cobalt acetate tetrahydrate, 3,3′,5,5′-tetramethyl-4,4′-bipyrazole in DMF, and acetonitrile into a Teflon autoclave that was heated at 160 °C for 72 h. Figure 8 summarizes the synthetic procedure of Fe_3O_4@Co-MONT. It was proved that the material can be used for the rapid enrichment and separation of PCBs and the developed method showed great analytical characteristics (Li et al. 2016a).

Liu et al. (2019) synthesized a metal azolate framework (MAF). MAF materials are a subfamily of MOFs that are also gaining attention in the recent years due to their remarkable structure. The research group used the novel sorbent as coating for SPME fibers for the preconcentration of polycyclic aromatic hydrocarbons from lake water and food samples prior to GC-FID analysis. For the synthesis of MAF-66, 3-amino-1,2,4-triazole and zinc hydroxide were mixed in an aqueous ammonia solution. For the construction of the SPME fiber, a stainless steel wire was dipped in hydrofluoric acid in order to obtain a rough surface. Subsequently, the wire was dipped into a methanolic solution of the MAF material and dried into the GC port. The layer-by-layer deposition procedure was performed 10 times before the fiber was finally aged at 250 °C for 1 h. The developed fiber showed long lifetime, low detection limit, and high enrichment factors.

Porous carbon materials are an interesting class of potential sorbents with good characteristics. MOFs can be carbonized to produce magnetic MOF-derived carbon materials. Due to the well-organized skeleton of MOF, carbons with uniform heteroatom decoration and superior extraction characteristics can be obtained (Li et al. 2016; Liu et al. 2017a). A magnetic porous carbon derived from a Zn/Co bimetallic MOF material was used as an adsorbent for the extraction of chlorophenols prior to high-pressure liquid chromatography-ultraviolet detection (HPLC-UV) analysis. The material was prepared by adding zinc nitrate hexahydrate and cobalt nitrate hexahydrate with 2-methylimidazole in methanol. The final Zn:Co ratio was 7:1. Accordingly, the bimetallic MOF was carbonized at 900 °C for 6 h. The material was successfully used for the analysis of tap water and honey tea samples (Li et al. 2016). In 2016, Liu et al. synthesized a magnetic porous carbon derived from a Zn/Co bimetallic metal-organic framework was also employed for the MSPE of organochlorine pesticides from drinking and environmental water samples prior to their detection with GC-MS. The novel sorbent exhibited high specific surface area as well as magnetization saturation (Liu et al. 2017a). MOF-derived carbons are promising materials that can be prepared from exhausted MOF after carbonization at high temperature to provide reusability and meet the terms of cyclic economy.

Conclusions

Metal-organic frameworks are novel hybrid organic–inorganic materials that have been successfully used in the

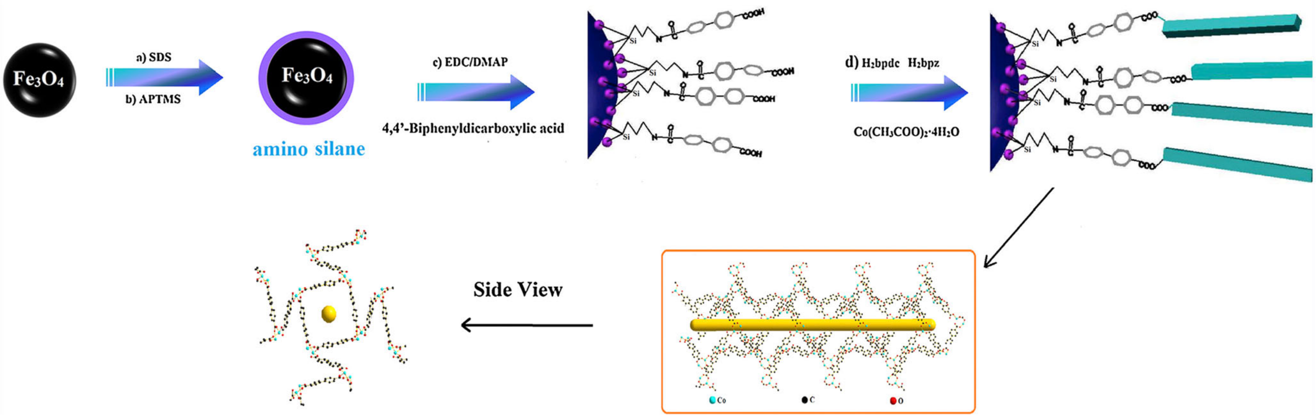

Fig. 8 Synthetic procedure of Fe_3O_4@Co-MONT. Reprinted from (Li et al. 2016a), Vol 1449, Zhang et al., Magnetic metal-organic nanotubes: An adsorbent for magnetic solid-phase extraction of polychlorinated biphenyls from environmental and biological samples, Page 40, Copyright (2016), with permission from Elsevier

field of sample preparation of various environmental samples. These materials offer an interesting possibility by enriching the analytical toolbox of environmental analysis. MOFs have been used for the SPE, d-SPE, MSPE, SPME, SBSE, and other extraction methods of various organic pollutants. In most cases, the extraction method was coupled with gas chromatography or high-pressure liquid chromatography for analytes' separation and detection.

Compared with other existing sorbents, MOFs exhibit superior properties such as flexible structure, high surface areas, tunable pore size, and high mechanical and thermal stability and are therefore promising materials for sample preparation. Due to the great variety of metal ions or clusters and organic linkers that can be used to build MOF materials, many novel sorbents can be synthesized. The main advantage of metal-organic frameworks is their high total pore volume which leads to high extraction recoveries. Moreover, with metal-organic frameworks, adsorption is based both on π–π and on hydrophobic interactions. On the other hand, extraction of organic pollutants with conventional SPE (e.g., C8 and C18), SPME (e.g., PDMS), and SBSE (e.g., PDMS) is mainly based on hydrophobic interactions. As a result, in most of the discussed analytical methods which used MOF materials as sorbents, higher extraction recoveries were observed.

The main drawback of MOFs is their low stability in aqueous solutions and their low stability after exposure to acidic or basic solvents/solutions. Due to potential structure decomposition of MOFs in aquatic environment, the regeneration, reusability, and recyclability of the sorbent after one cycle of adsorption and desorption of the target analytes is difficult.

In order to overcome the problem of the low chemical stability of MOFs in aqueous solutions, to provide satisfactory sorbent reusability, and to enhance the extraction efficiencies of the target analytes, many different approaches have been proposed. The most common approach is the modification or functionalization or the sorbent by attaching or inserting different functional groups. Change or modification of the metal (e.g., by changing the oxidation state or by metal ion doping) as well as surface modification of MOFs have been also examined. Functionalization can also enhance the selectivity of the extraction technique by introducing groups with higher selectivity towards the target analytes.

Zeolitic organic frameworks has been also widely used for the sample preparation of environmental samples combining the superior properties of MOFs and zeolites. Other MOF subfamilies that have been employed in analytical chemistry include metal azolate frameworks and metal-organic nanotubes. The use of these materials tends to be very promising for the development of simple, cost-effective, and environmental friendly sample preparation techniques. Moreover, exhausted MOF sorbents can be carbonized to produce MOF-derived carbon-based materials. These materials can be used either as sorbents or for alternative purposes (e.g., environmental remediation) to provide reusability and cyclic economy of MOFs.

Future perspectives regarding the synthesis of MOFs should be focused on the application of scalable processes which would lead to high amounts of MOFs as well as in greener ways to prepare MOF materials. As for the applications of MOFs, more research has to be done for the comparison of the performance of MOFs and other sorbents. Moreover, further application of the existing MOFs in other environmental friendly extraction methods, as well as the evaluation of other MOF types (for example, bio-MOFs), should be examined.

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