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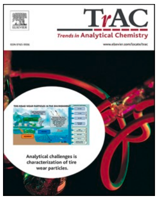

Novel materials for sorptive extraction techniques for the analysis of environmental water samples

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ABSTRACT

Developing new materials for improving the sample preparation step in analytical procedures is one of the most important research lines in analytical chemistry in order to improve the sensitivity or selectivity in this step. The sorptive extraction techniques most commonly used are solid-phase extraction (SPE), magnetic solid-phase extraction (MSPE), dispersive solid-phase extraction (dSPE) and solid-phase microextraction (SPME) or stir bar sorptive extraction (SBSE). The most important materials can be grouped into polymer-based, silica-based, carbon-based, metal organic frameworks (MOFs) and covalent organic frameworks (COFs). These materials can also be combined.

In this review, we present an overview of the most relevant in-house materials used in sorptive extraction techniques that have been reported for extracting contaminants from water samples since 2018. The most important properties that characterize each type of material and how they are exploited to extract the analytes are also presented. In addition, we discuss several examples of applications of these materials and the extraction procedures and highlight the most relevant aspects.

1. Introduction

The presence of contaminants in environmental water can affect public health and environmental integrity. There are many different groups of organic contaminants, such as pesticides [1], pharmaceuticals and personal care products (PCPPs) [2], endocrine disruptor compounds (EDCs) [3] and polycyclic aromatic hydrocarbons (PAHs) [4], among others. These contaminants reach environmental water through three main sources: urban wastewater disposal, industrial waste and agricultural runoff. Therefore, it is important to determine their levels to evaluate the possible effects on human health and the environment [5].

Although liquid chromatography (LC) and gas chromatography (GC) combined with mass spectrometry (MS) are powerful tools, in order to obtain reliable determinations, a sample preparation step must be included in analytical procedure to improve the selectivity and sensitivity of the determination. Sample preparation is often one of the most time-consuming step of the analytical procedure. Therefore, one of the most important research lines in the field of analytical chemistry is improving the current sample preparation procedures, focusing on improving the extraction step.

The extraction techniques for liquid samples can be divided into liquid-liquid extraction techniques and solid-liquid or sorptive extraction techniques. In the field of liquid-liquid extraction techniques, examples of the most commonly used solvents are chloroform, dichloromethane, toluene and hexane. However, due to their toxicity and environmental impact, they are being replaced by less toxic solvents, such as long-chained alcohols like 1-decanol or 1-dodecanol. Moreover, new liquid systems have also been developed with solvents such as switchable solvents, supramolecular solvents, ionic liquids and deep eutectic solvents [6]. The improvements on materials for sorptive extraction techniques have mainly focused on silica-based [7], polymer-based [8] and carbon-based materials [9,10]. Moreover, in recent years, other supports have appeared, such as covalent organic frameworks (COFs) [11] or metal organic frameworks (MOFs) [12]. These solid materials are commonly applied in sorptive extraction techniques such as solid-phase extraction (SPE), magnetic solid-phase extraction (MSPE), dispersive solid-phase extraction (dSPE) and solid-phase microextraction (SPME) or stir bar sorptive extraction (SBSE).

Several reviews have been published describing novel materials for sorptive extraction techniques [13–15], but in this case, we give an overview of the novel in-house materials that have been developed and applied since 2018 for determining contaminants in environmental waters. The materials are divided into polymer-based materials, silica-based materials, carbon-based materials, COFs and MOFs. The combination of two or more types has also been explored and there is also a miscellaneous section for materials not included in the mentioned groups. In addition, magnetic nanoparticles (MNPs) functionalized with

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Table 1

Selected examples of the application of novel in-house silica-based materials and optimized extraction conditions.

Type	Analyte	Ext. Tech.	Extraction procedure				Deter. technique	%R	LOD	Ref
			Amount	Loading/extraction	Washing	Elution/desorption				
Humic acids functionalized silica	Glucocorticoids	SPE	200 mg	1000 mL river, 250 mL effluent WW	–	2.5 mL MeOH	LC-MS/MS	79–123	0.02–0.9 ng/L	[19]
Amine, sulfonic and C$_{18}$ functionalized silica	Pharmaceuticals	SPE	200 mg	100 mL river, 50 mL effluent WW	5 mL MeOH	5 mL 5 % NH$_4$OH in MeOH	LC-MS/MS	40–85	1–5 ng/L	[20]
Mesoporous silica (UVM-7) doped with Ti	Flame retardants	SPE	200 mg	50 mL	–	0.25 mL EtOAc	GC-MS	66–109	0.019–0.21 µg/L	[23]
Perfluorobenzene functionalized silica	PAHs	SPE	200 mg	50 mL	–	2 mL DCM	LC-UV	32–89	2–80 ng/L	[21]
Carboxyl functionalized silica MNPs	Tetracyclines	On-line SPE	10 mg	pH 5	–	0.1 mL, MeOH, ACN and 0.02 M oxalic acid solution (10:20:70, v/v)	LC-MS/MS	97–111	12–74.1 ng/L	[25]
Quaternary amine functionalized silica MNPs	NSAIDs	MSPE	20 mg	4 mL pH 7, 45 min stirring	Water	0.1 mL 2 % AcOH in ACN, 30 min stirring	LC-UV	85–109	0.3–1.5 µg/L	[16]
Schiff base functionalized MNPs	Phenols	MSPE	15 mg	20 mL pH6, 4 min stirring	–	1 mL ACN	GC-FID	93–99	3–20 ng/L	[18]
Aldehyde functionalized mesoporous silica MNPs	EDCs	MSPE	10g	100 mL, 5 min vortex	Water	3 mL ACN, 2 min stirring	LC-HRMS	82–96	0.2–3 ng/L	[26]
C$_8$ and amino functionalized mesoporous silica	Herbicides	MSPE	5 mg	10 mL, pH 5, 1 min	–	1 mL of 2 % NH$_4$OH in acetone 1 min vortex	LC-MS/MS	88–115	5–20 ng/L	[27]
IL functionalized mesoporous silica (MCM-41)	Pesticides	MSPE	Not reported	10 min pH 6, 1 % NaCl	–	0.2 mL ACN, 3 min	GC-ECD	82–110	0.05–1.6 µg/L	[28]
Quaternary amine functionalized mesoporous silica (MCM-48)	EDCs	dSPE	15 mg	20 mL, 0.1 g NaCl, pH 3, 30 min stirring	Water	0.8 mL ACN 10 min USAE	LC-UV	95–102	1.2–2.6 ng/L	[24]
C$_{18}$ functionalized silica	PAHs	IT-SPME	–	25 mL	–	0.2 mL hexane:acetone (9:1, v:v)	GC-FID	79–104	0.22–0.47 µg/L	[17]
N-sulfonyl-4-hydroxymethyl-1,2,3-triazole functionalized mesoporous silica (SBA-15)	Phenolic compounds	SB-µ-SPE	–	10 mL, 2g NaCl, 30 min	2 mL 10 % MeOH in water	0.3 mL MeOH 20 min USAE	GC-MS	85–109	0.03–0.3 µg/L	[29]

Abbreviations: AcOH: acetic acid, ACN: acetonitrile, DCM: dichloromethane, dSPE: dispersive solid-phase extraction, ECD: electron capture detector, EDCs: endocrine disruptor compounds, EtOAc: ethyl acetate, FID: flame ionization detector, GC: gas chromatography, HRMS: high resolution mass spectrometry IT-SPME: in-tube solid-phase microextraction, LC: liquid chromatography, MeOH: methanol, MNPs: magnetic nanoparticles, MS: mass spectrometry, MS/MS: tandem mass spectrometry, MSPE: magnetic solid-phase extraction, NSAIDs: non-steroidal anti-inflammatory drugs, PAHs: polycyclic aromatic hydrocarbons, SB-µ-SPE: stir bar micro solid-phase extraction, SPE: solid-phase extraction, USAE: ultrasound assisted extraction, UV: ultraviolet, WW: wastewater.

the mentioned materials are included in the sections referring to the materials, since the MNPs are used to magnetize the sorbent.

A table is included in each section with selected examples of each type of material and some information about the material applied in each study as well as the extraction technique and its procedure, and the analytical technique used for the determination. In addition, each section includes the description of the most relevant properties of each material and some interesting examples in which we discuss how these properties are exploited in several applications.

2. Silica-based materials

Silica is an interesting material that has been applied in sorptive extraction for many years, it can be obtained at a low cost and it is easy to functionalize [7]. The silanol groups present on the surface of the silica can perform hydrogen bonding interactions with the analytes, being the most important retention mechanism, moreover, this silanol groups can be easily modified by inserting different functionalities, such as quaternary amine groups [16], C_{18} chains [17], or a Schiff Base [18]. As can be seen in Table 1, silica-based materials have been exploited in different sorptive extraction techniques. An example of silica functionalization is the study by Spelltini et al. [19], who thermally condensed humic acids in silica to extract glucocorticoids through SPE by allowing the sorbent to perform π stacking, H bond and dipole-dipole interactions. It should be highlighted that even when relatively high volumes (1000 mL of river water, 250 mL of effluent wastewater) were loaded in the 200 mg cartridges, no high matrix effects (less than 35 % signal suppression) were observed. A different approach was presented in our previous study [20], in which silica was functionalized with quaternary amines, sulfonic groups and C_{18} chains to selectively extract acidic and basic pharmaceuticals through ion-exchange interactions. A washing step with MeOH was included in which the acidic pharmaceuticals were rinsed from the sorbent. The acidic compounds were thus retained through reversed-phase interactions, and the basic compounds were retained through cation-exchange interactions. Therefore, the sorbent was applied to extract the basic analytes with matrix effects lower than ±25 %, as the washing step had removed the compounds retained through non-specific interactions. In another study, Yan et al. [21] functionalized silica with perfluorobenzene, allowing the material to perform π-hole bond interaction, which is a non-covalent interaction similar to a hydrogen bond. This material was applied to extract PAHs. Looking at the recoveries shown in Table 1, the results from these last two studies mentioned [20,21] seem to be low; however, in these studies the reported recoveries are “apparent recoveries”, which show the yield of the extraction and not the accuracy of the method (relative recoveries) as in other studies.

Mesoporous silica is a type of silica characterized by having a more ordered porous structure in which the pores have size uniformity (2–50 nm). It has a higher surface area and more homogeneous structure, which is appropriate for being applied in extraction techniques [7,22]. There are several studies with different modifications to mesoporous silica; for example, Pellicer et al. [23] added Ti to extract phosphorous flame retardants because Ti enhances the interactions with P-containing compounds. As shown in Table 1, the elution was made with ethyl acetate (EtAOc), which was selected over hexane, ACN, MeOH and ethanol (EtOH), because a solvent with intermediate polarity was needed. Moreover, the performance of the new sorbent was compared with a commercial C_{18} material, and it showed higher recoveries than the commercial one. Zhang et al. [24] and Ri et al. [25] functionalized mesoporous silica with quaternary amines and carboxylic acid groups, respectively, to enable the ion-exchange interactions. In the study performed by Zhang et al. [24], it was observed that adding quaternary amine groups compared to the unmodified silica enhanced the retention of some of the EDCs determined (estriol, estradiol, estrone and bisphenol A), due to the contribution of positive charges in the sorbent. However, the analytes were eluted with ACN without any acidic additive, and therefore, despite the ion-exchange contribution, the compounds were mainly retained through π-π and hydrogen bonding interactions. EDCs were also extracted with a modified mesoporous silica material functionalized with aldehyde groups [26].

Other examples of functional groups were the amine groups and C_8 chains to extract phenoxyacid herbicides through ion-exchange interactions [27]. As it can be observed in Table 1, pH 5 was selected for the extraction since it ensured the ionization of both analytes and sorbent, which enhances the ion-exchange interactions. In another study, the possibility to immobilize an ionic liquid in mesoporous silica was also explored [28], when an imidazolium ionic liquid was used for extracting multi-class pesticides (carbamates, OPPs and pyrethroids). Mesoporous silica has also been applied in stir bar supported micro-SPE (SB-μ-SPE) [29] when it was functionalized with N-sulfonyl-4-hydroxymethyl-1,2,3-triazole. This made it possible to perform hydrogen bonding and π-π stacking due to the hydroxyl groups and triazole groups, respectively, to extract phenolic compounds.

Although silica is a material that has been used extensively in sorptive extraction techniques, new silica-based materials including novel functional groups, continue to appear. Moreover, the development of mesoporous silica materials offers another interesting research line.

3. Polymer-based sorbents

Polymers are a type of material that has been widely used in sorptive extraction techniques for many years [8]. Their applicability led to the development of several commercially available materials that are widely applied. Examples of materials applied in SPE are Oasis, Bond Elute and Strata families. The most remarkable one is Oasis HLB, which, as we will point out in this review, has been widely used as a comparison with in-house materials. In SPME there are a few commercially available fibers, such as polydimethylsiloxane (PDMS) fiber, polyacrylate (PA) fiber and polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber. In SBSE, we can highlight the PDMS stir bar, which is also widely applied. Molecular imprinted polymers (MIPs) are another group of polymers that are used in different extraction techniques due to their enhanced selectivity. However, since they have been discussed in depth in other review studies [30,31], they will not be included in the present study.

Polymers give a wide range of flexibility, there is a huge diversity of monomers that can be used as building blocks, from simple molecules such as pyrrole [32] to the use of β-cyclodextrin [33], as can be observed in Table 2. It is very common to use two different monomers in order to combine their properties, such as N-vinylpyrrolidone and divinylbenzene [34] or divinylbenzene and vinylbenzene chloride [35]. Divinylbenzene is generally used as crosslinker monomer to form the structure, while the other monomers (i.e. N-vinylpyrrolidone or vinylbenzene chloride) are introduced to add functional groups. The variability can increase even more with the possibility to functionalize the polymer after the synthesis, and it is possible to add carboxylic acid groups [36], amines [37], a Schiff base [38], perfluorooctanoic acid groups [39] or γ-cyclodextrin [40], among others. Using polymers from natural sources has also been explored in recent years, such as amylodextrin [41], chitosan [42] and luteolin [43], following the principles of Green Analytical Chemistry.

According to the conditions shown in Table 2, there are diverse applications of in-house polymeric materials in SPE, as well as different extraction conditions. For instance, the amount of sorbent ranged from low quantities in the range from 25 to 60 mg to higher quantities in the range from 150 to 500 mg. The loading volume ranged from 8 to 250 mL; however, it is surprising that the lowest loading volume (8 mL) was used with the largest amount of sorbent (150 mg) [33], as it is usually the opposite tendency, although in the mentioned study the loading volume and the sorbent amount were not optimized. It is also surprising that in the study the quantity of the sorbent is expressed in mL [44]. The reason is that the polymer was prepared directly in the cartridge by adding a solution of 2-hydroxymethacrylate (monomer) and ethylene

Table 2
Selected examples of the application of novel in-house polymeric materials and optimized extraction conditions.

Type of polymer	Monomer	Analytes	Ext. tech.	Extraction procedure				Deter. tech.	%R	LOD	Ref
				Amount	Loading/ extraction	Washing	Elution/desorption				
Hydroxyl-functionalized polymer	Luteolin	Neonicotinoid insecticides	SPE	30 mg	100 mL, pH 6	3 mL 10 % MeOH in water	0.2 mL ACN	LC-UV	74–88	0.02–0.08 µg/L	[43]
Poly-2-HEMA	2 - HEMA	NSAIDs	SPE	0.465 mL (monolith precursor)	50 mL, pH 3.15	Water	1 mL ACN	LC-UV	42–53	1–2.6 µg/L	[44]
Hypercrosslinked DVB-VBC polymer	DVB and VBC chloride	MIX contaminants	SPE	200 mg	250 mL river, 100 mL effluent WW, pH 6	1 mL MeOH	5 mL 5 % NH_4OH in MeOH	LC-MS/MS	52–105	0.03–2 ng/L	[35]
PS-DVB functionalized with carboxylic acid groups	Styrene and DVB	Illicit drugs	SPE	60 mg	50 mL, pH 6,	4 mL MeOH	4 mL, 4 % TFA in MeOH	LC-MS/MS	83–116	0.17–1.67 ng/L	[36]
β-cyclodextrin polymer	β-cyclodextrin	Bisphenols	SPE	150 mg	8 mL	–	2 mL MeOH	LC-UV	95–102	0.3 µg/L	[33]
Amino functionalized triazine based HXL polymer MNPs	2,4-diamino-6-phenyl-1,3,5-triazine	EDCs	SPE	25 mg	100 mL	3 mL water	0,2 mL MeOH	LC-UV	84–107	20–60 ng/L	[45]
Polypyrrole MNPs	Pyrrole	β-lactams	MSPE	30 mg	40 mL, pH 4, 40 min stirring	–	2 mL 3 % NH_4OH in MeOH, 20 min stirring	MEKC-UV	83–93	0.8–1 µg/L	[32]
Polydopamine functionalized with γ-cyclodextrin	Dopamine	Microcystins	MSPE	4 mg	20 mL, pH 7, 30 min stirring	–	0.5 mL 20 % NH_4OH in MeOH, 7 min vortex	LC-MS/MS	87–102	0.8–2 ng/L	[40]
Polyethylene glycol functionalized with Schiff base	Ethylene glycol	Benzoylurea insecticides	MSPE	20 mg	10 mL, 2 min vortex	–	1 mL ACN, 1 min US, 1 min vortex	LC-UV	64–103	0.4–1 µg/L	[38]
PolyNVP-co-DVB MNPs	NVP and DVB	Pesticides	MSPE	50 mg	500 mL, 15 min USAE	–	3 mL 0.1 % HCOOH ACN	LC-MS/MS	63–117	0.13–0.42 ng/L	[34]
Amino functionalized HXL polymer MNPs	Styrene	Phenols	MSPE	20 mg	20 mL, pH 3, 10 min stirring	–	0.5 mL acetone, 5 min stirring	CE-UV	81–132	0.05–0.2 µg/L	[37]
Polysaccharide chitosan MNPs	Chitosan	PCBs	MSPE	50 mg	30 mL, pH 7, 25 % NaCl, 60 min stirring	–	1 mL hexane, 15 min USAE	GC-MS	93–106	20 ng/L	[42]
Perfluoroctanoic acid modified polyamideamine polymer MNPs	Ethylenediamine	Pesticides	MSPE	30 mg	8 mL, 1.5 min vortex	–	1.25 mL MeOH 2 min vortex	LC-UV	80–114	0.30–0.49 µg/L	[39]
o-hydroxyazobenzene polymer	2,6-diaminoan-thraquinone	Hormones and insecticides	dSPE	17.5 mg	5 mL, pH 6.5, 36 min USAE	–	1 mL MeOH, 30 min vortex	LC-MS/MS	94–100	0.4–1.3 ng/L	[46]
Ionic liquid polymer	1-vinylbenzyl-3-hexadecylimi-dazoliumbis [(trifluoromethyl) sulfonyl] imide	UV filters	HS-SPME	–	10 mL, 100 °C, 40 min,15 % NaCl	–	6 min, 250 °C	GC-MS	72–122	2.8–26 ng/L	[47]
Combination of hydrophilic acrylic polymer and amylodextrine	Acrylic acid and amylodextrine	Triazole fungicides	PT-SPE	6 mg	20 mL, pH 7.5	–	1.1 mL MeOH	CD-IMS	93–96	0.1–0.2 µg/L	[41]
Azo-linked polymer	4,4′-diamono-terphenyl and phloroglucinol	Benzotriazoles	SBSE	–	10 mL (diluted with 45 % of MeOH), 50 min stirring	–	0.15 mL 2 mM NaOH in acetone	LC-UV	96–118	0.12–0.33 µg/L	[48]
Polydopamine MNPs	Dopamine	Nitro musks	SBSDME	10 mg	25 mL, 15 % NaCl, 10 min stirring	Water	10 min, 275 °C	GC-MS	90–118	0.1–2.8 ng/L	[49]

Abbreviations: ACN: acetonitrile, CD-IMS: corona discharge-ion mobility spectrometry, dSPE: dispersive solid-phase extraction, DVB: divinylbenzene, EDCs: endocrine disruptor compounds, GC: gas chromatography, 2 – HEMA: 2-hydroxymethacrylate, HS-SPME: head-space solid-phase microextraction, LC: liquid chromatography, MEKC: micellar electrokinetic capillary chromatography MeOH: methanol, MNPs: magnetic nanoparticles, MS: mass spectrometry, MS/MS: tandem mass spectrometry, MSPE: magnetic solid-phase extraction, NSAIDs: non-steroidal anti-inflammatory drugs, NVP: N-vinylpyrrolidone, PCBs: polychlorinated bisphenols, PS: polystyrene, PT-SPE: pipette tip solid-phase extraction, SBSE: stir bar sorptive extraction, SBSDME: stir bar sorptive dispersive microextraction, SPE: solid-phase extraction, TFA: trifluoroacetic acid, USAE: ultrasound assisted extraction, UV: ultraviolet, VBC: vinylbenzene chloride, WW: wastewater.

glycol dimethacrylate (crosslinker), which solidified generating the extraction material.

Different types of interactions can be exploited to extract the analytes, which is related to the extraction conditions shown in Table 2. For instance, Guo et al. [43] exploited the π-π stacking and the Lewis acid-base interactions between the hydroxyl groups in the sorbent, which behaved as Lewis bases, and the NO_2 or CN groups in the neonicotinoid insecticides, which behaved as Lewis acids. Therefore, the pH selected was 6, ensuring that the analytes were in neutral form; and the compounds were eluted with acetonitrile (ACN), an adequate solvent to disrupt these interactions. Ning et al. [36] evaluated the exploit of ion-exchange interactions with a polystyrene-divinylbenzene (PS/DVB) polymer functionalized with mercaptosuccinic acid to perform weak cation-exchange interactions. Nadal et al. [35] also evaluated this with a hypercrosslinked polydivinylbenzene/vinylbenzene chloride (PDVB/VBC) polymer functionalized with amino acids to perform cation- and anion-exchange interactions simultaneously. In both cases, it was possible to include a washing step based on MeOH to remove the compounds retained through reversed-phase interactions, increasing the selectivity of the extraction. In the study performed by Wang et al. [45] with a triazine based polymer, the performance of the in-house material for extracting EDCs was compared with some commercial sorbents (Oasis HLB, MWCNTs, graphitized carbon and C_{18}). They obtained the highest recoveries with the in-house sorbent. This sorbent was also evaluated for extracting phenyl urea herbicides, chlorophenols and PAHs. Since the most important interactions were hydrogen bonding interactions, the sorbents showed good performances for all the compounds except the PAHs, which could not form this type of interaction.

Polymers have also been widely applied in dispersive techniques (MSPE and dSPE). As can be seen in Table 2, the loading volume ranged from 5 to 30 mL, according to the amount of sorbent, which ranged from 4 to 50 mg, except for the study performed by Liu et al. [34], which used 500 mL. Despite selecting a large extracting volume considering the amount of sorbent (50 mg) and the extraction time (15 min ultrasound assisted extraction), the recoveries are good. The performance of this sorbent (a copolymer of N-vinylpyrrolidone and DVB) was compared with a cartridge with 500 mg of Oasis HLB sorbent (also a copolymer of N-vinylpyrrolidone and DVB), presenting slightly higher recoveries, with ten times less sorbent thanks to the application of MSPE. Another interesting example is the study performed by Fan et al. [38], which presents a new functionalization of a polyethylene glycol sorbent that consisted of a Schiff base network (a system with high π density), which made it possible to extract benzoyl urea pesticides by exploiting π-π interactions and hydrogen bonding. In addition, Huang et al. [40] exploited hydrophobic interactions to extract microcystins with a sorbent functionalized with a γ-cyclodextrin. These interactions were also exploited in another study to extract polychlorinated biphenyls (PCBs) with a chitosan sorbent [42]. Other authors exploited ion-exchange interactions, such as Li et al. [32], who extracted lactams with a polypyrrole material, applying an acidic pH during the extraction step and a basic solution of MeOH to elute the analytes. In another study [46], hormones and insecticides were retained through electrostatic interactions, π–π stacking and hydrogen bonding with an *o*-hydroxyazobenzene polymer. However, in the elution step (1 mL MeOH), the π–π stacking and hydrogen bonding seem to be more relevant than the electrostatic interactions for retaining the analytes.

Polymeric materials have been applied in other techniques, as seen in Table 2, such as headspace SPME (HS-SPME) [47], pipette tip SPE (PT-SPE) [41], stir bar sorptive extraction (SBSE) [48] and stir bar sorptive dispersive microextraction (SBSDME) [49]. In the HS-SPME study [47], three different polymeric ionic liquids were developed for extracting UV filters. The best performing sorbent was the one in which 1-vinylbenzyl-3-hexadecylimidazolium bis [(trifluoromethyl)-sulfonylimide was used as the monomer. Moreover, using thermal desorption in the GC-MS made it possible to reach low detection limits (low ng/L), which can be seen in Table 2. Thermal desorption was also used for determining nitro musks through SBSDME [49], and low detection limits were also obtained. In this study, the extraction was performed with polydopamine MNPs. In both cases, they exploited the π–π stacking and hydrogen bonding interactions. In the SBSE study [48], the sorbent was rich in phenolic groups, which allowed it to interact with the benzotriazoles through π–π stacking, hydrogen bonding and hydrophobic interactions. Therefore, recoveries obtained with the in-house stir bar were higher than the ones obtained with the commercial PDMS stir bar it was compared with, and which can only perform hydrophobic interactions.

As highlighted, polymer-based materials have been widely used with different applications and it is expected that in the future novel materials will appear, new monomers will be tested and novel functional groups will be evaluated.

4. Carbon-based materials

Carbon can be found in different allotropic forms, such as diamond, graphite, fullerenes, graphene and carbon nanotubes. The last two are currently the most commonly applied in extraction techniques, as can be seen in Table 3.

Graphene a material widely used in different chemical fields, since it is characterized by properties like large delocalized π-density and high surface area. These properties make graphene (and graphene oxide) an interesting material to be applied in analytical chemistry for extraction techniques, mainly due to the π-π interactions that can perform with aromatic compounds [9,50]. The widest application of graphene is as MNPs in MSPE [51–55]. As can be observed in Table 3, the MNPs with graphene (or graphene oxide) can be applied without modification [53, 55], as Wang et al. [53] did when they applied it to extract imidazole antifungals. In this study, after a docking study to discern which type of interaction occurs (electrostatic attraction, cation-π interaction, hydrophobic interaction or π-π stacking), it was found that the major interactions between analytes and sorbent were, as expected, the π-π stacking. Moreover, they evaluated the matrix effect when river, effluent wastewater, and influent wastewater samples were analyzed. Low signal suppression was observed with river and effluent wastewater (less than 28 %) but higher suppression with influent wastewater samples (from 23 to 43 % signal suppression); however, this is acceptable considering the complexity of the matrix. This might be explained by the low specificity of this type of material.

The structure of the graphene (or graphene oxide) can be modified with ionic liquids [51], cyclodextrins [52], or carboxylic acid groups [54], among others. The ionic liquid (1-butyl-3-methylimizadolium bromide) [51] made it possible to extract microcystins through a combination of ion-exchange interactions and π-π stacking; pH 4 was selected since it combined negative charges in the microcystins with positive charges in the sorbent. The addition of carboxylic acid groups [54] also made it possible to perform ion-exchange interactions to extract sulfonamides. Comparing the performance of the carboxylated materials with non-modified graphene, the recoveries were 23 % higher on average. When a β-cyclodextrin was added to graphene MNPs [54], the combination of π-π interactions, due to the graphene, with the formation of host-guest complexes, due to the cyclodextrin, allowed PAHs to be extracted.

Regarding the conditions presented in Table 3, the amount of sorbent ranged from 10 to 80 mg and extraction times were similar, ranging from 10 to 20 min. In relation to the recoveries and detection limits, the recoveries were in all cases close to 100 % and the detection limits depended on the detection used, ng/L (or less) with tandem MS detection and μg/L if UV or FID detection was applied.

Apart from dispersive techniques, graphene was also applied to SPE [56,57] and SBSE [58], although to a lesser extent. In the example of the SPE application [56], a graphene aerogel was created in combination with ethylenediamine for extracting organophosphorus pesticides (OPPs). In this case, three of the compounds (fenitrothion, parathion and

Table 3
Selected examples of the application of novel in-house carbon-based materials and optimized extraction conditions.

Type	Analyte	Extraction technique	Extraction procedure				Deter. technique	%R	LOD	Ref
			Amount	Loading/extraction	Washing	Elution/desorption				
MNPs with graphene functionalized with ionic liquid	Microcystins	MSPE	10 mg	100 mL pH 4, 18 min stirring	–	1.8 mL 10 % NH_4OH in MeOH, 1.5 min vortex	LC-MS/MS	89–99	0.22–0.41 ng/L	[51]
MNPs with graphene oxide functionalized with β-cyclodextrin	PAHs	MSPE	25 mg	20 mL 27 % NaCl, 20 min stirring	–	0.3 mL toluene 6 min USAE	GC-FID	93–105	0.1–0.5 μg/L	[52]
MNPs with graphene	Imidazole fungicides	MSPE	80 mg	200 mL, 15 min stirring	Water	6 mL 2 % NH_4OH in acetone, 2 min vortex	LC-MS/MS	70–92	0.11–0.32 ng/L	[53]
MNPs with graphene functionalized with carboxylic acid groups	Sulfonamides	MSPE	15 mg	200 mL, pH 4, 20 min stirring	–	2x2 mL 1 % NH_4OH in MeOH, 1 min vortex	LC-MS/MS	73–90	0.49–1.59 ng/L	[54]
MNPs with graphene oxide	PAEs	MSPE	60 mg	25 mL, pH 6, 10 min stirring	–	4 mL DCM, 5 min stirring	LC-MS/MS	70–120	6–138 ng/L (LOQ)	[55]
Graphene aerogel	OPPs	SPE	–	40 mL, pH 6	–	5 mL THF	GC-MS	94–102	0.12–0.58 μg/L	[56]
Graphene oxide sponge	Benzotriazoles	SPE	15 mg	5 mL		0.8 mL acetone	LC-UV	89–105	0.02–0.08 μg/L	[57]
Nickel foam covered with graphene	Benzotriazoles	SBSE	–	10 mL, 50 min,	Water	0.15 mL 30 % EtOAc in acetone, 10 min USAE	LC-UV	83–112	0.33–0.50 μg/L	[58]
MNPs with MWCNTs	β-blockers	MSPE	200 mg	200 mL, 30 min stirring	–	6 mL 1 % HCOOH in MeOH, 2 min vortex	LC-MS/MS	49–92	0.54–1.45 ng/L	[60]
MNPs with β-cyclodextrin modified CNTs	PAHs	MSPE	15 mg	10 mL, 20 % NaCl, 20 min vortex	–	0.2 mL toluene, 10 min vortex	GC-FID	75–107	2–10 μg/L	[62]
MNPs with fluorinated CNTs	PFCAs and PFSAs	MSPE	30 mg	50 mL pH 4, 9 min stirring	–	0.5 mL 4 % TFA in acetone, 2 min stirring	LC-MS/MS	79–119	0.01–0.036 ng/L	[63]
MNPs with amino modified MWCNTs	Phenoxy acid herbicides	MSPE	5 mg	10 mL pH 5.4, 1 min vortex	5 mL 15 % MeOH in water	2x1 mL 2 % NH_4OH in acetone, 1 min vortex	LC-MS/MS	86–109	0.01–0.02 μg/L	[64]
MWCNTs	OPPs	SPE	50 mg	50 mL, pH 3	Water	2 mL EtOAc + 2 mL DCM	LC-MS/MS	88–125	0.07–3.33 ng/L	[59]
MWCNTs	Pharmaceuticals and metabolites	dSPE	4 mg	100 mL, pH 3, 30 min stirring	–	10 mL ACN:AcOH 3:7, 30 min stirring	LC-MS/MS	82–117	0.01–0.08 μg/L	[61]
MNPs with activated carbon	EDCs	MSPE	20 mg	0.75 mL, pH 10.5, 1 min, vortex	–	0.75 mL ACN:MeOH 1:1, 1 min vortex	LC-UV	56–81	0.10 mg/L	[65]
Carbon nanodots	OPPs and parabens	SPE	170 mg	50 mL pH 4.5	Water	6 mL 10 % AcOH in ACN	LC-MS/MS	63–123	15–125 ng/L	[66]
Activated carbon derived from corn straw	OPPs	MSPE	15 mg	40 mL, 35 min stirring	–	0.2 mL EtOAc, 4 min vortex	GC-MS	72–97	0.02–0.11 μg/L	[67]
Activated carbon derived from peanut shell	Emerging contaminants	RDSE	10 mg	15 mL, pH 2, 70 min stirring	Water	10 mL EtOAc, 20 min stirring	GC-MS	16–87	0.01–0.73 μg/L	[68]

Abbreviations: ACN: acetonitrile, AcOH, acetic acid, CNTs: carbon nanotubes, DCM: dichloromethane, dSPE: dispersive solid-phase extraction, ECD: electron capture detector, EtOAc: ethyl acetate, FID: flame ionization detector, GC: gas chromatography, LC: liquid chromatography, MeOH: methanol, MNPs: magnetic nanoparticles, MS: mass spectrometry, MS/MS: tandem mass spectrometry, MSPE: magnetic solid-phase extraction, MWCNTs: multiwalled carbon nanotubes, OPPs: organophosphorus pesticides, PAEs: phthalate esters, PAHs: polycyclic aromatic hydrocarbons PFCAs: perfluoroalkyl carboxylic acids, PFSAs: perfluoroalkyl sulfonic acids, RDSE: rotating disc sorptive extraction, SPE: solid-phase extraction, TFA: trifluoroacetic acid, THF: tetrahydrofuran, USAE: ultrasound assisted extraction, UV: ultraviolet, WW: wastewater.

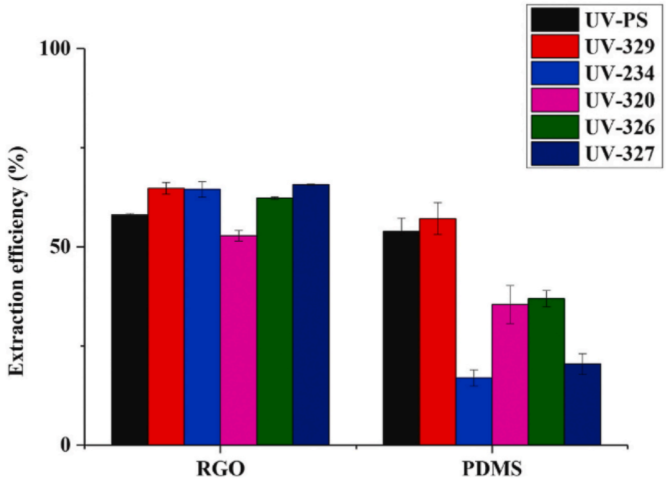

Fig. 1. Comparison of the graphene stir-bar (RGO) with the commercial PDMS stir-bar (PDMS) for extracting UV filters. Reprinted from Ref. [58] of Elsevier.

fenthion) could be retained through π-π stacking, and the other OPPs (trichlorfon, ethoprophos and dimethoate) could possibly be retained through hydrophobic interactions since they do not have benzene rings. For SBSE [58], a nickel foam was covered with graphene for extracting benzotriazoles, and good extraction efficiencies were obtained. This can be seen in Fig. 1 as they were over 50 % for all compounds. Moreover, it can be seen in the figure that the developed stir bar performed better than the PDMS commercial stir bar. Both materials were compared under the same extraction conditions (50 min) and it was observed that the in-house stir bar had faster extraction kinetics because with the same time, the extraction yields were significantly higher.

Carbon nanotubes are the other allotropic form of carbon that is widely used in extraction techniques. Since carbon nanotubes are essentially a graphene sheet rolled into a cylinder, their properties are similar to graphene (high surface area, inertness, high π-density). They can appear as single walled carbon nanotubes (CNTs), which are similar to a single graphene layer, or multiwalled carbon nanotubes (MWCNTs), which consist of multiple concentric layers of graphene [50]. As can be seen in Table 3, carbon nanotubes have been mainly applied in dispersive techniques (dSPE and MSPE); however, some applications in other extraction techniques are reported, such as SPE [59]. Table 3 shows that different amounts of sorbent have been used, ranging from 4 to 200 mg. As expected, the study in which 200 mg were applied matched with the highest volume (200 mL) [60]; however, it should be pointed out that the study that used 4 mg, was able to extract up to 100 mL [61]. Focusing on the applications, CNTs modified with β-cyclodextrin were applied to extract PAHs [62], as well as in the study that combined graphene and β-cyclodextrin [52]. The combination of π-π interactions with the formation of host-guest complexes due to the cyclodextrin enhanced the extraction of the PAHs in both studies [52,62]. CNTs can also be functionalized with fluorine, as Huang et al. [63] did to extract perfluoroalkyl carboxylic and perfluoroalkyl sulfonic acids. The presence of fluorine in the CNTs allowed F–F interactions, which increased the recoveries from 1.1 to 1.9 times compared to the non-fluorinated material. pH 4 was selected because it was observed that basic pH inhibited the F–F interactions. Focusing on MWCNTs, Wang et al. [60] applied non-modified MWCNTs to extract β-blockers, exploiting π-π stacking. The matrix effect was evaluated for river, effluent wastewater and influent wastewater samples. It was found to be less than −17 % for river and effluent wastewater; however, influent wastewater samples had a significant matrix effect (ranging from −19 to −48 %), which can be explained due to the complexity of the sample and the high capacity of the material.

Jakubus et al. [61] presented an interesting study. They extracted pharmaceuticals and their metabolites with different types of MWCNTs: non-modified, OH-modified, COOH-modified and helical MWCNTs. It was observed that the modifications with –OH and –COOH groups decreased the π-π stacking. Comparing the non-modified and the helical MWCNTs, it was observed that the retention in the non-modified MWCNTs was more effective because the compounds were extracted completely with only 4 mg of the sorbent, whereas in the case of helical MWCNTs, the amount of sorbent was 10 mg, which is also a low amount of sorbent. In another study, amino groups were added to the MWCNTs [64] for determining phenoxy acid herbicides. This study is interesting since a washing step with 15 % of MeOH was included to remove some interferences that were not retained through ion-exchange interactions, which was the mechanism for retaining the analytes. This washing step benefited the selectivity of the extraction.

In addition to graphene and carbon nanotubes, other formats of carbon have been reported, such as activated carbon [65] or carbon nanodots [66]. Activated carbon, which was widely used in the beginning of sorptive extraction techniques, was applied for the MSPE of EDCs, exploiting the hydrophobic and π-π interactions [65]. Moreover, activated carbon from biomass is gaining attention and it could be obtained from subjecting materials such as corn straw [67] or peanut shell [68] to high temperature (400–800 °C). The material derived from corn straw was applied for the determination of OPPs meanwhile the one derived from peanut shell was applied to determine emerging contaminants. The application of nanodots in extraction techniques is interesting since they are not usually applied in these techniques [66], and are more applied in sensors [69]. Carbon nanodots were used for the SPE of pesticides (OPPs and parabens) from wastewater samples and the performance of carbon nanodots was compared with a commercial sorbent (Oasis HLB). They showed slightly lower recoveries than the commercial sorbent. The matrix effect was also evaluated, showing values that are considerably high (ranging from −50 to +43 %). This means that the sorbents had a high capacity but low specificity for the pesticides extracted.

As it has been pointed out, the current trends in the development of carbon-based for sorptive techniques are focused on graphene and carbon nanotubes. It is expected that in future years, the research lines will continue with these two materials, evaluating new applications and novel modifications to enhance the extraction procedure.

5. Metal organic frameworks

Metal organic frameworks (MOFs) are based on a metal ion surrounded by organic ligands, forming dimensional structures. Using different metal centers and organic ligands leads to a wide variety of MOFs with different properties [12]. The most applied MOFs are MIL-101 (either with Cr or Fe as metal ion), UiO-66 (Zr) and ZIF-8 (Zn). We will not cover them individually in this section, but rather they are present in some studies in which several MOFs are compared. Moreover, some applications of them will be discussed in the section of composite materials. Applications of these materials can be consulted in reviews focused on MOFs [12,70].

The applications presented in Table 4, show that MOFs have been more commonly applied in dispersive techniques (dSPE and MSPE) and SPME. The interactions performed by MOFs use to be hydrogen bonding, hydrophobic and π-π interactions, and for this reason, the analytes more feasible to be extracted with this material are non-ionizable compounds (PAHs, PCBs, OCPs …) [71,72] or ionizable compounds in their non-charged form [73].

Table 4 presents some studies that compare different MOFs [72,74,75]. For instance, Gao et al. [74] compared MIL-101 (Cr), MIL-100 (Fe), MIL-53 (Al) and UiO-66 (Zr) for extracting estrogens and glucocorticoids by dSPE. These authors observed that MIL-53 (Al) showed the highest sorption capacity, which was due to the simple channel structure of the sorbent promoting the extraction of the analytes. In relation to the extraction conditions, it can be observed that pH 4 was used to prevent

Table 4

Selected examples of the application of novel in-house metal organic framework (MOF) materials and optimized extraction conditions.

Material	Analyte	Extraction technique	Extraction procedure			Deter. technique	%R	LOD	Ref
			Amount	Loading/extraction	Elution/desorption				
MIL-101(Cr), MIL-100(Fe), MIL-53(Al) and UiO-66 (Zr)	Estrogens and glucocorticoids	dSPE	8 mg	10 mL pH 4, 15 % NaCl, 30 min vortex	1 mL MeOH, 20 min USAE	LC-MS/MS	79–107	0.0015–1 μg/L	[74]
HKUST-1, MOF-5(Zn), MIL-53(Al) UiO-64 and MOF-74(Zn)	MIX contaminants	dSPE	5 mg	10 mL, 5 min vortex	3x0.2 mL ACN 5 min vortex	LC-TOF	13–51	0.013–0.04 μg/L	[75]
Na–Bi MOF	PAEs and adipate esters	dSPE	5 mg	5 mL, 5 min vortex	0,5 mL 2,2-dimethoxypropane	GC-FID	52–80	0.66–1.2 μg/L	[82]
MOF on MOF (Co-MOF and Fe-MOF)	Benzodiazepines	dSPE	40 mg	20 mL, 1 % NaCl, 5 min US	0,137 mL MeOH, USAE	LC-UV	88–98	0.06–0.09 μg/L	[81]
Carbonized MOF-71 (Co)	PAHs	MSPE	28 mg	25 mL, 10 % NaCl, 15 min stirring	0.13 mL ACN, 2 min vortex	LC-UV	52–82	0.06–0.18 μg/L	[80]
MIL-100 (Fe)–NH_2	NSAIDs	MSPE	25 mg	50 mL pH 5, 45 min stirring	1 mL 1 % HCOOH in ACN, 15 min USAE	LC-MS/MS	75–105	0.02–0.09 μg/L	[73]
MIL-125 (Ti)–NH_2	Fluoroquinolones	MSPE	25 mg	50 mL, pH 7, 30 min stirring	2 mL 30 % NH_4OH MeOH, 20 min stirring	LC-UV	85–109	0.05–0,2 μg/L	[78]
MIL-53 (Al)– NH_2	Phenols	MSPE	50 mg	50 mL, 10 s vortex	0.5 mL acetone, 10 s vortex	LC-UV	80–111	1.8–42 μg/L	[77]
ZIF-90 (Zn), MOF-199 (Cu), MIL-101 (Cr), MOF-5 (Zn)	PCBs	SPME	–	20 mL, 50 °C, 40 min	230 °C 13 min	GC-MS	87–99	0.0013–0.053 ng/L	[72]
NU-1000 (Zr)	Organochlorine pesticides	SPME	–	10 mL, 40 °C, 40 min	260 °C, 6 min	GC-MS	83–122	0.011–0.058 ng/L	[76]
Carbonized ZIF-67 (Co)	PAHs	SPME	–	15 mL pH 7, 25 % NaCl, 35 °C, 35 min	4 min, MeOH:water (85:15)	LC-UV	82–120	5–42 ng/L	[79]
MAF-66 (Zn)	PAHs	HS-SPME	–	10 mL, 25 % NaCl, 25 °C, 40 min	250 °C, 5 min	GC-FID	90–108	0.1–7.5 ng/L	[71]

Abbreviations: ACN: acetonitrile, dSPE: dispersive solid-phase extraction, FID: flame ionization detector, GC: gas chromatography, HS-SPME: head-space solid-phase microextraction, LC: liquid chroma-tography, MeOH: methanol, MNPs: magnetic nanoparticles, MS: mass spectrometry, MS/MS: tandem mass spectrometry, MSPE: magnetic solid-phase extraction, NSAIDs: non-steroidal anti-inflammatory drugs, PAEs: phthalate esters, PCBs: polychlorinated biphenyls, SPME: solid-phase microextraction, TOF: time of flight, USAE: ultrasound assisted extraction, UV: ultraviolet.

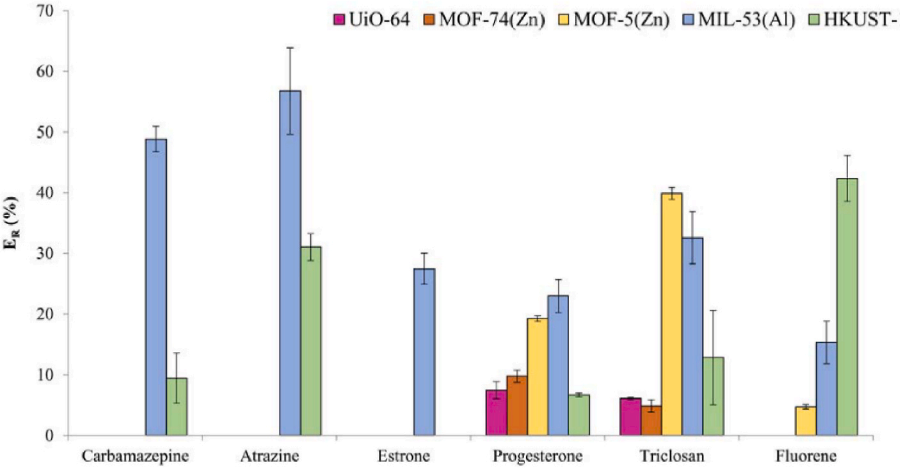

Fig. 2. Comparison of the different MOFs for extracting the target compounds. Reprinted from Ref. [75] of Elsevier.

the ionization of the analytes to enhance the hydrophobic interactions. In another study, Rocío-Bautista et al. [75] also selected MIL-53 (Al) among other MOFs (HKUST-1 (Cu), MOF-5 (Zn), UiO-64 (Zr) and MOF-74 (Zn)) since as can be observed in Fig. 2, it performed better for the extraction of a mixture of contaminants (one PAH, two hormones, two drugs and one disinfectant), with apparent recoveries (not relative recoveries) ranging from 13 to 51 % in wastewater samples. Moreover, Zhang et al. [72] evaluated different MOFs to determine PCBs using SPME, and selected ZIF-90 (Zn) over MOF-199 (Cu), MIL-101 (Cr) and MOF-5 (Zn). Its performance was also compared with commercial fibers (PDMS/DVB, PDMS and PA) and the in-house material was the one that performed best.

Liu et al. [71] developed MAF-66 (Zn) and Gong et al. [76] synthesized NU-1000 (Zr) for the extraction of PAHs and OCPs, respectively, exploiting the π-π interactions occurring between the MOF and the analytes. The performance of NU-1000 was compared with commercial fibers (PDMS/DVB and PA), and the in-house material performed best. As was described previously, MOFs can be applied to extract ionizable

Table 5
Selected examples of the application of novel in-house covalent organic framework (COF) materials and optimized extraction conditions.

Monomers	Analyte	Extraction technique	Extraction procedure			Deter. technique	%R	LOD	Ref
			Sorbent amount	Loading/ Extraction	Elution/ desorption				
N, N, N′, N′-Tetrakis (4-aminophenyl)-1, 4- benzenediamine (TPDA) and 2, 6-pyridinedicarboxaldehyde (PCBA)	Parabens	MSPE	20 mg	10 mL pH 7, 20 min US	2x1 mL ACN, 5 min USAE	LC-UV	82–110	0.15–0.20 μg/L	[87]
1,3,5-tris(4-aminophenyl) benzene (TAPB) and terephthalaldehyde (TPA)	PFAAs	MSPE	30 mg	25 mL pH 4, 15 min stirring	2 mL 5 % NH_4OH in MeOH, US 3 min	LC-MS/ MS	72–115	0.05–0.38 ng/L	[84]
3,3’ -diaminobenzidine (DAB) and 1,3,5-triformylphloroglucinol (Tp)	Phenyl urea herbicides	MSPE	30 mg	120 mL, 5 % NaCl, 25 min stirring	1 mL ACN, 1 min vortex	LC-UV	84–105	0.3–0.5 μg/L	[86]
1,3,5-triformylphloroglucinol (Tp) and benzidine (BD)	Aromatic disinfection byproducts	MSPE	10 mg	50 mL pH 0.5, 6 min vortex	1 mL 4 % HCOOH in MeOH, 1 min vortex	LC-MS/ MS	78–115	0.07–1.81 ng/L	[85]
1,3,5-triformylbenzene (TFB) and 4,4′-diaminobiphenyl (BD)	NSAIDs	dSPE	15 mg	10 mL pH 2, 5 min USAE	0.5 mL 1 % NH4OH in MeOH, 10 min USAE	LC-UV	78–112	0.2–1.4 μg/L	[88]
2,3,5,6-tetrafluoro-4-pyridinecarbonitrile (TFPC) with 2,3,6,7,10,11-hexahydroxy triphenylene (HHTP)	PFAs	SPME	–	10 mL, pH 7, 25 min	1 mL 0.6 % TFA in MeOH, 10 min	LC-MS/ MS	90–105	0.002–0.0045 ng/L	[89]
1,3,5-tri-(4-aminophenyl) benzene (TAPB) with 2,5-dimethoxyterephthaldehyde (DMTA)	Polar phenols	SPME	–	10 mL pH 6, 30 % NaCl, 50 °C, 60min	280 °C, 5 min	GC-MS/ MS	81–112	0.0048–0.015 ng/L	[90]
1,3,5-Tris (4-aminophenyl) benzene (TPB) and 2,5-dimethoxyterephthalaldehyde (DMTP)	OCPs	HS-SPME	–	10 mL, 80 °C, 40 min	280 °C, 6 min	GC-MS/ MS	83–107	0.001–14 ng/L	[92]
1,3,5-triformylphloroglucinol (Tp) and 2,5-dichloro-1,4-phenylenediamine (2,5-DCA)	PCBs	HS-SPME	–	10 mL, 60 °C, 15 min	260C, 5 min	GC-MS	79–124	0.0015–0.0088 ng/L	[91]

Abbreviations: ACN: acetonitrile, dSPE: dispersive solid-phase extraction, GC: gas chromatography, HS-SPME: head-space solid-phase microextraction, LC: liquid chromatography, MeOH: methanol, MNPs: magnetic nanoparticles, MS: mass spectrometry, MS/MS: tandem mass spectrometry, MSPE: magnetic solid-phase extraction, NSAIDs: non-steroidal anti-inflammatory drugs, OCPs: organochlorine pesticides, PCBs: polychlorinated biphenyls, PFAAs: perfluoroalkyl acid substances, PFAs: perfluoroalkyl substances, SPME: solid-phase microextraction, TFA: trifluoroacetic acid, USAE: ultrasound assisted extraction, UV: ultraviolet.

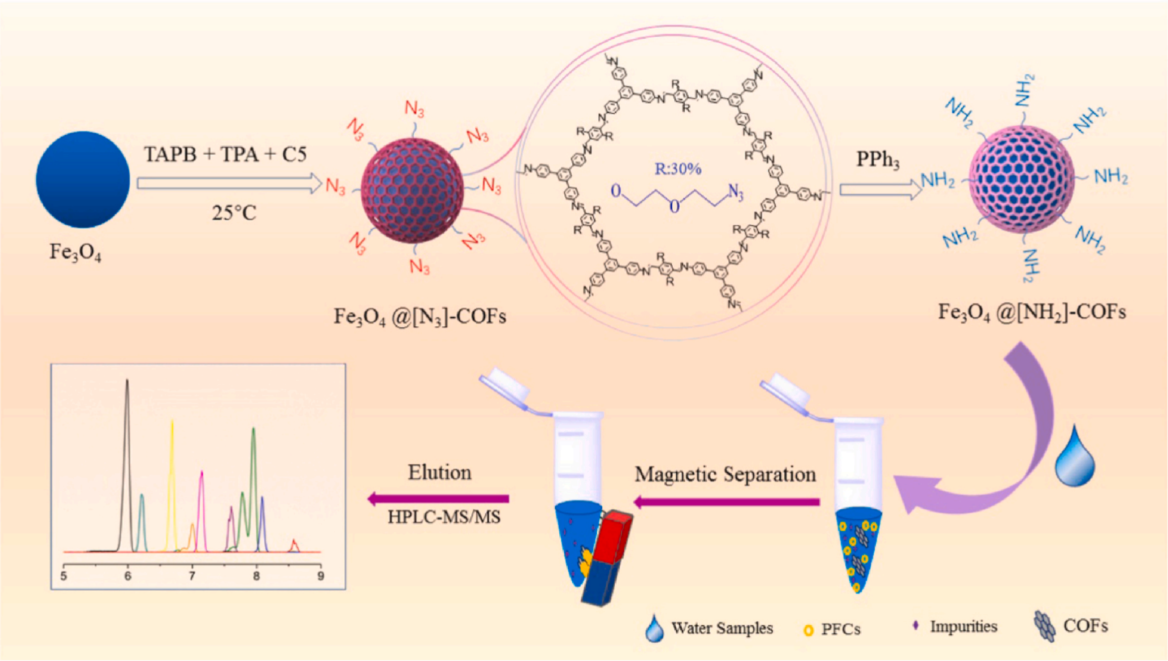

Fig. 3. Preparation and application of the MNPs modified with aminated COF. Reprinted from Ref. [84] of Elsevier.

analytes in their non-charged state, as Liu et al. [73] did when extracting non-steroidal anti-inflammatory drugs (NSAIDs), selecting a pH that prevented the deprotonation of these acidic analytes, and exploiting hydrogen bonding and π-π interactions. The best performing pH was 5, which is surprising considering that the pK_a of these analytes ranged from 3.7 to 5. However, pH 3 and pH 4 had lower recoveries than pH 5, which is difficult to explain considering the mentioned pK_a.

To extract ionizable compounds in their charged form, MOFs can be modified to add functional groups, and the amine groups are the most commonly used for this [77,78]. For instance, Lian et al. [78] developed MIL-125 (Ti) with amine groups to promote the extraction of fluoroquinolones, combining the ion-exchange interactions with the π-π interactions. Moreover, cysteine was included in the structure of the material to increase the shell thickness and improve the extraction.

The MOFs can be subjected to high temperatures to carbonize the material, creating a porous carbon material [79,80]. The properties of these materials can be controlled by the structure of the precursor MOF and the temperature of carbonization. For instance, Akbar et al. [80] subjected MOF-71 (Co) to 600 °C during 2 h to obtain a carbonaceous material that was used to extract PAHs thanks to the combination of hydrophobic and π-π interactions.

It is interesting to consider the use of MOF-on-MOF structures, which are obtained by growing a MOF on the surface of another MOF. Abad et al. [81] combined a MOF based on Co with another based on Fe for extracting benzodiazepines. Another interesting study is the one performed by Pezhhanfar et al. [82], who applied a heterometallic MOF based on Na and Bi. It should be highlighted that 2,2-dimethoxypropane (DMP) was used as the desorption solvent in that study. This solvent is transformed to methanol and acetone in the presence of water. Therefore, the inherent moisture of the MOF particles resulting from vortexing them in the aqueous solution led to the partial conversion of DMP to methanol and acetone. The in-situ-generating ternary solvent (methanol, acetone, and unreacted DMP) led to the desorption of the target compounds from the MOF via vortexing for 5 min.

Other MOF materials apart from ZIF-8, MIL-101 and UiO-66 have also been developed and applied, and it is expected that even more materials will be developed and applied. Moreover, the possibility to functionalize or carbonize them expands the diversity of MOFs.

6. Covalent organic frameworks

Covalent organic frameworks (COFs) are one of the new trends in recent years in the field of extraction techniques. Table 5 shows some relevant examples of their applications. They are based on monomers formed by light elements (C, B, O, N …) that are connected through strong covalent bonds to form a network. The wide diversity of monomers available and the capability to predict how the monomers will assemble make them an interesting material to be applied in analytical chemistry. Despite the diversity among them, all of them are characterized by low density, large surface areas and good chemical stability [11,83]. The monomers employed usually have benzene rings (at least one of the monomers presented in Table 5 for each study), so one of the most common mechanisms to extract the analytes is π-π stacking; for instance, both 1,3,5-tris(4-aminophenyl)benzene and terephtaldehyde [84] have aromatic rings in their structures.

In terms of the dispersive techniques, Table 5 shows that the amount of sorbent ranges from 10 to 30 mg and that the limits of detection are around μg/L when UV detection is used and around ng/L when MS detection is applied. As has been highlighted, most of the studies exploit the π-π interactions to extract the analytes. For instance, when a COF was applied for extracting disinfection byproducts [85], the pH used for the extraction of the compounds was very acidic (pH 0.5) compared to the pH usually applied in extraction techniques, because when pH was higher than 2, then negative charges appeared in the analytes and the COF. Therefore, electrostatic repulsions were generated and the π-π stacking was hindered. However, in some cases, the presence of hydroxyl groups or amines allowed the materials to perform hydrogen bonds [86,87]. Moreover, in some examples COFs have been functionalized with amine groups to exploit ion-exchange interactions, as to extract perfluoro alkyl acid substances (PFAAs) [84]. Their synthetic and extraction procedures are shown in Fig. 3. The extraction procedure was based on using an acidic pH (pH 4) for the extraction to promote the ion-exchange interactions and an elution step with ammonium hydroxide to disrupt these interactions. The addition of the amines was compared with the unmodified sorbent, showing better extraction yields, especially for the smaller PFAAs. Moreover, Li et al. [88] also exploited the ion-exchange interactions to extract NSAIDs, using a molecular imprinted COF (MICOF) that used ibuprofen as template to

Table 6
Selected examples of the application of novel in-house composite materials and optimized extraction conditions.

Type	Description	Analytes	Extraction technique	Extraction procedure			Deter. technique	%R	LOD	Ref
				Amount	Loading	Elution				
Polymer/ Carbon	Alginate, polyvinylpyrrolidone and activated carbon	Nevirapine and zidovudine	dSPE	100 mg	20 mL, pH 6.5, 15 min US	5 mL ACN, 10 min USAE	LC-UV	91–99	0.20–0.23 μg/L	[99]
	Polyethylene glycol and CNTs	OPPs	SPE	–	70 mL	0.8 mL ACN	GC-FID	95–99	0.01–0.03 μg/L	[97]
	Polystyrene and GO	Bisphenols	dSPE	10 mg	10 mL, 30 min vortex, pH 6	6 mL MeOH	LC-MS/MS	71–88	0.02–0.11 μg/L	[93]
	Polystyrene and graphene (aerogel)	Pyrethroids	In syringe SPE	–	10 mL	0.5 mL EtOAc	GC-MS	66–106	0.012–0,11 μg/L	[94]
	Polyamidoamine and MWCNTs (MNPs)	Heterocyclic aromatic hydrocarbons	MSPE	50 mg	60 mL pH 7, 15 % NaCl, 50 min stirring	7.5 mL ACN, 12 min	GC-MS/MS	87–115	0.001–20 μg/L	[98]
	Polyaniline and GO (MNPs)	PAHs and NitroPAHs	MSPE	2.5 mg	20 mL, 15 min USAE	0.15 mL ACN, 5 min USAE	GC-MS	92–113	0.04–0.05 μg/L	[96]
	Polycaprolactone and graphene	Contaminants	RDSE	–	150 mL, 2 h stirring	1 mL MeOH, 1 min shaking	LC-UV	52–120	3–7.6 μg/L	[95]
Polymer/ MOF	HKUST-1 (Cu)-polyMAA	Fluoroquinolones	Online SPE	0.1 mg	pH 7	2 % HCOOH in MeOH	CE-UV	92–100	30 ng/L	[121]
	TMU-4 (Zn) and polyethersulfone	OPPs	HS-SPME	–	10 mL, 30 % NaCl, 75 °C, 40 min	220 °C, 6 min	GC-NPD	91–108	5–8 μg/L	[105]
	Polyvinylidene fluoride UiO-66 (Zr)–NMe3+	Phenoxy acid herbicides	DME	–	50 mL, 30 min stirring	2x2.5 mL 1 % NH4OH in MeOH	LC-MS/MS	80–117	0.03–0.59 ng/L	[100]
	Chitosan + MIL-53 (Al) USED, MIL-53 (Fe), MIL-101 (Cr), MIL-101 (Fe), UiO-66 (Zr) and MIL-100 (Fe)	Parabens	dSPE	–	10 mL pH 5, 20 min US	1 mL EtOAc, 15 min vortex	LC-MS/MS	79–102	0.09–0.45 μg/L	[101]
	MIL-101 (Cr), MIL-100(Fe), ZIF-8 (Zn), MOF-199 (Cu), MIL-53 (Al) and PVA	NSAIDs	SPE	–	10 mL, pH 6, 1 h vortex	1 mL ACN USAE	LC-MS/MS	78–106	7–37 ng/L	[102]
Polymer/ MOF	UiO66 (Zr)–NH2 and poly-4 vinylpyridine	Sulfonylurea herbicides	SBSE	–	5 mL, pH 5, 30 min	0.2 mL 10 % AcOH in MeOH, 30 min	LC-UV	69–98	0.04–0.84 μg/L	[103]
	Polydopamine and MIL-101 (Fe) (MNPs)	Sulfonylurea herbicides	MSPE	60 mg	25 mL pH 5, 3 min vortex	7 mL MeOH, 3min USAE	LC-UV	91–109	0.12–0.34 μg/L	[104]
Polymer/ COF	Polyacrylonitrile - COF (terephthalaldehyde and 1,3,5-tris (4-aminophenylbenzene)	OCPs	SPME	–	20 mL pH 6, 10 % NaCl, 30 min 40 °C	250 °C, 5 min	GC-ECD	79–116	0.05–20 ng/L	[107]
	poly (styrene-divinyl benzene-glycidyl-methacrylate) - COF (1,3,5-triformylbenzene and 4,4′-diamino-biphenyl)	NSAIDs	In syringe SPE	20 mg	3x10 mL, pH 4	3x0.5 mL EtOH	LC-UV	93–100	0.54–2.74 μg/L	[106]
MOF/ Carbon	MIL-101 (Cr) and GO (MNPs)	Neonicotinioid insecticides	MSPE	20 mg	10 mL pH 7, 4 % NaCl, 20 min USAE	1 mL 30 % 3-ethyl-amine in EtOH, 6 min USAE	LC-UV	89–102	19–22 ng/L	[108]
Silica/ Polymer	Mesoporous silica and polydopamine (MNPs)	Amphetamines	MSPE	50 mg	50 mL, pH 11, 15 min stirring	5 mL 5 % HCOOH in ACN, 3 min vortex	LC-MS/MS	95–107	0.5–2.5 ng/L	[109]
Silica/ Carbon	Silica and graphene (MNPs)	Benzothiazoles, benzotriazoles and benzenesulfonamides	SPE	200 mg	100 mL river, 50 mL effluent WW and influent WW	5 mL MeOH	LC-HRMS	48–85	10–455 ng/L	[110]
Silica/MOF	Cu/Ni MOF and silica MNPs	Aflatoxins	MSPE	39 mg	15 mL, pH 7.7, 0.3 g NaCl, 6 min USAE	0.265 mL MeOH, 7 min USAE	LC-FLD	94–96	0.01–0.04 μg/L	[111]

Abbreviations: ACN: acetonitrile, AcOH: acetic acid, dSPE: dispersive solid-phase extraction, ECD: electron capture detector, EtOAc: ethyl acetate EtOH: ethanol, FLD: fluorescence detector, GC: gas chromatography, HRMS: high resolution mass spectrometry, HS-SPME: head-space solid-phase microextraction, LC: liquid chromatography, MeOH: methanol, MNPs: magnetic nanoparticles, MS: mass spectrometry, MS/MS: tandem mass spectrometry, MSPE: magnetic solid-phase extraction, NPD: nitrogen-phosphorous detector, NSAIDs: non-steroidal anti-inflammatory drugs, OCPs: organochlorine pesticides, OPPs: organophosphorus pesticides, PAHs: polycyclic aromatic compounds, SBSE: stir bar sorptive extraction, SPE: solid-phase extraction, USAE: ultrasound assisted extraction, UV: ultraviolet, WW: wastewater.

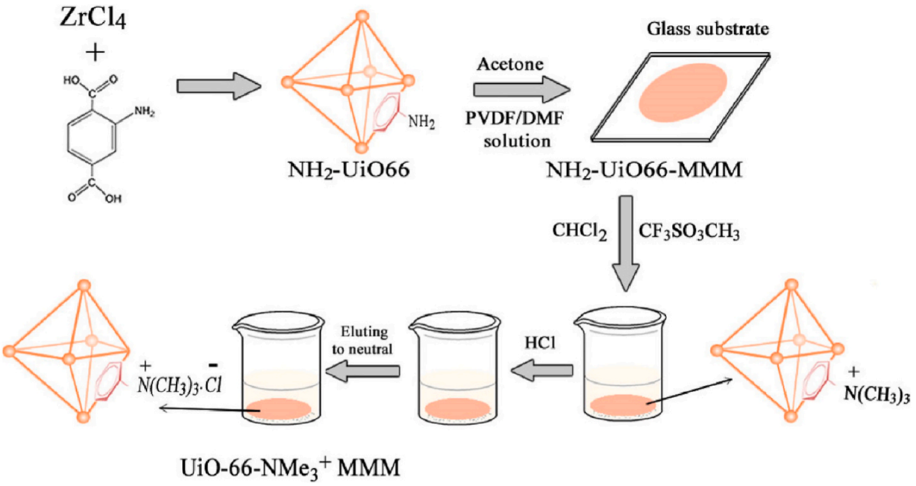

Fig. 4. Illustration for the synthesis of UiO-66-NMe$_3^+$ membranes. Reprinted from Ref. [100] of Elsevier.

promote the selectivity of the extraction.

In the case of SPME applications, when this technique was combined with GC/MS determination, significantly low detection limits were achieved (Table 6), even with liquid desorption [89]. It should be noted that some COFs applied in SPME had high surface areas, reaching values such as 1254 [89] or 1560 m^2/g [90]. Similarly to the sorbents applied in dispersive techniques, the π-π interactions and the hydrogen bonding were the mechanisms exploited to extract the analytes [89–92]. The fibers developed were compared with the commercial fibers most commonly used, such as DVB/CAR/PDMS, PA, PDMS and PDMS/DVB [90–92]. The in-house material was the one that performed best in all cases. In another comparison with commercial fibers, the COF based on the combination of 1,3,5-triformylphloroglucinol (Tp) and 2, 5-dichloro-1,4-phenylenediamine (2,5-DCA) [91], also showed a better performance than PDMS and PDMS/DVB fibers for extracting PCBs. The commercial fibers had lower extraction yields as the chlorine atoms of the PCBs increased. This behavior was not observed in the COF developed.

Although COFs are a relatively new material in the field of sorptive extraction techniques, interesting applications have already been demonstrated. More applications of these materials with new combinations of monomers are expected to be reported in the future with successful results.

7. Combination of materials

The described materials can be combined to exploit the properties of both in a synergistic way. As seen in Table 6, the material that had the most combinations was polymers, mainly with carbonaceous materials and MOFs. Focusing on the combinations between carbonaceous and polymer materials, similarly to the trend with carbon-based materials, most of the applications are with dispersive techniques. Graphene and graphene oxide have been combined with polystyrene [93,94], polycaprolactone [95] and polyaniline [96], among others. For instance,

Table 7
Selected examples of the application of novel in-house miscellaneous materials and optimized extraction conditions.

Material	Analytes	Extraction Technique	Extraction procedure			Deter. technique	%R	LOD	Ref.
			Amount	Loading	Elution				
ZSM-5 (Zeolite) MNPs	NSAIDs	MSPE	40 mg	20 mL pH 2.2, 2.5 % NaCl, 2 min vortex	0.424 mL MeOH, 2 min USAE	LC-UV	86–107	0.5–3 μg/L	[116]
Boron nitride MNPs	Phenoxy carboxylic acid herbicides	MSPE	7 mg	10 mL pH 3, 10 min vortex	3 × 0.5 mL 5 % NH_4OH in ACN, 3 min vortex	LC-MS/MS	77–107	5.6–10.3 ng/L	[113]
Hydroxypatite MNPs	Parabens	MSPE	2 mg	50 mL pH 3, 7 min USAE	0.1 mL ACN, 5 min USAE	GC-MS	95–104	5–10 ng/L	[115]
MoS_2 MNPs	Neonicotinioid insecticides	MSPE	40 mg	30 mL pH 7, 10min stirring	3x1 mL acetone: EtOAc (1:1) 30 s vortex	LC-UV	66–91	0.48–0.67 μg/L	[112]
Surfactant modified MNPs	Parabens	MSPE	20 mg	80 mL, pH 7, 10 min stirring	0.28 mL MeOH, 15 min USAE	LC-UV	87–116	2.4–6.3 μg/L	[114]
Paper modified with deep eutectic solvent	Triazine herbicides	dSPE	–	25 mL, 60 min stirring	1 mL MeOH, 5 min stirring	GC-MS	89–106	0.4–0.6 μg/L	[118]
Fabric	Pesticides	FPSE	–	100 mL 5 % NaCl, 50 min stirring	0.25 mL acetone, 2 min vortex	GC-MS	20–100	3–160 ng/L	[120]
ZnAl-LDH	UV filters	SPME	–	15 mL pH 9.5, 3 % NaCl, 35 min, 35 °C	Liquid desorption	LC-UV	80–109	17–52 ng/L	[117]
Cork	Contaminants	RDSE		35 mL	1 mL MeOH: EtOAc (1:1)	GC-MS	80–120	0.11–1.44 μg/L	[119]

Abbreviations: ACN: acetonitrile, dSPE: dispersive solid-phase extraction, EtOAc: ethyl acetate, FPSE: fabric-phase solid extraction, GC: gas chromatography, LC: liquid chromatography, LDH: layered double hydroxide, MeOH: methanol, MNPs: magnetic nanoparticles, MS: mass spectrometry, MS/MS: tandem mass spectrometry, MSPE: magnetic solid-phase extraction, NSAIDs: non-steroidal anti-inflammatory drugs, RDSE: rotating disc solid extraction, SPE: solid-phase extraction, USAE: ultrasound assisted extraction, UV: ultraviolet.

Song et al. [93] combined polystyrene microspheres with graphene oxide to extract bisphenols. They compared the recoveries of the components separately and observed that the performance was better when the components were combined. The authors attributed this improvement to the synergistic effects of the polymeric microspheres that increased the surface available to interact with the analytes while graphene enhanced the π-stacking with their high π density. In terms of the methodology of this study (Table 6), the elution volume used (6 mL) is surprisingly high compared to the low amount of sorbent (10 mg) although a lower elution volume might have been used if this variable was optimized. The study does not report which elution volumes were tested, so this volume might be reduced without reducing the recoveries. Another application combined polystyrene and graphene to generate an aerogel [94]. After the generation of the aerogel, the polymer was removed and the final product was applied in the in-syringe SPE for pyrethroids, which allowed on-site sampling. It stands out that in another study [96], an elution volume as low as 0.15 mL of ACN was used when 2.5 mg of sorbent based on the combination of polyaniline and graphene oxide was applied to extract aromatic compounds through π-π interactions. Moving to the combination with carbon nanotubes, Amiri et al. [97] combined polyethylene glycol with CNTs to extract OPPs. The polymer provided a 3D network while the CNTs enhanced the π-π interactions. Moreover, Zhou et al. [98] also exploited the structure of the polymer, in their case polyamidoamine, and the π density of MWCNTs to extract heterocyclic aromatic hydrocarbons. Apart from CNTs and graphene, activated carbon has been combined with polyvinylpyrrolidone and alginate to extract nevirapine and zidovudine [99], it can be highlighted that alginate is a natural biopolymer, so using it follows the trends of Green Analytical Chemistry.

The combination of polymer and MOF has been also deeply investigated, some examples are shown in Table 6. The structural possibilities that allow working with polymers combined with MOFs created some interesting formats, such as membranes [100], foams [101] and cryogels [102]. For example, Wu et al. [100] combined UiO-66 (Zr) – NMe_3^+ with polyvinyl fluoride to create membranes for extracting phenoxy carboxylic acid pesticides through dispersive membrane extraction (DME), as can be observed in Fig. 4. Since the extraction is based on ion-exchange interactions, it is surprising that there was no pH adjustment to control the ionization of the analytes. In another study, Li et al. [101] created foams by combining chitosan (a biopolymer) with several MOFs: (MIL-53(Al), MIL-53 (Fe), MIL-100(Fe), MIL-101(Cr), MIL-101 (Fe) and UiO-66(Zr). It was observed that MIL-53 (Al) performed the best for extracting parabens through a combination of hydrophobic and π-π stacking because the extraction pH was 5 (analytes in neutral form) and ethyl acetate was used for the elution. It stands out that a low matrix effect was observed, being lower than ±20 %. Moreover, Wang et al. [102] also tested different MOFs (MIL-101 (Cr), MIL-100(Fe), ZIF-8 (Zn), MOF-199 (Cu), MIL-53 (Al)) in combination with polyvinyl alcohol (PVA) to produce cryogels for extracting NSAIDs. The best performing material was MIL-101 (Cr) and the adsorption mechanism discussed was a combination of H-bonding (hydroxyl groups in PVA) and π-π stacking due to the π density on the MOF. These three applications [100–102] are examples in which the structure of polymers makes it possible to create formats to exploit MOFs in an easier way in comparison to powder. Moreover, Yang et al. [103] and Deng et al. [104] combined UiO-66 (Zr) and poly-4-vinylpyridine and MIL-101 (Fe) and polydopamine, respectively, to extract sulfonyl urea herbicides. As can be seen in Table 6, the two studies used pH 5 for the extraction since the interactions exploited were π-π stacking and H-bonding, preventing the analysis from being charged. In addition, Bagheri et al. [105] developed a new fiber for HS-SPME by combining TMU-4 (Zn) and polyethersulfone to extract OPPs. In this case, the MOF contributes with high surface area (although it is not reported) and the polymer with a high π density.

Table 6 shows that other combinations have been reported, such as polymer with COF [106,107], MOF with graphene [108] and silica with polymer [109], graphene [110] or MOF [111]. In most cases, one of the materials acted as a substrate (due to their structure) to promote the interactions of the other material. This is the case of the combinations of polymer and COF [106,107] and the one of silica and graphene [110], in which the extraction was based on the π-π interactions due to the inclusion of COFs or graphene in the silica structure. In the case of combining MOF and graphene [108], the combination of MIL-101 (Cr)–NH_2 and graphene oxide made it possible to perform H-bonds due to the amine groups in the MOF, as well as π-stacking due to the graphene for extracting neonicotinoid insecticides. Silica also acted as the substrate to enhance the retention of the analytes when it was combined with polydopamine [109] and a bimetallic MOF (Cu–Ni) to extract amphetamines and aflatoxins through π-stacking and H-bonding [111].

Although different combinations have been presented in this review, it is expected that in the future more and more composite materials will be developed, exploiting the properties of each component synergistically.

8. Other materials

In this section, we discuss some relevant applications that did not fit in the previous sections. As can be seen in Table 7, most of these applications are based on modified MNPs with different functionalities. The use of materials with a similar structure to graphene was evaluated by combining MNPs with MoS_2 [112] and hexagonal boron nitride [113]. Regarding the similarity of these compounds with graphene, the π-stacking is the governing interaction between the S–Mo–S rings and the extracted neonicotinoid pesticides [112] or between the BN rings and the phenoxy acid herbicides [113]. Materials that are regularly used in other fields of chemistry were evaluated for functionalized MNPs, such as a surfactant (DC193C) [114], hydroxyapatite [115] and a zeolite (ZSM-5) [116]. In addition to MNPs, using a ZnAl layered double hydroxide (LDH) in SPME can be highlighted for extracting UV filters [117]. In this study, the performance of the in-house fiber was compared with commercial fibers (PA and PDMS) and showed a better performance than both the commercial fibers. This improved performance was related to the higher surface area that LDH involved (although the surface area was not reported) and also to the capability of the sorbent to perform cation-π interactions with the aromatic compounds.

Some interesting new formats have also been reported that follow the principles of Green Chemistry, such as paper [118], cork [119] and fabric [120]. Paper is very interesting and promising due its hydroxyl groups and also because its porosity can be impregnated with liquids, for instance using a deep eutectic solvent (thymol-vanillin) to extract triazine herbicides [118]. Cork also has an interesting structure with good hydrophobicity and a large number of aromatic rings due to the presence of lignin and suberin. These were exploited for extracting multiclass contaminants through rotating stir disk extraction (RSDE) [119]. The easy modification of fabric through sol-gel reactions makes it possible to introduce several modifications. For instance, Ferracane et al. [120] modified fabric with Carbowax 20 M, a mixture of polycaprolactone and polydimethylsiloxane and polytetrahydrofuran, to extract up to seven different families of pesticides (carbamates, morpholines, nitrosamines, OCPs, OPPs, pyrethroids, and triazines). It was observed that combining Carbowax 20 M and polytetrahydrofuran provided the best results. Since green chemistry is becoming increasingly relevant nowadays, it is expected that the application of these sustainable formats will increase significantly in future years.

9. Conclusions

In this review we have emphasized the appearance of numerous homemade materials to be applied in sorptive extraction techniques for determining contaminants in water samples. A wide variety of materials have been applied through the diverse extraction techniques, exploiting the properties of each material to extract the compounds and improve the extraction features. It is also highlighted that depending on the structure and features of the materials, different type of interactions can be exploited to interact with the target compounds.

This area of research is expected to continue evolving and improving analytical procedures. The most frequently reported applications involved the use of different materials in combination, taking advantage of their synergistic properties. It is anticipated that most new materials will follow this trend.

The growing importance of green chemistry is expected to influence the development of new materials, and the search for more sustainable substrates is also likely to increase in the coming years.

CRediT authorship contribution statement

Alberto Moral: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Francesc Borrull:** Project administration, Funding acquisition, Conceptualization. **Rosa M. Marcé:** Supervision, Project administration, Methodology, Conceptualization. **Núria Fontanals:** Validation, Supervision, Conceptualization.

Declaration of competing interest

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

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Data availability

No data was used for the research described in the article.

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