Chapter 7

Application of various metal-organic frameworks in analytical methods: recent trends and future perspectives

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Abstract

Water scarcity and pollution are serious environmental problems and global concerns that affect millions of people. For this reason, there is increasing demand for frequent water quality monitoring. Therefore, there is a need for the development of efficient analytical platforms and methodologies that combine high accuracy, affinity, sensitivity, and selectivity towards various pollutants. Metal-organic frameworks (MOFs) have emerged as promising adsorbents, stationary phases, supports, and active coating for pollutant detection, extraction, sample clean-up, and separation. This chapter summarises the recent advances and trends in the application of MOFs in various analytical methodologies such as solid-phase extraction, solid-phase microextraction, and electrochemical sensors. A brief discussion of the synthesis strategies and their incorporation into various nanomaterials to increase the affinity of the resultant adsorbent towards various analytes is made. The application of MOF-based adsorbents for extraction, preconcentration, separation, and detection of pollutants in water systems is reported.

Keywords: Metal-organic frameworks, Solid phase extraction, Solid phase microextraction, Electrochemical sensors, Environmental pollutants

1. Introduction

Water pollution is considered one of the severe problems faced worldwide, and it needs to be solved urgently [1]. Several pollutants resulting from different activities and diffuse pollution are continually detected in the aquatic environment. These pollutants enter the aquatic environment and have a great potential to have various adverse ecological and human health effects [2]. These chemicals are classified as highly hazardous compounds because most of them are known to be endocrine disruptors, and the rate at which they are released cannot be effectively controlled since a number of these are used all over the world [3]. A significant number of pollutants have been detected in different aquatic environments due to the advanced analytical detection levels. These chemicals include dyes, heavy metals, and pharmaceuticals which are used as medicine for both animals and humans as well as in farming industries [4]. Their presence in the environment has drawn much attention [5], because most of these contaminants are pharmacologically active, non-degradable, persistent in the environment, and they also have potentially negative effects on ecology and human health [4]. Attention continues to grow in finding analytical methodologies for the detection and monitoring of these substances in the environmental water systems. Their presence in water systems causes several negative health effects such as hormonal, nervous, and reproductive system disorders. Other related health effects include obesity, cardiovascular as well as cancer [6]. In the past few years, the discovery of various pollutants in different environmental matrices has increased and these pollutants are found at concentrations that are capable of causing harmful effects on humans and other living organisms [7].

Given the above, analytical chemistry played a significant role in the development of methodologies for the detection, control, and monitoring of numerous environmental pollutants in a selective, sensitive, accurate, precise, and reliable way. Due to the complexity of environmental samples and low analyte concentrations, the analysis process undergoes various steps that affect analytical performance [8]. These steps include sampling, sample preparation, detection, and data processing. It is worth mentioning that even during a chromatographic separation or electrochemical detection or spectroscopic/spectrometric analysis, the presence of interferences is the major challenge in environmental analysis where organic, inorganic, and biological components co-exist and interact [9]. As a result, sample preparation plays a vital role in the sample matrix elimination, sample clean-up, and preconcentration of target analytes before the detection process [8,9]. Additionally, the improvement of stationary phases in chromatography applications and the use of functional materials in the modification of electrodes in electrochemical detection have recently received more attention [10,11].

Advancements in functional materials have received great interest in modern analytical chemistry due to their potential applications in numerous analytical methodologies [11–13]. Owing to their captivating features, metal-organic frameworks (MOFs) have been used in a wide range of applications (Figure 1). As seen in Figure 1, MOFs have been designed to meet the analytical challenges in sampling, sample preparation (that is, extraction, preconcentration, and sample clean-up), sensing, and chromatographic separation to improve analytical instrumentations' selectivity, sensitivity, and detection limit [11,13].

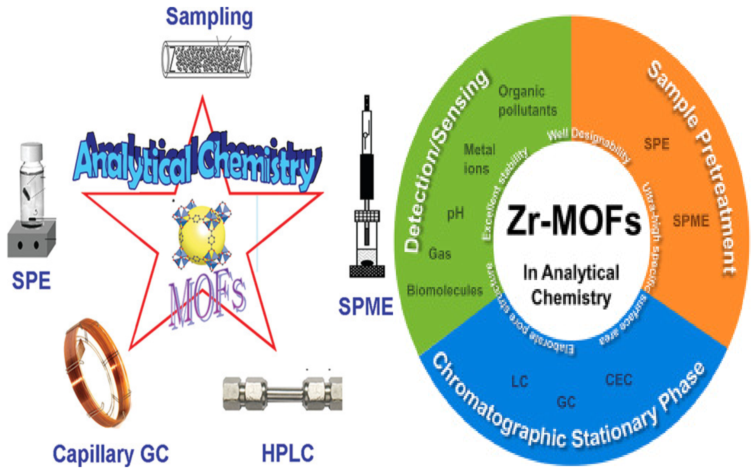

Figure 1: Application of metal-organic frameworks in various areas of analytical chemistry. Adapted and reproduced with permission from refs [11,13].

Considering the rapid developments in the application of MOFs in the analytical chemistry field, this chapter reviews the recent trends in the utilisation of analytical MOF-based methods. This chapter places particular emphasis on trends in the utilisation of MOFs in sample preparation (sorbent-based extraction methods) and electrochemical sensing. The overview will be limited to articles published between 2019 and 2022. This chapter also highlights a brief introduction of MOFs and MOFs-nanocomposites.

2. Metal-organic frameworks

Metal-organic frameworks (MOFs) are a group of porous materials that have attracted significant attention in different fields of research [14]. They are crystalline clusters or metal centres linked with organic ligands through coordination bonds creating stretched, arranged networks [15]. The richness of the geometry and connectivity of metal nodes and ligands can lead to the preparation of MOFs with specific structures and topology, which can be tailored for a specific application [16]. Furthermore, MOFs pose high surface area, thermal and chemical stability, versatile architectures, tunable pore size, simple metal nodes, and ligands modification as well as mild synthetic conditions [17]. Several metal ions and organic ligands with different functional groups have been used in the preparation of MOFs. As a result, most MOFs have been prepared using transition metals such as Cr, Cu, Fe, Mn, Co, Ni, , Zr, and Zn [18][19] and organic linkers containing various functional groups [20]. Sundriya ***et al.***, [21] reported the synthesis of manganese MOF using a one-step solvothermal method. In their study, 1,4-benzenedicarboxylate was used as an organic linker. The resultant MOF displayed a high specific surface area, chemical, and thermal stability. Some of the ligands used in the synthesis of metal-organic frameworks are shown in Table 1, where they are used in different applications and have shown high performance.

The MOFs formed from carboxylate ligands and N-donor ligands are said to be water-stable [28-30]. The ligands used in the synthesis of MOFs should be water stable because the water molecules may easily replace the ligand leading to the collapse of MOFs or this can block the active sites [31]. The strength of the ligand-metal bond plays an important role in the MOF water stability. MOF instability is caused by (i) ligand displacement, when a water molecule is inserted into the ligand-metal bond causing ligand escape and formation of cation hydrate. Also, (ii) hydrolysis, where the ligand-metal bond is broken by water and a hydrated cation is formed as well as a protonated ligand [32]. MOFs that are formed by mixed linkers (ligands) like carboxylates and nitrogen donors have been studied [33]. Abazari and co-workers have synthesised MOF from N-donor piperazine and imidazole-4,5-dicarboxylate for the degradation of cloxacillin, ampicillin, and amoxicillin antibiotics with 89, 88, and 92.5%, respectively. The ligands assist in MOF stability and reusability in adsorption studies and photodegradation [34].

Table 1: Various ligands used in MOF preparation and their application

Metal ions	**Ligand**	**Application**	**Performance**	**References**
Cd(II) and Co(II)	bis-pyridyl-tris-amide ligand benzene-1,3-diacrylic acid (BDA) 4,4′-oxybisbenzoic acid (OBA	Gas adsorption	High adsorption capacity	[22]
Ho(III)	H_2dtp = 4′-(3,5-dicarboxyphenyl)-4,2′:6′4″-terpyridine)	Th(IV) separation from rare earth metals (REEs)	Separation factor Th/La (19.2); Th/Eu (7.5); Th/Y (21.6); Th/Lu (6.2); Th/Ce (18.9)	[23]
Cd(II)	1,4-bis(benzimidazol-1-yl)-2-butylene	Sensing $Cr_2O_7^{2-}$ and acetylacetone	N/A	[24]
Ni(II) and Cd(II)	$[Cd(5\text{-}BrIP)(TIB)]_n$ (1) $[Ni_2(5\text{-}BrIP)_2(TIB)_2]_n$ (2) 1,3,5-tris(imidazol-1-ylmethyl) benzene (TIB)	Sensing of picric acid [2,4,6-trinitrophenol, TNP]	paper strip at 365 nm radiation by Cd(II) LMOF (**1**)-coated paper strip	[25]
Zr(IV)	2-Aminoterephthalic acid	Photo degradation	94% Cr(VI) reduction	[26]
Zr(IV)	2-(thiophene-2-carboxamido) benzene-1,4-dicarboxylic acid	Catalysis	94% and 95% yields	[27]

Carboxylates are considered as hard ligands and they can form strong bonds when bonded to strong metal ions such as Zr, Zn, and Cu among others [35]. In addition, carboxylate can easily coordinate with metals in the first row of transition metals under hydrothermal and solvothermal conditions. For instance, Jasuja and co-workers synthesised new water-stable MOFs using the first-row transition such as nickel, cobalt, copper, and zinc. The MOFs were obtained by incorporating structural factors such as catenation and ligand steric [36]. Li ***et al***. synthesised uranium-based MOF that was found to be stable with large pores [37]. The MOF was prepared by combining the negatively charged uranyl carboxylates $[UO_2(RCOO)_3]^-$ metal node with a square-like tetracarboxylate organic ligand. According to the BET results obtained, the prepared MOF gave a high surface area of about 2100 $m^2 g^{-1}$. In addition, the carboxylate -based MOF was water stable and was selectively absorbing positively charged species [37]. When N-donor ligands were compared to amines, they showed better donor ability towards metal ions forming a more stable compound [30]. The metal N-coordination bond is labile when compared to the metal-carboxylate bond. This reduces the porosity of networks even though it makes it easy to rearrange during self-assemble. It is said that the use of mixed linkers, for example, N-donor and carboxylates leads to a framework that is doubly interpenetrated reducing its pore size [38].

Gao and others used a solvothermal method to prepare a series of Cu, Zn, Co, and Mn-based MOFs with mixed N-donor ligands and carboxylates [39]. Transition metals are the choice of metals to be used with these carboxylates as they form variations of coordination geometries to obtain different networks, also the use of two carboxylates to form high porous MOFs [40]. Several researchers have modified MOFs to enhance their removal performance and photocatalytic degradation; herein we combine the properties of MOFs with other nanomaterials to achieve/obtain high removal efficiency. Such nanomaterials include chitosan, magnetic nanoparticles, graphene oxide, and multi-walled carbon nanotubes.

2.1 Synthesis of MOFs

The synthesis of nanoscale MOFs has gained much attention. This is done to assist in accomplishing the application of MOFs than bulk MOFs. Top-down and bottom-up methods have been used in the MOF synthesis. The top-down method includes solvent-induced delamination exfoliation (SIDE), sonication-assisted liquid exfoliation (SALE), and micromechanical exfoliation (ME) (Du ***et al***., 2019; Xie ***et al***., 2020) [42]. The bottom-up method includes interface-mediated synthesis (ImS), hydrosolvothermal synthesis (HsS) [43] 44], and Langmuir-blodge Hm

(LBm). These methods are widely used in the synthesis of single-crystal MOF and ultrathin MOFs which are in the range of 2–10 nm [45]. In the interface-mediated method, ultrathin materials such as MOFs grow through liquid/air /solid interface. Various materials can be modified to provide specific functional groups responsible for different applications; MOFs can be modified by the addition of pyridyl or amine moieties. Post-synthetic modification to prepare MOFs with high mechanical and physical properties, an organic ligand, can be altered to accommodate functional groups introduced [46].

3. Application of metal-organic frameworks in analytical methods

3.1 MOFs in sample preparation

In most environmental water analyses, direct identification and quantification of analytes are not suitable due to the complexity of the sample matrix (which may contain a mixture of the analytes with different chemical properties and co-existing substances) [47]. Therefore, a suitable sample preparation that could be converting any environmental sample type into a format that is ideal for precise and accurate quantification of the analytes is required. Sample preparation plays a remarkable influence on total analysis time and the quality of the analytical data obtained after instrumental analysis [8,47,48]. Therefore, the selection of a suitable sample preparation method depends on the chemical properties of the analytes, sample matrix, and the analytical detection method to be used [49]; [50]. Sample preparation methods such as solid phase extraction (SPE), dispersive solid-phase extraction (DSPE), magnetic solid-phase extraction (MSPE), and different modes of solid-phase microextraction (SPME) (in-tube, stir-bar, fabric, fibre, and thin-film) have been developed as seen in Figure 2 [48]. The success of these analytical methods depends on the selection of suitable adsorbent or coating material [48,51]. As a result, a substantial number of adsorbent materials with attractive characteristics have been used in the above-mentioned analytical sample preparation methods. These include molecularly imprinted polymers [52,53], porous organic polymers [54], covalent organic frameworks [55,56], zeolites [57], layered double hydroxide [58], carbon nanomaterials [59,60], and MOFs [11,48,61,62], among others. The application of MOFs as adsorbents in various solid phase-based extraction methods has recently emerged due to their remarkable properties.

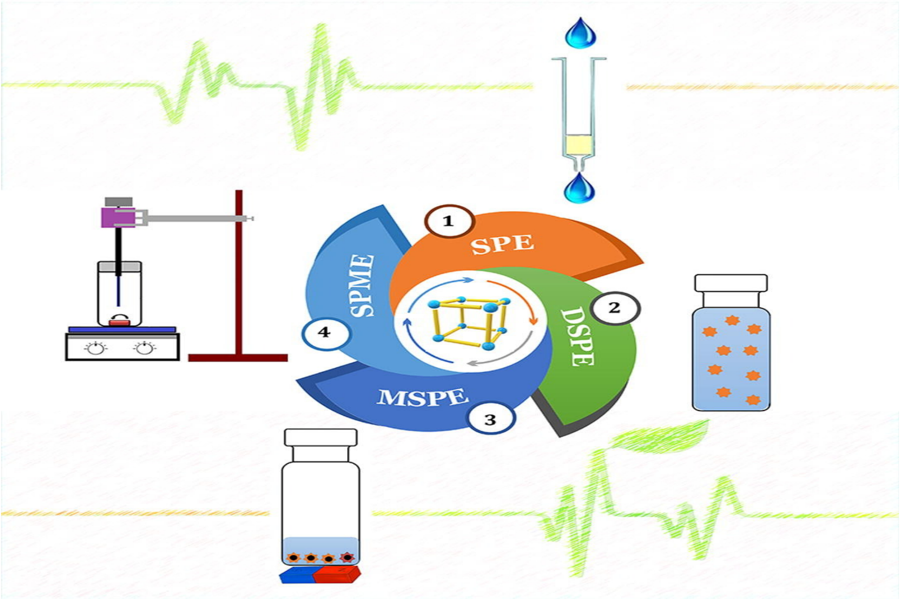

Figure 2: Application of metal-organic frameworks in different sample preparation methodologies. Adapted and reproduced with permission from Ref [48]

3.2.1 *Solid phase extraction*

Solid-phase extraction (SPE) is one of the extensively used sample preparation techniques that utilise an adsorbent to extract, isolate, and preconcentrate the target analytes from a specific sample [63,64]. Various types of adsorbents [65–67] and formats [51,63,65] have been reported in the literature and they cover all potential interactions with the analytes [63,64]. This study will briefly review the application of MOFs in traditional SPE, DSPE, micro SPE (µ-SPE), pipette tip SPE (PT-SPE) and MSPE for environmental analysis.

Traditional SPE can be performed as an offline or online preconcentration procedure. Both these modes enhance the detection sensitivity of the analytical instrument [68]. In a study reported by Amini and co-workers [69], an online micro solid-phase extraction (online-µSPE) used electrospun polyacrylonitrile/ Zn-metal organic framework 74 @graphene oxide (PAN/Zn-MOF-74@GO) nanocomposite as an adsorbent [69]. The method was used for extraction and preconcentration of chlorobenzenes complex environmental samples before a high-performance liquid chromatography analysis. The incorporation of MOF-74 in the nanocomposite enhances the affinity, surface area, and performance of the adsorbent material [69]. As a result, acceptable linearities in the range of 0.25–700 ng mL^{-1} with the coefficient of determination ≥ 0.9991 were obtained under optimum conditions. Furthermore, limits of detection (LODs), intra-day, and inter-day precisions were 0.08–1.10 ng mL^{-1}, 4.1%–9.5% and 5.8%–12.1%, respectively.

Martínez-Pérez-Cejuela ***et al.*** [70] developed on-line solid-phase extraction capillary electrophoresis with ultraviolet detection (SPE-CE-UV). The online SPE method used a hybrid material composed of nano-metal organic framework (HKUST-1) @organic polymer (nano-MOF@ polymer) as illustrated in Figure 3. The developed SPE was investigated for extraction and preconcentration of fluoroquinolones (FQs) in several real complex samples, including river water. The developed SPE-CE-UV method showed low LODs and acceptable accuracy as well as very high preconcentration factors (up to 500,000 times). The high sensitivity of the developed method was accredited to the porous structures and nanostructures of the hybrid MOF nanocomposite. The use of hybrid MOF nanocomposite also enabled good separation between the investigated analytes (see typical chromatogram in Figure 3).

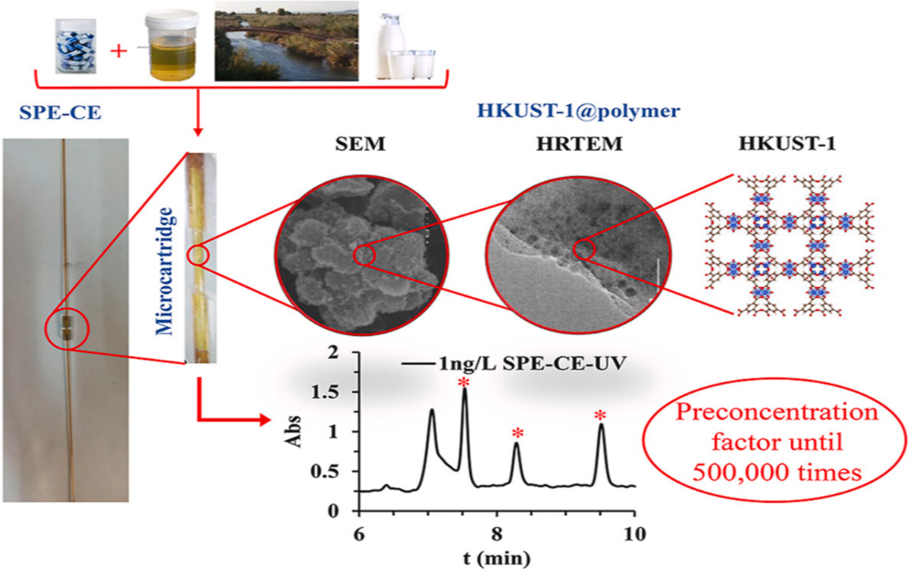

Figure 3: Schematic diagram illustrating the development of an online solid-phase extraction capillary electrophoresis. Adapted and reproduced with permission from Ref [70].

In traditional SPE, an adsorbent is often prepared or packed in a cartridge and the interaction between the solid phase material and target analyte is driven by the sample flow rate [64]. This feature becomes a critical challenge when nanomaterials are used as adsorbents because the small particles block the frits, thus generating backpressure, which makes it difficult for the sample to pass through [64]. Therefore, alternative approaches to conventional SPE have been developed. These include DSPE, MSPE, and D-µSPE, among others. In these SPE approaches, the adsorbent is dispersed into the sample matrix using a mechanical shaker, ultrasonication, or vortex. These methods allow close contact and effective interaction between the adsorbent and the analyte, thus increasing the overall extraction efficiency. The advantage of these methods is that the conditioning of sorbent is eliminated. Additionally, the extraction process is achieved by using low amounts of adsorbents (low milligram range).

Ghaemi ***et al.*** [71], developed a D-µSPE utilising a microcrystalline cellulose/metal-organic framework 199 hybrid (MCC/MOF-199) as a solid material. The developed D-µSPE method was used for preconcentration of chlorophenols in water before high-performance liquid chromatography-ultraviolet detection (HPLC-UV) determination. The combination of MCC on MOF-199 led to enhanced extraction capabilities. Under optimum conditions, the LODs, linearity, and %RSD were 0.1-200 ng mL^{-1}, 0.03-0.05 ng mL^{-1} and 6.8%, respectively. Moreover, the applicability of the D-µSPE-HPLC-UV method was investigated by analysing chlorophenols in different real water samples (mineral, river, and wastewater samples) and acceptable recoveries ranging from 95.8–99.5% were obtained. Duo and co-workers [72] designed a novel fusiform-like magnetic metal-organic framework material (Fe_3O_4-NH_2@MOF-235) as an adsorbent in MSPE of benzoylurea insecticides in tap water samples before HPLC. Acceptable linearity (1.0-300.0 µg L^{-1}), LOD (0.25-0.5 µg L^{-1}) and extraction recoveries (84.0-99.6%) were obtained. The adsorption mechanism was dominated by the hydrophobic and π–π stacking interactions between Fe_3O_4-NH_2@MOF-235 and benzoylurea insecticides. The remarkable properties of the MOF- based adsorbents allowed the use of very little adsorbent at a very short analysis time (<10 min).

In response to Green Analytical Chemistry (GAC), miniaturised SPE methods such as pipette tip solid-phase extraction (PT-SPE) employing MOFs as adsorbents have been reported [73-78]. For example, Su ***et al.*** [78] developed PT-SPE based on amino functionalised MOF@COF hybrid adsorbent combined with HPLC-UV for the analysis of sulfonamides in environmental water. Some researchers synthesised cotton@UiO-66 by growing UiO-66 on the surface of cotton fibre at room temperature. The resultant cotton@UiO-66 adsorbent was found to be effective for PT-SPE of herbicides in tap water samples. The combination of MOF-based PT-SPE with HPLC resulted in a facile and efficient analytical method with remarkable analytical characteristics. These include a wide linear range (1.4-280 µg/L), low LOD (0.1-0.3 µg/L), acceptable recoveries (83.3-

107%), and precision (<6.7%). Table 2 indicates that SPE approaches are powerful sample preparation strategies and with a suitable adsorbent, they allow a wide variety of analytes to be analysed. As shown in Table 2, the use of MOFs shows that these methods are effective enough to improve the performance of a wide range of analytical instruments. Furthermore, it can be seen from this table that a series of water-stable MOF materials have been used.

In most cases, the adsorption mechanism of ionic pollutants is driven by the surface charge of the MOF material, and this limits their applications for the extraction of nonionic organic pollutants. Such challenges are usually solved by the incorporation of other nanomaterials or functional groups. For example, Gao ***et al.*** [79] introduced amino groups on the surface of MIL-101(Cr) which promoted the increase of Lewis base sites (LBSs) density in surface modification of nanosised material thus allowing better interactions between the dyes and adsorbent. Functionalisation or modification of MOF materials proved to be beneficial to adsorption capacity and increases selectivity and affinity of the adsorbent. Environmental matrices are very complex, therefore, used hybrid materials to increase porosity and crystallinity have been explored (Table 2). For instance, hybrid MOF-based nanocomposite materials in Table 2 proved to be effective adsorbents for the MSPE, DPE, and online SPE, among others.

3.2.2 Solid phase microextraction

The basic principle of SPME methods is based on two steps, that is, extraction and desorption of target analytes from sample matrix [89,90]. The extraction step encompasses the partitioning of target analytes to the coating material (adsorbent). These methods are known as non-exhaustive and rely on the equilibrium between the sample matrix and the solid phase material [89,90]. The desorption step is performed after equilibrium and is achieved by placing the coated fibre into a vial containing elution solvent or the injection port of a GC [89,90]. MOFs and MOF-nanocomposite have been used as active materials in various SPME methods. For instance, Wang *et al.*, [60] developed a novel spiral-SPME fibre coated with zeolitic imidazolate framework-67 (ZIF-67) derived hollow multi-shelled structures Co_3O_4/carbon nanomaterials. The coating was used to capture trace concentrations of polycyclic aromatic hydrocarbons (PAHs) in environmental water samples. The use of MOFs-based adsorbent composition in the spiral fibre demonstrated higher selectivity for extraction of PAHs compared with brominated flame retardants and endocrine chemicals. The high affinity of the fibre coating towards PAHs was attributed to strong π-π stacking force, hydrophobic

Table 2: Application of MOFs and nanocomposite in various solid phase extraction methods for environmental water analysis

Analytes	**Analytical methods**	**Adsorbent**	**Linearity**	**LOD**	**%RSD**	**Refs**
Sulfonamides	MSPE/HPLC-DAD	Magnetic MOF@COF hybrid nanosphere	10–2000 ng/mL	0.1–0.5 ng/mL	3.9	[80]
Malathion	DSPME/UHPLC-MS/MS	Cu-BTC-MOF	-	4.0 µg/L	<10	[81]
Non-steroidal anti-inflammatory drugs (NSAIDs)	MSPE/UPLC-MS/MS	Core-shell magnetic Fe_3O_4@MIL-100(Fe)	0.1–30 µg L^{-1}	0.02-0.09 µg L^{-1}	<9.6	[82]
Phthalic acid esters	DSPE/LC-MS	Basolite® F300 MOF	5–500 µg L^{-1}	6.6-21 ng/L	<20%	[83]
Organophosphorus pesticides	DSPE-GC-FID	Zinc-based MOF	0.1–100 ng mL^{-1}	0.03–0.21 ng mL^{-1}	5.4-8.5	[84]
Polar estrogens	µ-SPE/ UHPLC-MS/MS	MIL-101(Cr)	0.005–100 µg L^{-1}	0.95-23 ng L^{-1}	<9.9	[85]
Cr^{3+}, Pb^{2+}	DSPE/FAAS	ZIF-8/ZIF-67 core-shell	0.5–200 µg L^{-1}	0.10-0.15 µg L^{-1}	1.9-2.7	[65]
Cu^{2+}	MSPE/UV-Vis	Fe_3O_4@MOF@COF	0.05-1.2 µM	37.6 nM	4.14	[86]
Silver	MSPE/FAAS	MIL-101(Cr)/Fe_3O_4@SiO_2@2-ATP	0.2–200 ng mL^{-1}	0.05 ng mL^{-1}	4.5-9.3	[87]

Analytes	Analytical methods	Adsorbent	Linearity	LOD	%RSD	Refs
Allergenic disperse dyes	DSPE/UHPLC-MS/MS	NH_2-MIL 101 (Cr)	0.010-10 µg L^{-1}	0.36–16.9 ng/L	2.1-7.8	[79]
Polycyclic aromatic hydrocarbons	D-µSPE/UHPLC-FD	Silica@MOF CIM-80(Al)	0.02–1.0 µg L^{-1}	0.005-0.1 µg L^{-1}	<14	[88]
Malachite green, rhodamine B, methyl orange and acid red 18 dyes	PT-SPE/HPLC	Co-MOF	0.5–200.0 µg/L	0.09–0.38 µg/L	<6.4	[74]
Fluoroquinolones	PT-SPE/HPLC-FLD	Zeolitic imidazole framework-8/cellulose aerogel	1.0–512 ng L^{-1}	0.34–1.7 ng L^{-1}	<6.0	[76]
Nitrazepam, oxazepam	PT-SPE/HPLC	Polyacrylonitrile/MIL-53(Fe) electrospun nanofiber	5.0–1000 ng mL^{-1}	1.5-2.5 ng mL^{-1}	≤7.6	[73]
Parabens	PT-µSPE/HPLC-UV	Cr-MOF adsorbent	1.0–200.0 µg/L	0.24-0.25 µg/L	5.78	[75]

interactions. In addition, the spiral fibre was reported to have the potential of increasing the contact area between adsorbent and PAHs. The developed S-SPME method exhibited wide linearity (0.005–1000 µg L^{-1}), low LOD (0.002–2.7 µg L^{-1}) and acceptable precision (0.7–10.7%). The performance of the developed S-SPME fibre proved to have excellent extraction efficiencies and enrichment abilities for the analysis of PAHs compared with commercially available SPME fibres.

In another study, Amini ***et al***., [91] reported the application of novel electrospun polyacrylonitrile/nickel-based metal-organic framework nanocomposite (PAN/Ni-MOF) nanosorbent as the coating on a stainless-steel wire. The PAN/Ni-MOF coated stainless-steel wire was employed for headspace solid-phase microextraction (HS-SPME) of organophosphorus pesticides in water samples and food samples. The analytes of interest were quantified using corona discharge ion mobility spectrometry (CD-IMS). The developed HS-SPME exhibited remarkable analytical performance such as linearity (0.5–300 ng mL^{-1}), LODs (0.2-0.3 ng mL^{-1}), and intra-day precision (≤ 5.2%). The application of MOFs and MOF-based nanocomposites in various modes of SPME proves to be receiving great attention in environmental analysis. Table 3 shows that MOFs and MOF-based nanocomposites are suitable candidates for extraction of pharmaceuticals and personal care products, polycyclic aromatic hydrocarbon, per- and polyfluoroalkyl substances (PFASs), organic dyes, heavy metals in complex environmental waters samples.

3.4 Electrochemical sensors

An electrochemical sensor is an analytical device that has a sensitive component that undergoes chemical changes upon interactions with an analyte and a transducer that converts the chemical changes into measurable signals [12,98]. Electrochemical sensors are one of the promising analytical methods for the detection and identification of various analytes that can be easily oxidised or reduced in environmental water matrices [12,98]. The electrochemical oxidation or reduction reactions occur on the surface of the electrode. Therefore, for better sensitivity and selectivity, the surface of the electrode is usually modified by immobilising the active materials as shown in Figure 4 [12]. The modified electrode provides more active sites for the electrochemical redox reaction with the target analyte [12], thus resulting in a rapid reaction rate and enhanced sensitivity toward the target analytes (Figure 4).

Table 3: Application of MOFs and nanocomposite in various SPME modes for environmental water analysis

Analytes	**Analytical method**	**Sorbent**	**Linearity**	**LOD**	**%RSD**	**Refs**
Nonsteroidal anti-inflammatory drugs (NSAIDs)	SPME/GC	Zr-MOF@GO	0.01–500 µg L^{-1}	0.001–0.030 µg L^{-1}	-	[92]
Fluoroquinolones	In tube SPME/HPLC-FLD	ZIF-8@monolith composite	0.001-5.0 µg/L	0.14–0.61 ng/L	<10	[93]
Odorants	SPME/	MOF-74	0.005–100 µg/L	0.01–0.9 ng L^{-1}	<8.7-9.4	[62]
Polycyclic aromatic hydrocarbons	HS-SPME/GC	Metal azolate frameworks (MAF-66)	0.01–100 µg L^{-1}	0.1–7.5 ng L^{-1}	0.23–4.2	[94]
Perfluorooctanoic acid (PFOA)	SPME/MS	Water-resistant MOFs: ZIF-8, UiO-66, MIL88-A, and Tb2(BDC)3	-	11 ng L^{-1}	-	[95]
Polycyclic aromatic hydrocarbons	SPME/GC-MS	HKUST-1 membrane	0.01–10 µg L^{-1}	0.12–9.9 ng L^{-1}	2.6–14	[96]
Polycyclic aromatic hydrocarbons (PAHs), personal care products (PCPs	DI-SPME-GC-FID	ZIF-8	2.0–100 µg L^{-1}	0.6-2.0 µg L^{-1}		[97]

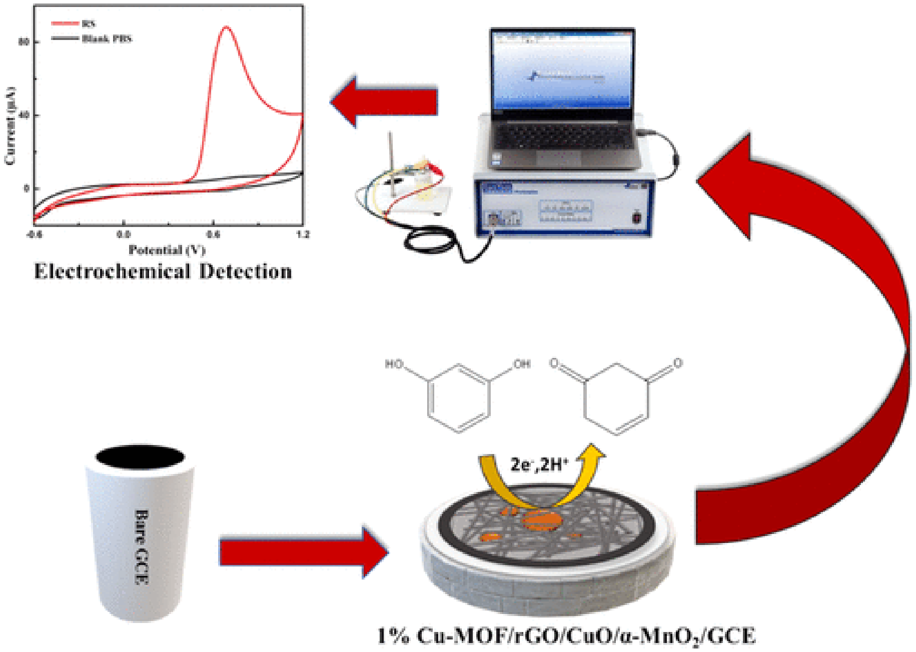

Figure 4: Schematic illustrating the fabrication of an electrochemical sensor. Adapted and reproduced with permission from ref [99].

Metal-organic frameworks have proven to be promising electrochemical sensing platforms due to their remarkable characteristics [98,100,101], namely:

- Unique structural characteristics (tunable porosity, large surface areas, and cavities) and unsaturated metal coordination sites (See Figure 5). The unique features give MOFs and MOF-based nanocomposites superior catalytic capabilities, which warrants them to be useful candidates as effective coating materials for electrochemical electrodes.
- The large surface area and high porosity MOF materials become beneficial in the preconcentration and mass transfer of the analytes from the sample to the surface of the electrode, thus effectively amplifying the analytical signal response and enhancing the sensitivity of the electrochemical sensor.
- The unique particle size and shape of the MOF cavities and channels (Figure 5) allow enhanced selectivity towards the target analytes via a process called size exclusion effects.

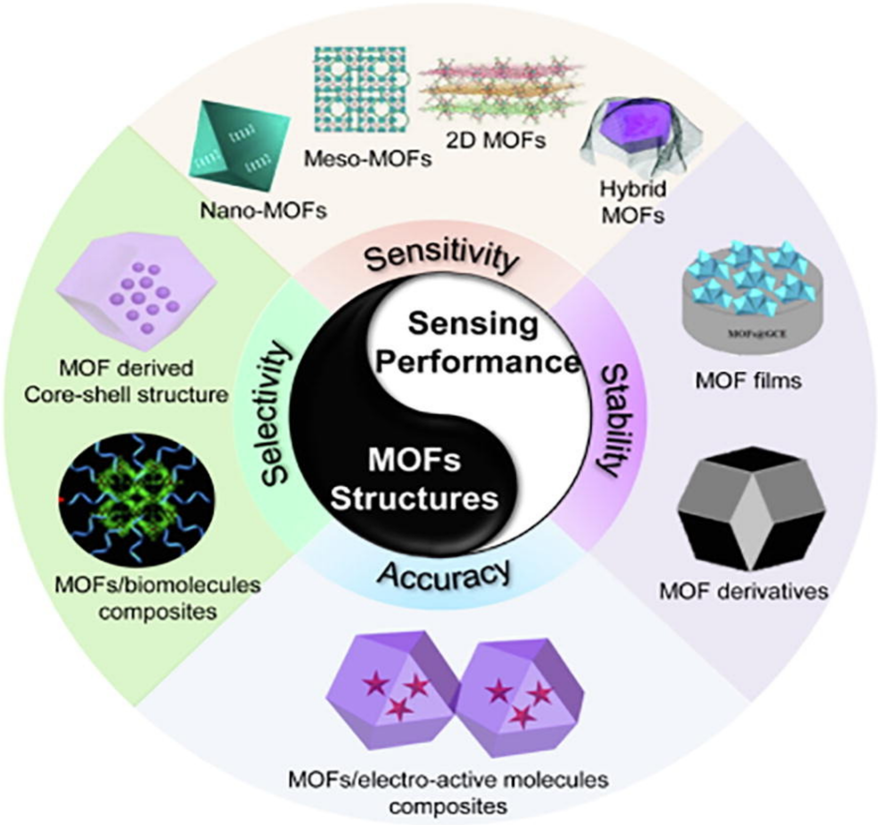

Figure 5: Structure-performance relationship of MOF-based materials for advanced electrochemical sensing applications. Adapted and reproduced with permission from ref [101].

Inspired by the above-mentioned attractive features, a wide range of MOFs and nanocomposites with improved and superior electroactivities have been used as electrochemical sensing platforms of inorganic and organic pollutants in water systems (Table 4). Kokkinos ***et al.***, [102], reposted the combination of 3D-printing technology and a highly efficient calcium-based metal-organic framework (Ca-MOF) as a glassy carbon electrode (GCE) sensing platform for determination Hg(II). The Ca-MOF was prepared using N,N'-bis(2,4-dicarboxyphenyl)-oxalamide and N,N-dimethylacetamide), which proved to increase the selectivity of the electrochemical sensor towards Hg(II). In another study, Wan ***et al.***, [66] constructed an electrochemical sensor for the simultaneous detection of Cd^{2+}, Pb^{2+}, and Cu^{2+}. The electrochemical sensing platform was fabricated using ferrocenecarboxylic acid-functionalised UiO-66 (Fc-NH_2-UiO-66) and thermally reduced graphene oxide (trGNO) to give an overall final material termed trGNO/Fc-NH_2-UiO-66 nanocomposite. The porous structure and large specific surface area of NH_2-UiO-66 were beneficial to the effective extraction, adsorption, and preconcentration of the target analytes. Additionally, the incorporation of trGNO and Fc improves the electrochemical activity and electron conductivity of the trGNO/Fc-NH_2-UiO-66/GCE sensing platform.

The MOF-based electrochemical sensors have also received more attention in the determination of fast and efficient tracking of emerging contaminants. For instance, Chen ***et al.***, [103] developed an electrochemical sensor based on nitrogen-doped Cu MOFs modified electrode (N-Cu-MOF/GCE). The designed N-Cu-MOFs had an average particle size of 450 nm, unique octahedral shapes, and a large surface area of 1184 m^2 g^{-1}. These extraordinary properties demonstrated excellent electroanalytical capability for the detection of dopamine and sulfonamides. The designed N-Cu-MOF/GCE exhibited wide linear ranges (0.50 nM-1.8 mM), low LOQ (0.15 nM-0.003 µM). Song ***et al.***, [104], designed a novel electrochemical aptasensor based on NH_2-MIL-101(Fe)/CNF@AuNPs electrode for the detection of tetracycline antibiotics in environmental water samples. The authors mentioned that the analytical signals generated from the interaction between tetracycline antibiotics and the electrode were amplified by the NH_2-MIL-101(Fe)/CNF@AuNPs, which resulted in the lowest detection limits and good selectivity. Additionally, the NH_2-MIL-101(Fe)/CNF@AuNPs electrode exhibited high stability.

4. Conclusion and future perspectives

Recent developments and applications of MOF and MOF-based nanocomposites on sample preparation and electrochemical sensor have been reviewed and discussed. To date, the reported findings indicate that the application of MOF and MOF-based nanocomposites in analytical methods is gaining popularity. Depending on the nature of the analytes, literature findings showed that the MOFs and MOF-based nanocomposites have different selectivity and adsorption mechanisms. Other than a large surface area, unique cavities, thermal stability and porosity, $\pi-\pi$ stacking, electrostatic and hydrophobic interactions drive the adsorption mechanism. These properties of MOF materials gain more attention as electrochemical sensing platforms for both inorganic and organic pollutants.

In this review, a concise report on the recent applications of MOF materials as efficient adsorbents for the extraction and pre-concentration of different target organic and inorganic pollutants (pharmaceutical and

Table 4: Summary of the applications of MOFs materials as an electrochemical sensing platform for the detection of environmental pollutants

Analytes	**Electrochemical sensing platform**	**Linearity**	**LOD**	**%RSD**	**Refs**
Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}	UiO-66-NH_2/GaOOH/GCE	0.10–2.50 μM	0.006-0.028 μM	3.4-5.8	[10]
Cu^{2+}, Pb^{2+}, Cd^{2+}	Fc-NH_2-Ni-MOF/GCE	0.001–2.0 μM	0.2-7.1 nM	4.1-7.4	[66]
Cd^{2+}	Fe^{3+}@MOF-867@PPy/GCE	0–130 μg L^{-1}	0.29 μg L^{-1}	-	[105]
Pb(II), Cu(II), Hg(II)	MIL-47(as)/CPE	1–10 μM	29.01-87.80 nM	-	[106]
As	GO/Zn-MOF-GCE	0.2-25 μg L^{-1}	0.06 μg L^{-1}	2.1	[107]
Resorcinol	Cu-MOF/rGO/CuO/α-MnO_2/GCE	0.2 to 22 μM	0.2 μM	-	[99]
paraoxon and chlorpyrifos.	TiO_2 functionalized graphene oxide@UiO-66 (TGO@UiO-66)/GCE	1.0–300.0 nM	0.2-1.0 nM	<4.6	[108]
Nitrites	Cu-MOF/Au/GCE	0.1–4000 and 4000–10000 μM	82 nM	4.3	[109]
Dichlorophen	RGO@Ce-MOF/GCE	0.02-10 μM	0.007 μM	3.6	[110]
Mercury (II)	Thioether-Zr-MOF/ screen-printed carbon electrodes	0.01 nM–3 μM	7.3 fM	2.2-4.0	[111]
Ciprofloxacin	NH_2–UiO-66/RGO sensor	0.02 to 1 μM	6.67 nM	-	[112]
Pb^{2+} and Cd^{2+}	MWCNTs-COOH/UiO-66-NH_2/MWCNTs-COOH/GCE	1-511 μg L^{-1}	0.071-0.090 μg L^{-1}	5.9-6.8	[113]
Nitro-aromatic compounds	Cu-MOF(JUC-62)@pOMC-3/GCE	0.05–420 μM	18 μM		[114]

personal care products, dyes, phenols, polycyclic aromatic hydrocarbons, and heavy metals) from environmental water samples. Additionally, the porous nature of MOF materials proved to be a candidate to replace conventional adsorbents used in SPE and SPME. Furthermore, MOF materials are promising adsorbent materials in the analysis of challenging contaminants such as emerging micropollutants and organic dyes. The future applications of MOFs as adsorbents in analytical chemistry still need a lot of research in terms of green synthesis of new MOFs (prepared from waste materials) with impressive properties such as good selectivity, higher chemical stability, and super adsorption capacity as well as better reusability and separability. Furthermore, combining MOFs with other novel nanomaterials has proven to further enhance the adsorption and conductivity properties of MOFs. The resultant adsorbent materials could be used in various extraction methods (SPME, DSPE, SPME, and SPE) and electrochemical sensing techniques to assist the researchers to improve the performance of their analytical techniques for the analysis of a wide range of pollutants present in complicated environmental matrixes. Finally, this chapter has proven that the opportunity and future of using MOF-based materials in the field of analytical science look highly promising.

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