Malaysian Journal of Analytical Sciences (MJAS)
Published by Malaysian Analytical Sciences Society
ANALIS Persatuan Sains Analisis Malaysia

METAL-ORGANIC FRAMEWORKS AS SORBENT- BASED EXTRACTION: A REVIEW

(Rangka Kerja Logam-Organik Sebagai Penjerap Berasaskan Pengekstrakan: Satu Ulasan)

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Received: 27 July 2021; Accepted: 2 October 2021; Published: xx October 2021

Abstract

Metal-organic frameworks (MOFs) are highly ordered porous crystalline structures and full of cavities. They are formed by inorganic centers (metal ion atoms or metal clusters) and organic linkers connected by covalent coordination bonds. Depending on the ratio of such precursors and the synthetic conditions, the characteristics of the resulting MOFs vary significantly, thus drifting into a countless number of interesting materials with unique properties. This review offers an overview on the current state of the use of MOFs in different microextraction configurations, in all cases covering extraction devices coated with (or incorporating) MOFs, with particular emphasis in their preparation. Moreover, recent analytical applications reported from 2018 to 2020 will be discussed critically.

Keywords: metal-organic framework, microextraction method, sorbent, extraction

Abstrak

Rangka kerja logam-organik (MOFs) adalah struktur kristal berliang yang sangat tersusun dan berongga. MOFs dibentuk oleh logam pusat tak organik (atom ion logam atau kluster logam) dan penghubung organik yang dihubungkan oleh ikatan koordinasi kovalen. Bergantung pada nisbah bahan pemula dan keadaan sintetik, ciri-ciri MOFs yang dihasilkan berbeza-beza, sehingga menjadikan MOFs sebagai penarik kepada bahan penyerap dan bersifat unik. Ulasan ini memberikan gambaran umum mengenai keadaan semasa penggunaan MOFs yang berbeza-beza dalam konfigurasi pengekstrakan mikro yang meliputi kaedah pengekstrakan yang disaluti dengan (atau menggabungkan) MOFs, dengan penekanan khusus dalam penyediaannya. Tambahan pula, aplikasi analisis terkini yang dilaporkan dari tahun 2018 sehingga 2020 akan dibincangkan secara kritikal.

Kata kunci: rangka kerja logam-organik, kaedah pengekstrakan mikro, bahan penyerap, pengekstrakan

Introduction

Metal-organic frameworks (MOFs) are a new class of crystalline materials with three-dimensional (3D) organic inorganic complexes and highly porous nanostructures comprising metal ions/clusters and organic linkers [1]. They may be defined as supra-molecular solids but they consist of strong bonding and linking units that are available for modification by organic synthesis, a geometrically well-defined structure and robustness [2, 3]. In one-dimensional (1D) MOFs, coordination bonds are spread over the polymer in one direction. In two-dimensional (2D) MOFs, the single type layers are superimposed through either edge to edge or staggered type of stacking by weak interactions and guest species can be accommodated in the space between grids of the layers and the space between the layers. 3D MOFs are highly porous and stable since coordination bonds spread in three directions. According to Zhang et al. [4], these intriguing porous crystalline materials have been studied as promising candidates for various applications including gas separation and chemical sensing [5], energy storage [6, 7], homogenous and heterogeneous catalysis [8] and drug delivery [9]. Emam et al. [2] stated that in the last 20 years, a great variety of MOFs were widely designed due to main advantages such as their well-known features of large surface areas [10], high micropore volumes and the tunable pore sizes [11], uniform nanoscale cavity, specific adsorption affinities [12], good thermal and chemical stability [7], and the availability of post-synthetic modification. Overall, MOFs have been attractive candidates as advanced sorbents in sample preparation due to the unique-microenvironment and have been proved to be good catalysts [13]. Consequently, MOFs have been preferably recommended as a reliable and novel sorbent material in sample preparations, including pollutants, large molecules, and heavy metals and others which have led to a rise in the number of published papers [14, 15].

Until now, various MOF materials have been used in different extraction modes, for example, solid-phase extraction (SPE) [16], dispersive-micro solid phase extraction (D-µSPE) [17], solid-phase microextraction (SPME), thin-film solid-phase microextraction (tf-SPME), in-tube solid-phase microextraction (it-SPME) [18], stir-bar solid-phase microextraction (sb- SPME), and lastly, needle trap device [19]. Therefore, MOFs have been applied in many different scientific fields and applications of MOFs have been reported, whereby the most popular applications of the use of MOFs in analytical chemistry are in the field of sample preparation as absorbents for the extraction of a wide range of analytes in different matrices [20]. Other applications of MOFs include MOFs in chromatography and as a sensor in spectroscopic and electro analytical methods [3], MOFs as therapeutic agents, drug carriers, imaging agents and biosensors in cancer biomedicine [21], hydrogen storage in MOFs [10], MOFs in applications like catalysis or separation, and MOFs as substrates for paper spray mass spectrometry (MS) [22].

Metal-organic framework design in analytical separation

There are many kinds of MOFs used in various sample preparation strategies such as metal-organic framework (MOF) family, University of Oslo (UiO) [7], zeolite imidazolate frameworks (ZIF), Matériaux de l'Institut Lavoisier (MIL) and isoreticular metal-organic framework (IRMOF). Among all, IRMOF is the most widely studied as an excellent drug carrier material [7,23].

According to Li et al. [24], the first appearance was reported in the middle of the 1990s by the Yaghi group [25], who claim that MOFs have attracted extensive attentions due to their fascinating structures and unique properties. As a milestone in the history of MOFs, MOF-5 is known for its robust and open framework structure [24]. This material comprises $Zn_4O(CO_2)_6$ octahedral secondary building units (SBUs), each linked by 1,4-benzenedicarboxylate (BDC_2-) units to give a cubic framework. Its Brunauer-Emmett-Teller (BET) surface area reaches 2320 m^2/g. MOF-199 (also called HKUST-1) and is composed of Cu paddle wheel $[Cu_2(CO_2)_4]$ SBUs and a tropic organic linker benzene-1,3,5-tricarboxylate (BTC_3) [23]. This material shows merits in good stability against moisture, relatively easy synthesis procedure, and excellent thermal stability [14].

The UiO family has a Zr-based cuboctahedral SBU building block. As a representative member of this family, UiO-66 composes zirconium clusters and terephthalate ligands [26]. Zirconium is highly resistant to corrosion and has a strong affinity for hard oxygen donor ligands, therefore it is very stable even in strong acid and base solutions. In other words, this MOF UiO-66 exhibits extraordinary thermal stability even at 540 °C [8].

The ZIF family is built by metal ions with imidazolate ligands through nitrogen atoms. Among the ZIFs family members, ZIF-8 (Zn atoms coordinated tetrahedrally with 2-methylimidazolate (MeIM)) is the most studied because it exhibits a large surface area, high porosity, and exceptional chemical stability in organic solvents or boiling sodium hydroxide solution [27]. Recently, Emam et al. [2] in their research on the adsorptive performance of MOFs and MOF containing composites for clean energy and safe environment show that other members (e.g. ZIF-8 (Zn), ZIF-68 (Co)) have been utilised in hydrothermal/in-situ and infrared/in-situ techniques.

As for IRMOF-1, also known as MOF-5 to IRMOF-16 is synthesized with expanded and various functionalized organic linkers with zinc while keeping the same topology [7]. In hydrothermal synthesis, different ditopic carboxylate linkers would yield the same type of framework under closely related conditions. IRMOF-74-I to XI is synthesized from its original linker of one phenylene ring (I) to eleven (XI), respectively, with pore apertures increasing from 14 Å to 98 Å [28]. Different pore sizes of IRMOF could be used to conduct size-exclusion extraction according to the kinetic diameters of analytes.

As for the MIL family, it is constructed by trivalent metal centers and carboxylic acid bridging ligands. Among the MIL family members, MIL-53(Cr) MIL-100(Fe) and MIL-101(Cr) are widely studied in solid-phase extraction (SPE). Meanwhile, [5] stated that MIL-53(Cr) is built up with trimeric chromium octahedral clusters and terephthalate ligands, which exhibits unique pore expansion or contraction behavior with guest molecules. Both MIL-101 (Cr)-SO_3H and MIL-101 (Cr) were functionalized by post-treating them with ethylene diamine and tris (2-aminoethyl) amine (TAEA), ethanolamine (EA), receptively to produce MIL-101 (Cr)-SO_3H-TAEA, MIL-101 (Cr)-EA, and MIL-101 (Cr)-ED [2].

In addition, there are hundreds of novel MOFs reported and named by different researchers, such as PCN [29], BCF [30], NOTT [31], and BioMOF [32], and so on. Even for the same topology, mixed-metal and mixed-ligand MOFs greatly multiplied their diversity. For example, MOF-74 could contain 10 different metal ions (Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Zn, and Cd) coordinated with the same ligand in one framework [7]. Goyal, 2019 in his study stated that the most flexible MOF (named MOF-5) have a neutral framework of composition Zn_4O(BDC) in which Zn_4O groups are linked by terephthalate where BDC means 1,4-dicarboxylate has been synthesized and its name has been taken from a known zeolite ZSM-5. Figure 1 shows several representative examples of MOFs structures and their respective SBUs. One of the most representative examples is the family of isoreticular metal–organic frameworks (IRMOFs). This group of MOFs present the same topology and skeleton but different functionalization and pore dimensions to provide new perspectives for developing highly functional flexible MOFs.

MOFs as sorbent for small organic analytes

According to Sajid et al. [34], the following features of metal-organic frameworks (MOFs) include high porosity, designable and tunable structures, ultra-high surface area, utilization of functionalities as well as outer space, high thermal stabilities, and structural cavities that justify their use as sorbents in analytical chemistry as shown in Figure 2.

Relying on metal ion geometry and bridging ligands, different topologies and dimensionalities of MOFs can be attained. MOFs have been widely employed in analytical extractions [3]. Other than polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), volatile organic compounds (VOC), pharmaceuticals, herbicides, pesticides, toxins, dyes, endocrine-disrupting chemicals (EDCs) are the examples of MOFs in small organic analyte. MIL-101 (Cr) has been widely used as an adsorbent [35]. Magnetic MIL-100(Fe) microspheres also showed excellent performance for extraction of (PAHs), and the adsorbent can be used150 times without significant loss in extraction [36].

The magnetization (Fe_3O_4 MNPs) of the MOFs makes their dispersion as well as retrieval easier in the extraction process. A facile method based on the mixing of MOF (MIL-101) and silica-coated magnetic microparticles in the sample solution was suggested for in situ magnetization and micro solid-phase extraction (MSPE) applications. In this case, hydrophobic and π-π interactions with the framework terephthalic acid molecules, and the π -complexation with the Lewis acid sites in the pores of MIL-101 contributed towards extraction of PAHs [2]. In another work, the magnetization of ZIF-7 was achieved through polydopamine (PDA) coating of Fe_3O_4 MNPs, where the NH_2 groups on PDA can form noncovalent and covalent interactions with ZIF-7 giving it magnetization as well as stability and reusability as sorbents. High surface area, accessible internal pores, unsaturated π -complextion, and π- π interactions of bridging ligand benzimidazolate with PAHs contribute toward extraction [4].

MOFs can also be employed in combination with magnetic nanoparticles (MNPs) to enhance their retrieval after extraction [3]. HKUST-1 and MNPs were prepared separately and used together in the extraction of PAHs from water samples. This work does not involve any chemical reaction between HKUST-1 and MNPs to ensure chemical binding. MOF and MNPs were taken in a vial before the addition of the water sample. Ultrasound dispersed the mixture in a sample solution that was retrieved with the help of the magnet after extraction. This simplified the synthesis as well as magnetic extraction [3].

Similar to PAHs, PCBs in environmental samples are usually difficult to determine for their low concentration and to overcome this issue, MIL-101(Cr) was packed into hollow fiber to prepare a novel µ-SPE device where this fiber device was robust and could prohibit the leakage of sorbents and due to the thermal stability of this MOF, it could be used for more than 80 extractions without performance loss and shape change [37].

PBDEs were another aromatic persistent organic pollutants and one type of widely used flame retardants and the application of MOFs as sorbents in PBDEs was quite limited. Su *et al.* [38] stated that $Cd_3(L)_2(bpy)_2.5(H_2O)_2$ was prepared as a sorbent for the dispersive SPE of seven PBDEs in environmental water samples and the Box-Behnken design was used through response surface methodology in method development to get optimum extraction parameters where the limit of detection (LODs) for seven PBDEs were in the range of 0.08–0.15 ng/L.

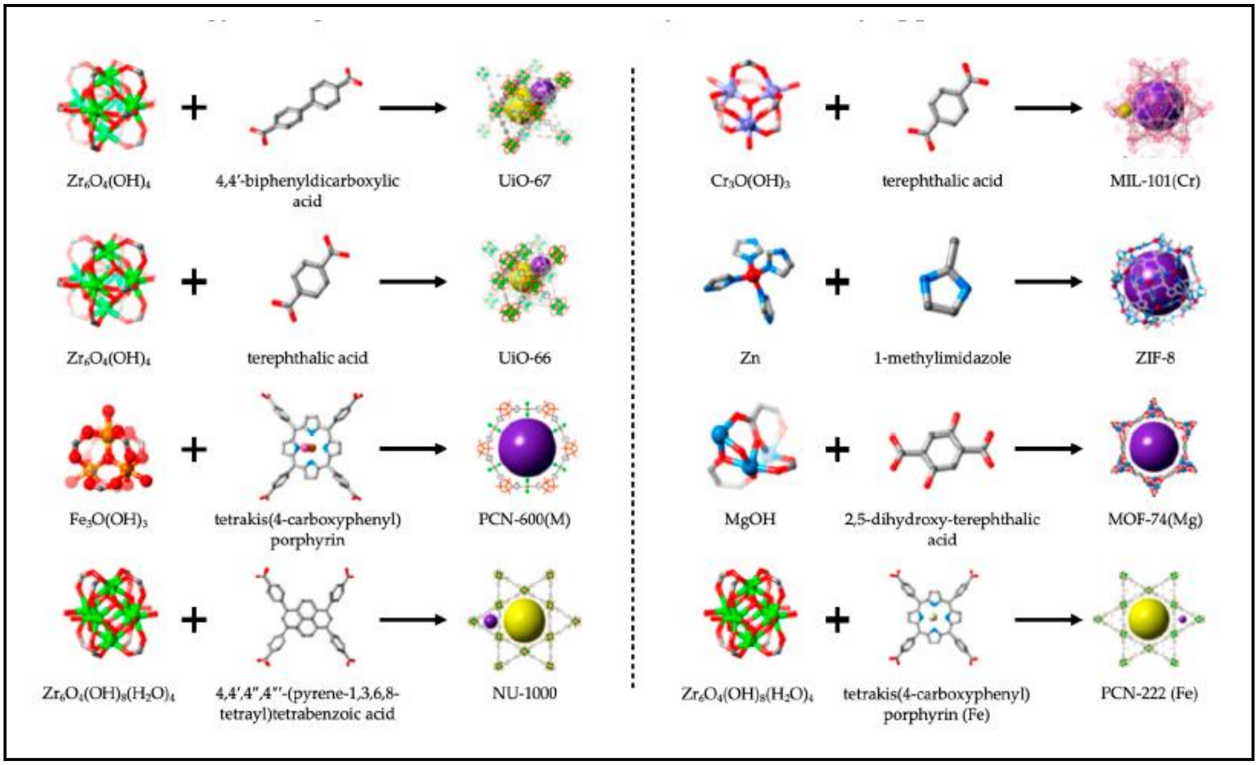

Figure 1. Schematic representation of different metal-organic frameworks structures with their corresponding metallic clusters and organic linkers [33]

Figure 2. Features of metal-organic frameworks (MOFs)

MOF in solid phase extraction

In recent years, applications of MOFs in separation science have been investigated intensively. One of the most important advantages of MOFs is that they can be designed to pertain to preferable (either chemical or physical) properties [16]. Generally, several factors (including flexibility and porosity of the framework, shape, and size of the pores) are considered as the most crucial factors determining the selective adsorption of guest molecules into the bulk structure of these solid materials in the solid-phase extraction (SPE) procedure. Therefore, the selective sorption of target compounds by MOFs is possible based on their shape, size, hydrophilic, and hydrophobic properties. It is important to note that many conventional sorbents used in SPE had either limited selectivity or adsorption capacity towards environmental pollutants such a Å s octadecyl-modified silica (C_{18}), graphitized carbon black (GCB), porous graphitic carbon (PGC), and activated carbon (AC) [39]. In this respect, MOFs are quite flexible to overcome such drawbacks through modification of the pore surface (for different adsorption preferences) against different target molecules [18], for example, MOF DUT-60 holds the world record regarding the highest surface area and pore volume. This MOF has a pore volume of 5.02 $cm^3 \cdot g^{-1}$ and a surface area of 7,800 $m^2 \cdot g^{-1}$ where it is formed by $Zn_4O_6^+$ clusters and an expanded topic ligand 1,3,5-tris(4′-carboxy[1,1′-biphenyl]-4-yl)benzene in combination with a ditopic linker 1,4-bis-p-carboxyphenylbuta-1,3-diene [40]. In general, MOFs with surface areas over 6,000 $m^2.g^{-1}$ are termed ultrahigh porosity crystalline frameworks.

In 2006, Zhou and co-workers stated the first example of using MOF in solid phase extraction was demonstrated by using an on-line flow injection SPE system using copper (II) isonicotinate (Cu $(4\text{-}C_5H_4N\text{-}COO)_2$ $(H_2O)_4$) as sorbent followed by HPLC-UV for trace determination of polycyclic aromatic hydrocarbons (PAHs) where these target PAHs contained in environmental samples (coal fly ash and local water samples) were concentrated and extracted onto the surface of copper isonicotinate coordination polymer based on the pore size of the hydrophobicity and polymer of the guest molecules.

In another case, an SPE procedure based on a magnetic porous carbon derived from an MIL-53-C was developed for pre-concentration of three steroid hormones (methyltestosterone, testosterone propionate, and nandrolone) from both urine samples and water where MIL-53-C with a good magnetic behavior and large surface area was prepared through its direct carbonization which it was exposed to 100 mL of sample solution containing steroid hormones to remove the target compounds from either human urine samples (LODs: 0.1-0.3 μg L^{-1}) and water (LODs: 0.005-0.01 μg L^{-1}) [36].

Furthermore, pure MOFs can be used as efficient sorbents for SPE of inorganics such as, Zn (II)-MOFs (TMU-4, TMU-5, and TMU-6) for the extraction of heavy metals (Cu (II), Cd (II), Pb (II), Cr (II), and Co (II)) from environmental water samples and TMU-5 was selected for the subsequent SPE analysis of heavy metals because it exhibited the maximum extraction efficiencies [36]. The proposed SPE procedure is known to possess several advantages including high extraction efficiency, simplicity, and low organic waste while, MOFs maintained either high water stability or wide pH range stability, it was recognized as the suitable sorbent for the extraction and pre-concentration of the target analytes from water samples [16].

MOF in dispersive-micro solid phase extraction

Chisvert et al. [17] in their research stated that sorbents used in dispersive-micro solid phase extraction (D-μSPE) play a crucial role in the overall extraction procedure. Both efficient clean-up and enrichment depend on the affinity they present concerning the target analytes, i.e., the facility to entrap them. Nevertheless, as important as the entrapping step is for desorption, the interaction sorbent-analytes should be reversible under different conditions to desorb them readily. This last step could be obviated in case the determination is carried out directly on the sorbent surface.

As mentioned before, the efficiency of both sorption and desorption processes depends on the contact surface area between the sample and the sorbent, and between it and the desorption solvent. In this sense, nanostructured sorbents with a high surface area to volume ratio provide higher adsorption capacity compared with micro-scale materials [41].

To this regard, the development of new materials as sorbents has a great impact in micro extraction techniques, including D-μSPE, to improve the efficiency and selectivity, and their chemical or physical stability and consequently their lifetime. Many of the sorbents used in D-μSPE, which could be classified by attending to several criteria. Here, they have been divided into three groups: firstly, the micro materials, basically conformed by (but not limited to) the classic sorbents coming from SPE (e.g., the well-known octadecyl silica (C_{18})) that were proposed at the beginning of D-μSPE, and other more selective materials used later; secondly, nanostructured sorbents, especially nanoparticles (NPs) with special emphasis in magnetic NPs (MNPs); and finally, hybrid materials (composites) [42].

Boontongto and Burakham [6] stated that (NH_2-MIL-101(Fe)) has been proposed as a sorbent for dispersive micro-solid phase extraction (D-μSPE) of ten priority phenolic pollutants and the entire D-μSPE process was optimized by studying the effect of experimental parameters affecting the extraction recovery of the target analytes. Meanwhile, MOF functionalised with amino groups, was employed as the sorbent for D-μSPE to pre-treat eight nitrobenzene compounds from environmental water samples [42]. According to Ghorbani *et al.*[43], regarding trends in sorbent development for D-μSPE, it was stated that the most widely used MOFs was D-μSPE sorbent including HKUST-1 and MIL-101, respectively. Furthermore, Ghaemi & Amiri also stated that (MCC/MOF-199) was applied as a sorbent for the (D-μSPE) of chlorophenols, where the D-μSPE method combined with high-performance liquid chromatography-ultraviolet detection (HPLC-UV) was employed to determine four chlorophenols including 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,3-dichlorophenol (2,3-DCP), and 2,5-dichlorophenol (2,5-DCP) in aqueous [44].

MOF in solid phase microextraction

Solid-phase microextraction (SPME), developed in the early 1990s by Arthur and Pawliszyn, is a novel sample preparation method that is fast, highly sensitive, and less solvent consumptive. When it is comparable with other conventional sample preparation methods and can be coupled with gas chromatography (GC) or high-performance liquid chromatography (HPLC). SPME has been successfully used in biological, food, and environmental analyses [27]. In the past two decades, great progress has been made in the thermal and chemical stability of prepared SPME materials as well as the sensitivity, selectivity, and reproducibility of specific analytes. In addition, substantial effort has been made to explore novel SPME coating materials [45].

More recently, MOF-based SPME fibres have garnered increasing interest for efficient extraction and determination of different compounds such as, PAHs, VOCs, and penicillin while in 2009, Cui and co-workers have introduce the first example of using MOFs as SPME coating where hydrothermal procedure was applied to produce a thin film of MOF-199 on the surface of SPME fiber with result offered large enhancement factors (19,613-1,10,880), wide linearity (36-23,000 ng L^{-1}), and low LODs (8.3-23.3 ng L^{-1}) for SPME of benzene homologues. The outstanding efficiency of SPME-based MOF-199 resulted from such features as porous structure and large surface area of MOF-199, π-π interactions between aromatic rings of target compounds and Lewis acid sites of MOF-199 pores.

Furthermore, developing novel fibre materials on Cd (II)-MOF, MOF-199, and MIL-101 have been applied to analyze volatile polycyclic aromatic hydrocarbons and benzene homologs using headspace SPME [13,24,46]. While, Venna et al. stated that SPME fibres coated with some MOFs such as MOF-199, ZIF-7, and ZIF-8 were applied to investigate the selectivity of these adsorbents in separation procedure of n-alkenes [47]. Composite of MOFs with graphite oxide (GO) has been introduced as a new fibre coating for SPME-based separation of organochlorine pesticides (OCPs) and this composite was formed by reaction between the oxygen groups of GO and copper sites in MOF-199 where it provided large surface area, high porosity, strong dispersive forces and good thermal stability (above 300 ℃) [48].

MOF in thin film solid phase microextraction

According to Gutiérrez-serpa et al.[18], while it is clear that the enlargement of the thickness of the sorbent material in film solid-phase microextraction (tf-SPME) devices implies an increase in the amount of extracted analyte, it also comes with long extraction times to reach the equilibrium due to the radial diffusion of the analytes. Thin-film solid-phase microextraction (tf-SPME) appears as a solution to increase the sensitivity (using larger sorbent amounts) without increasing the extraction time. Wilcockson and Gobas, were the first to propose the tf-SPME configuration. This first device consisted of a glass coverslip coated with a 0.33 µm thin film of ethylene- vinyl acetate (acting as sorbent coating) [49]. The device was tested in the analysis of toxic organic chemicals in aqueous extracts of fish samples.

In tf-SPME, the sorbent material covers the surface of flat material or forms a free membrane with a reduced thickness, with the increasing amount of sorbent being related to the extension of the surface, thus maintaining a high surface area to volume ratio. In this mode, higher sensitivities can be reached given the increased amount of sorbent but requiring shorter times (similar to those of tf- SPME) because there were no extra difficulties in diffusion (same as those in tf-SPME) [50]. Figure 3 below shows a schematic of the tf-SPME configuration reported in the literature.

The main challenge for the different sampling formats of tf-SPME is to avoid film folding. Among formats, it is possible to cite free-membrane, stainless steel rods, cotter pin, and mess holder configurations. Furthermore, it is possible to automate this extraction technique using 96-blades, which is a variety of the commercial 96-well plates system [52].

It is possible to distinguish two different kinds of tf-SPME devices attending to their thermal stability: thermostable and non-thermostable films. Thermostable films can be coupled to a temperature desorption unit and directly injected into the GC. As a disadvantage, there is a limited number of thermostable films reported in the literature and most of them are the same as the polymeric coatings used in conventional tf-SPME. Regarding thermo-labile films, they are used in solvent-assisted desorption applications (implying longer sample preparation times due to the slower diffusion of the analytes in the liquid phase). In addition, the increased size of the tf-SPME device requires the use of higher amounts of eluent solvent (in turn requiring a final step of solvent removal and reconstitution) [53]. Solvent desorption from tf-SPME is more challenging compared to thermal desorption which is related to the lack of conventional interfaces for on-line coupling of tf-SPME device to the workflow of the analytical instrument. This would facilitate the direct introduction of the extracted analytes into the analytical instrument. Furthermore, during the desorption process, the relatively large tf-SPME device requires a larger volume of eluent. According to Olcer et al. [53], only a small portion of the solution is introduced to the instrument after solvent desorption and this does not take full advantage of the large extractive phase, unless reconstitution steps and additional evaporation are employed to generate a smaller, more concentrated sample volume to account for the extra dilution.

The tf-SPME modality recently benefited from the introduction of MOFs. The preparation of MOF-based tf-SPME is easier than other SPME configurations because the increased surface facilitates the MOF growing. MOFs reported in tf-SPME devices include MIL-53(Al) and ZIF-67(Co) [54-55]. Other MOFs studied as sorbent material in tf-SPME are UiO-66(Zr), MIL-53(Fe), MIL-100(Fe), MIL-101(Cr), and ZIF-8(Zn) but presented poor analytical performance when compared with the abovementioned MOFs) [54]. Other thin films incorporate MOFs reported in the literature, but they are used as sorbent material in µ-SPE applications instead of tf-SPME strictly [56-57].

In the case of MIL-53(Al), it is incorporated in the thin-films by embedding the MOF which is previously synthesized in a polymer. This method involves the dispersion of the MOF in a volatile solvent (i.e., acetone), and the addition of such suspension to a polyvinylidene difluoride (PVDF) solution in dimethylformamide under sonication to ensure homogeneity. Then, the volatile solvent is evaporated, and a dense ink is obtained [54]. The bar coating technique forms the thin film by spreading the ink over a surface. It requires an applicator with an adjustable gap to control the thickness of the film, followed by the ageing of the film and solvent removal to ensure the solidification of the film [53]. The final shape of the tf-SPME device can be easily modulated by proper cutting of the solid membrane obtained. These composites combine the flexibility of the polymers and the high porosity offered by MOFs. The amount of MOF powder cannot be extremely high in the film because it becomes more fragile and flakier. The highest charge reported for a MOF into a membrane for tf-SPME application is 67% (w/w) [54].

Recently, Mohammadi et al. [55], have proposed a method that combines electrospinning and the in-situ solvothermal growth to prepare a ZIF-67(Co)-based tf-SPME device. The electrospinning implies forming a composite of polyacrylonitrile and Co_3O_4 nanofibers. By heating, the polyacrylonitrile suffers calcination and the polymer is removed from the film structure. Afterwards, this film gets in contact with the organic linker required for the preparation of the ZIF-67(Co) (2-methylimidazole) at adequate conditions to ensure formation of the nanofibers. The main advantage of this method is that the MOF is self-supported without the use of a mesh or a polymer, while still maintaining a flexible membrane.

Regarding the applicability of the MOF-based tf-SPME devices, just the self-supported ZIF- 67(Co) film permitted a thermal desorption. In this last case, the application was the determination of pesticides [55]. In terms of analytical performance, they present adequate intra- and inter-device precision, with reported relative standard deviation values lower than 11.4%. Samples analyzed include water and biological fluids for the determination of estrogens and pesticides [54-55].

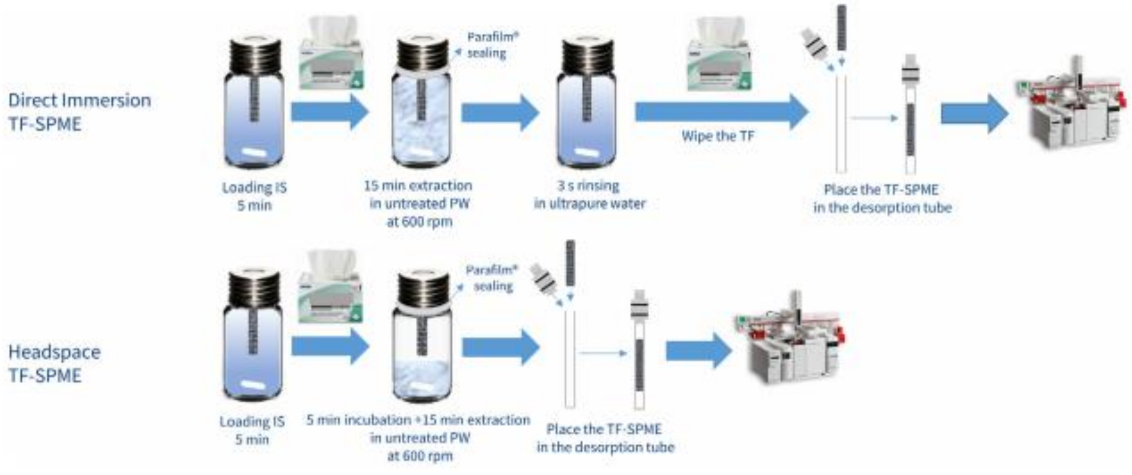

Figure 3. Scheme of the tf-SPME configuration [51]

MOF in in-tube solid phase microextraction

The in-tube solid-phase microextraction configuration (it-SPME) was developed practically after the development of the conventional tf-SPME, mainly to improve the drawbacks related to the coupling of the technique with liquid chromatography (LC). Although the high success of tf-SPME devices in many analytical applications, the extraction of non-volatile, semivolatile, and or thermo-labile compounds (not adequate for GC) was a significant hurdle to overcome.

The introduction of it-SPME devices facilitates the online and direct injection in a LC system, and even more importantly, its automation [58]. The first it-SPME devices consisted of 60 cm sections of a GC capillary column, with an internal diameter of 0.25 mm and an internal thin film of the stationary phase coating the capillary. Depending on the nature of the stationary phase, the film thickness varies, exhibiting slightly different internal volumes among the devices. Nevertheless, the nature of the film is the main factor responsible for the difference in behavior [58]. Nowadays, most developed it-SPME devices use open tubular fused-silica capillaries, with a thin film of the extractant material on the inner walls. The development of other capillary modes shifts to the incorporation of novel materials and the improvement of the technique. Other capillary modes include sorbent-packed, fibre-packed, and monolithic phases [59-61].

There are several operational modes for it-SPME depending on the number of pumps and valves. Nevertheless, they can be divided mainly into two configurations attending to the introduction of the sample: the flow-through system and the draw or eject system. In the first one, the injection of the sample can be performed manually or automated, and the sample is continuously injected into the device following a unique direction. In the draw/eject mode, it requires an automatic sample introduction system (programmable). The sample is injected, flows through the device, and goes back to the sample vial through the device again completing a cycle. In this modality, it is important not only to optimize the sample flow, but also the number of required cycles to obtain the maximum extraction efficiency [59, 61]. Up to date, the use of MOFs as sorbent material in it-SPME is not extended, and only few studies have been reported so far using MIL-101(Cr), MIL-53(Al) [62-63] and ZIF-8(Zn), in all cases for the determination of environmental pollutants in water.

In the cases of MIL-101(Cr) and MIL-53(Al), the devices consist of a glass capillary filled with a monolith composed of a polymer and the MOF. Thus, the glass capillary was cut in sections of 4-10 cm length, followed by washing with concentrated NaOH to activate the silanol groups. Then, the inner walls of the capillary were vinylated to guarantee the attachment of the monolith [62]. Afterwards, the mixture suspension containing the necessary amount of MOF (as prepared and already activated), butyl methacrylate as monomer, ethylene dimethacrylate as cross-linker agent, azo-bis-isobutyronitrile as radical initiator, and a porogenic solvent fills the capillary. Once the sides of the capillary are sealed, a microwave-assisted polymerization takes place. It is important to ensure the correct dispersion and homogenization of the mixture suspension before filling the capillary to get a homogenous it-SPME device. Finally, there is a clean-up step to remove the unreacted chemicals from the device) [63]. One of the most important factors to optimize in this kind of device is the amount of MOF in the monolith. If large amounts of MOF are used, the monolith structure would be more compact, thus making the diffusion of the sample and solvents difficult (and in turns resulting in a decreasing of the extraction efficiency of the final device) [63].

Regarding the ZIF-8-based it-SPME device proposed by Ling and Chen, it consisted of a fiber-packed capillary [64]. In this case, the incorporation of the MOF requires an electrodeposition step followed by an *in-situ* crystal growth. The general procedure starts by using a strong acid and a base in order to activate the surface of carbon fibers (bundle of 13 cm). Then, the electrodeposition of ZnO takes place by immersing the carbon fibers (as the working electrode on a three-electrodes system) in a solution of zinc nitrate. The deposition of the oxide takes place by cyclic voltammetry. Once the ZnO is formed all over the surface of the fibers, the cyclic voltammetry is stopped, and the fibers bundle is washed and heated at 100 °C to ensure the immobilization of the oxide. This strategy renders supported ZnO crystals of 30-80 nm. Consecutively, the solvothermal synthesis ensures the growth of the MOF ZIF-8 by immersing the ZnO-based carbon fibers bundle into a solution of the organic linker under adequate growing conditions, followed by packing it in a polyetheretherketone (PEEK) tube. The analytical applications involved the determination of Sudan dyes in environmental waters [64].

MOF in stir-bar solid-phase microextraction

Baltussen et al. [65] introduced the stir-bar solid-phase microextraction (sb-SPME) configuration as an alternative to conventional f-SPME, particularly useful for compounds with low octanol/water partitioning coefficient (non-polar compounds). The device consisted of a magnetic stir bar coated with PDMS. The sample was stirred with the bar at an adequate agitation rate. The bar was removed after proper extraction time, and a direct thermal desorption step took place in a specific GC injection port called a thermal desorption unit. In this configuration, part of the sorbent was in contact with the bottom of the sample container thus blocking possible interactions between the analytes and a portion of the extractant material. Stir-cake solid-phase microextraction (sc-SPME) emerged as a solution to this problem. The sorbent (in general a monolith) was located in a cylindrical device avoiding the contact between the sorbent and the bottom of the vessels thus improving the entire extraction efficiency [66].

Both configurations followed the same extraction fundamentals as conventional SPME. However, the amount of the sorbent material in both modes sb-SPME and sc-SPME were ~50–200 times bigger than the amount used in conventional f-SPME, thus permitting not only an increase of the extraction capacity towards target analytes but also an increase in the extraction time [67].

Currently, there are only two commercially available sb-SPME devices distributed by Gerstel: one coated with PDMS and the other with a PDMS/ethylene glycol copolymer. Although these coatings possessed many merits such as high sensitivity and good reproducibility, they also had low selectivity and required long extraction times to reach the equilibrium conditions. In addition, recoveries for polar compounds are poor due to the non-polar nature of the sorbent, being necessary a derivatization step for their extraction. Given these drawbacks, recent developments of sb-SPME devices focused on the development of more selective coatings with faster extraction kinetics, with MOFs not being an exception [68].

MOFs used as sorbents in sb-SPME include IRMOF-3(Zn), MIL-53(Al)-NH_2, MOF-5(Zn and Fe), ZIF-8, MIL-101(Cr) and it is amino- functionalised version, MIL-68(Al), ZIF-67(Co), and UiO-66-NH_2 [45, 67, 69-73]. The main procedure followed incorporation of MOFs in sb-SPME devices that followed the sol–gel approach. The devices prepared by this procedure have three components which are an iron wire or metallic rod of ~1-3 cm length, a glass jacket, and the sorbent. The iron wire or metallic rod is responsible for the agitation under the magnetic field while the glass jacket isolates the metallic wire from the water sample, avoiding its corrosion. The glass jacket also offers a homogeneous tunable surface for the immobilization of the coating when immersing the bar into the sol–gel solution containing the MOF dispersed into a polymeric solution. Then, the device is removed from the sol–gel solution and the self-assembly of the coating finishes by heating [67].

An alternative to sol-gel is the synthesis of monoliths by polymerization. The general procedure implies filling a template with a pre-polymeric solution (containing the MOF powder dispersed or its precursors), polymerization, removal of the template, and a final wash to clean the monolith [5,74]. Thus, the shape and dimension of the devices depends on the template and not on the support. Even the use of support is not required if magnetic nanoparticles are dispersed in the pre- polymeric suspension [31]. Recently, Du et al. [75] took advantage of this strategy for the preparation of the first MOF-based sc-SPME device by dispersing Fe_3O_4 @HKUST-1 core-shell particles in a pre-polymeric solution of 2-ethylhexylacrylate/divinylbenzene/methyl methacrylate. Although the MOF composite monolith does not utilize classical sc-SPME support, its visual geometry and shape resemble that of the classical sc-SPME device.

Another option is the in-situ solvothermal growth of the crystals onto other types of supports. Hu et al. [45] used this strategy with a porous copper foam as support. The foam is immersed in the solution containing the precursors of MOF-5(Zn) and, after impregnation, the support and the solution are set on the Teflon-lined autoclave, which is heated to form the MOF. In this case, the sb-SPME device is used in the headspace solid (HS) mode and uses a lab-made rotor to stir the device. As the direct growth of crystals over the support surface is not easy in terms of ensuring homogeneity, a similar approach to atomic layer deposition (ALD) strategy was used, to promote the crystal growth out of the metal nanoparticles previously electrodeposited all over the surface of the support [73]. The main disadvantage of these devices is the weak union MOF-support. The friction between the stir bar and the sample container causes a progressive loss of the MOFs, thus reducing the lifetime of the device. Wang et al. developed the use of a dumbbell-shaped PEEK jacket to improve mechanical strength. However, PEEK material is a highly inert material, requiring several aggressive pre-treatment steps to obtain an activated surface before the in-situ growth [74].

MOF in needle trap device

Needle trap device (NTD) is a microextraction technique that was first introduced by Pawliszyn et al. in 2001 [76]. In recent years, NTD has attracted much scientific interest from many researchers, due to its advantages [77]. In this regard, in previous researches, a wide variety of commercial and synthetic adsorbents have been used in NTD for the determination of different compounds [78]. These adsorbents, compared to other commercial adsorbents, have unique specifications like controllable pore sizes, super porosity, high selectivity, uniform cavities, high thermal stability, high specific surface area (>1000 m^2/g) with regular and uniform cavities, and various functional groups and sorbent flexibility to design and prepare a new adsorbent with desired specifications consistent with the target analytes [79].

Due to the possibility of using various organic linkers and metals, these types of adsorbents have been recently used in the extraction of a wide variety of analytes (like sulphonamides, polychlorinated biphenyls, volatile compounds, and polycyclic aromatic hydrocarbons) from various matrices (water and air) at different concentrations [46]. Until now, MOFs have been used in SPE and SPME for the extraction of phenolic derivatives [74]. The use of needle packed with Zn-MOF as a sorbent in sampling a number of PAHs including naphthalene, anthracene, phenanthrene, and pyrene in the air was conducted in the present study and the performance of this method was assessed using the gas chromatography-flame ionization detector (GC-FID) while to determine the temperature and time of desorption, storage time of the sample, and breakthrough volume (BTV) was exploited by using response surface methodology (RSM) [19].

Furthermore, the NTD packed with MIL-125 was used for extraction of phenol derivatives such as phenol, o-cresol, p-cresol, and 2-chlorophenol followed by gas chromatography analysis which shown the proposed of NTD offered was a high repeatability and accuracy. Also, the values of LOD and LOQ indicated a high sensitivity for the suggested sampler that proved the NTD packed withMIL-125 adsorbent can be used as a sensitive, accurate and fast method for determination phenolic derivatives from workplace air [77].

Conclusion

MOFs are known as well-established sorbents due to their advantages such as robustness, high surface area (provide large adsorption capacity), and highly ordered pores with specific size (selective adsorption for target analytes) over other alternatives. Currently, MOF examples, especially for analytical applications (various sample preparations and chromatographic separations), are limited to UiO-n, MIL-n, ZIF-n and MOF-n series, and a few other MOFs. Overall, MOFs or MOF-based composites with excellent properties as sorbents provide many new opportunities for sample pretreatment in the analytical extraction field. Finally, applications of MOFs and their composites as sorbents in SPE, D-μSPE, SPME, tf-SPME, it-SPME, sb-SPME, and MOF in needle trap device are highlighted. These developments and sustained research efforts will spark more interest in expanding the application of MOFs in sample pretreatment methods. Given the extensive knowledge about MOFs and their composites, we believe that this subject will become of great interest and continue to improve performance in analytical applications and beyond.

Acknowledgements

The authors would like to thank the Ministry of Higher Education, Malaysia for FRGS-RACER grants

(RACER/1/2019/STG01/UITM//5) and (RACER/1/2019/STG01/UITM//2). The authors would like to acknowledge the Faculty of Applied Sciences, Universiti Teknologi Mara (UiTM), Cawangan Negeri Sembilan, Kampus Kuala Pilah Campus and Faculty of Applied Sciences, Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia for facilities and services provided for the analysis.

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