

# Use of Nanomaterials in the Pretreatment of Water Samples for Environmental Analysis



Sandra C. Bernardo, Ana C. A. Sousa, Márcia C. Neves and Mara G. Freire

**Abstract** The challenge of providing clean drinking water is of enormous relevance in today's human civilization, being essential for human consumption, but also for agriculture, livestock and several industrial applications. In addition to remediation strategies, the accurate monitoring of pollutants in water supplies, which most of the times are present at low concentrations, is a critical challenge. The usual low concentration of target analytes, the presence of interferents and the incompatibility of the sample matrix with instrumental techniques and detectors are the main reasons that render sample preparation a relevant part of environmental monitoring strategies. The discovery and application of new nanomaterials allowed improvements on the pretreatment of water samples, with benefits in terms of speed, reliability and sensitivity in analysis. In this chapter, the use of nanomaterials in solid-phase extraction (SPE) protocols for water samples pretreatment for environmental monitoring is addressed. The most used nanomaterials, including metallic nanoparticles, metal organic frameworks, molecularly imprinted polymers, carbon-based nanomaterials, silica-based nanoparticles and nanocomposites are described, and their applications and advantages overviewed. Main gaps are identified and new directions on the field are suggested.

## 1 Introduction

Since the beginning of industrialization and due to the continuous population growth, anthropogenic activities have been constantly rising, allowing many toxic compounds to reach the aquatic environment (Hussain and Kharisov 2016). According to the United Nations Environmental Program (UNEP) and the Food and Agriculture Organization of the United Nations (FAO), the contamination of the aquatic environment and consequently water pollution is a global challenge, both in developed and developing countries (UNEP/UNECE 2016; FAO 2017; WWAP 2017). The contamination

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of the aquatic environment has negative impacts on ecosystems and human health and, consequently, undermines economic growth. To address this important problem it is necessary to understand the extension of water contamination, where environmental monitoring is essential. However, some of the compounds that are being accumulated in the environment are sometimes close or under the detection limits of the currently available analytical techniques, despite being toxic at very low concentrations. In order to assess the current levels of these pollutants in the environment it is crucial to modernize and improve the performance of analytical techniques, so that pollutants that are present at ultra-low concentrations in environmental samples could be detected and quantified with accuracy and consistency (Scragg 2005; Hussain and Kharisov 2016).

Pollutants are occasionally ubiquitous contaminants; most of them can migrate from the point sources and contaminate other areas where they are not used (Scragg 2005). According to the United Nations Environmental Program (UNEP, UNEP b) and the Food and Agriculture Organization of the United Nations (FAO), the sources of contamination are diverse and include, for example, agriculture and food (e.g. land based farming, agroindustry, fisheries and aquaculture), energy (e.g. fossil fuels, biomass), industry (e.g. chemical, mining, and petrochemical), manufacturing (e.g. pharmaceuticals, home appliances, electronics), services (e.g. health care, tourism), transports (e.g. fuel use, engine emissions) and waste (e.g. municipal and industrial solid waste, hazardous waste, wastewater effluents, leachates) (Fig. 1).

The most common pollutants found in the environment (water, soil and air) include metals, polycyclic aromatic hydrocarbons (PAHs), persistent organic pollutants (POPs), pesticides, and pharmaceutical drugs (Liang and Guo 2009; Hussain and Kharisov 2016).

**Metals** are naturally occurring elements that due to human activities are being re-introduced in the environment, e.g. from agriculture activities and wastes from industrial processes (Scragg 2005; UNEP 2013). Once released, some metals such as cadmium, lead, copper, chromium, mercury, uranium, nickel, cobalt, zinc, arsenic, selenium, thallium, and antimony, tend to bioaccumulate (Akpór 2014). Some of these metals, such as mercury, are also able to bioconcentrate along the food chain and they can even cross the blood brain barrier, being considered as extremely toxic (Bjørklund et al. 2017). These pollutants have been extensively studied since water contamination with metals poses serious health risks due to their high toxicity (most are carcinogenic and teratogenic substances) (Scragg 2005; Vunain et al. 2016; Carolin et al. 2017). Hence, these toxic metals have been prioritized as the major inorganic contaminants in the environment; furthermore, they are non-biodegradable, highly persistent and present high mobility between ecosystems (Vunain et al. 2016).

**Polycyclic aromatic hydrocarbons (PAHs)** are hydrocarbons with two or more fused aromatic rings. PAHs are produced from the incomplete combustion or pyrolysis of carbonaceous and organic matter (coal, diesel, gas, wood, etc.). Their major anthropogenic sources into the atmosphere and environment include industrial processes, vehicle exhausts, energy producing plants, waste incineration, and domestic heating emissions (Pandey et al. 2011; Sajid et al. 2018). PAHs are highly toxic and some of them are mutagenic and carcinogenic (Scragg 2005; Sajid et al. 2018). PAHs

**Fig. 1** Schematic representation of examples of human activities and pollutant's sources of water contamination



are ubiquitous in the environment being detected in all compartments (air, soils and water). In what concerns aquatic systems, PAHs have been detected in river, lakes, oceans and also in groundwater and drinking water (Menzie et al. 1992; Burgess et al. 2003).

**Persistent organic pollutants (POPs)** are a group of manmade chemicals that are persistent, toxic and globally distributed. These chemicals are even found at high levels in regions where they were not used, including the Arctic. POPs include different classes of chemicals, as for example, polychlorinated biphenyls (PCBs), dioxins and furans, organochlorine pesticides [e.g. dichlorodiphenyl trichloroethane (DDT), polybrominated diphenyl ethers (PBDEs), short-chained chlorinated paraffins or perfluorooctane sulfonic acids (PFOS)]. Their deleterious effects include cancer, neurotoxicity, immunotoxicity and endocrine disruption. They are regulated under the Stockholm convention and their use is mostly banned (UNEP a).

Another commonly found type of pollutants, especially due to agriculture activities, are **pesticides**, which include herbicides, fungicides and insecticides (UNEP c). Pesticides are a wide-ranging group of chemical compounds, including organochlorines, organophosphates, carbamates, chloroacetanilide, pyrethroids and neonicotinoids (Kaur et al. 2014; Wang et al. 2017). They are widely used to prevent crops destruction by any plague and to increase the agriculture productivity, leading to

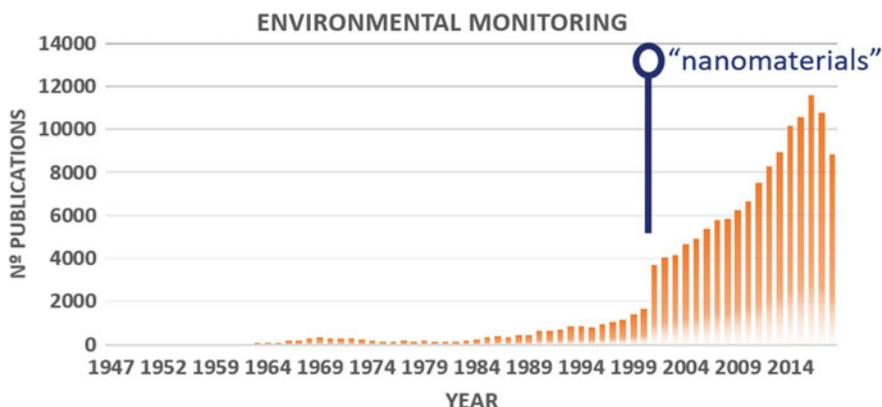
their accumulation in the food chain and in the contamination of air, water and soil (Kaur et al. 2014; Wang et al. 2017).

Despite the important role of **pharmaceuticals** for assuring public health safety, their excessive and prolonged use poses serious environmental concerns. Pharmaceuticals are not completely metabolized by the human body, being mainly discharged by urine and reaching wastewater treatment plants (WWTPs) (Lolic et al. 2015). Furthermore, daily tons of these compounds are directly loaded in the sewage systems. However, most of the pharmaceutical drugs and their bioactive metabolites are not completely removed since WWTPs are mainly designed to remove suspended solids and organic loadings, leading to a continuous discharge of these compounds into the environment (Lolic et al. 2015). Antibiotics, for instance, are amongst the pharmaceutical drugs presenting a higher threat; they induce toxic effects at very low concentrations and can in a long-term contribute to the growth of antibiotic-resistant bacteria (Wang et al. 2018). But other drugs are also of high concern due to their large consumption and release into the environment, such as non-steroidal anti-inflammatory drugs (NSAIDs), analgesics,  $\beta$ -blockers, lipid regulators and psychiatric drugs. The European Union established regulatory guidance to assess the presence of pharmaceuticals in the aquatic environment, in which several drugs are included in the watch list, namely the hormones 17- $\alpha$ -ethinylestradiol and 17- $\beta$ -estradiol, and the NSAID diclofenac, as they may pose a significant risk to the aquatic environment and for which monitoring data are insufficient (European Commission 2013; Lolic et al. 2015).

Due to the serious concern associated to these pollutants, the European union implemented the Water Framework Directive (WFD) (European Commission 2013), requiring their determination down to the  $\text{ng L}^{-1}$  range (Liang and Guo 2009). Accordingly, the improvement of the sensitivity of analytical techniques currently used to identify and quantify the several pollutants present in aqueous samples is in high demand (Liang and Guo 2009; Hussain and Kharisov 2016). However, the key difficulty in environmental analysis is connected to the low sensitivity and selectivity of the used analytical techniques. Most of the times these are insufficient for determining the low concentration levels and to eliminate interferences arising from the complex environmental matrices, turning mandatory a sample treatment step prior to analysis (Liang and Guo 2009). However, sample pretreatment is still one of the most time- and labor-consuming parts in environmental analysis, and has been subject of intensive research over the past 20 years (Hussain and Kharisov 2016).

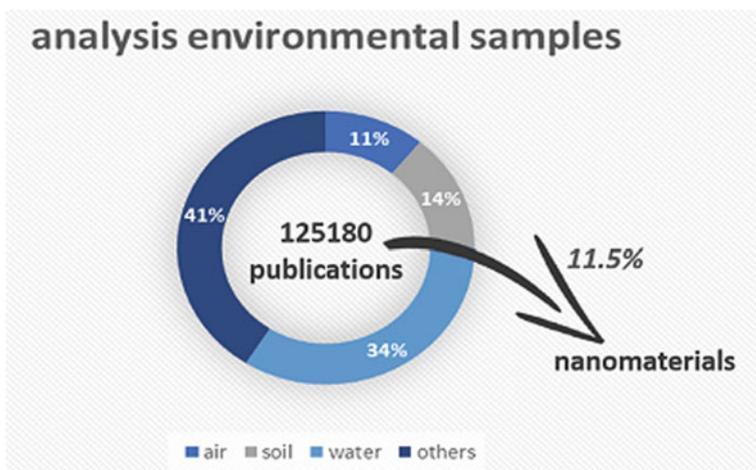
## 2 Improvement of Environmental Analysis Using Nanomaterials

Environmental analysis can be defined as the use of analytical chemistry techniques to detect and quantify pollutants in the environment (Nilsson et al. 2007). The high demand for environmental monitoring is confirmed by the increasing number of



**Fig. 2** Number of publications *per* year (from 1947 to 2018) focusing on environmental monitoring. The search was carried out in the PUBMED database in December 2018 using the keywords “environmental monitoring”. The search was refined using the additional keyword “nanomaterials”. Publications dealing with nanomaterials in environmental monitoring appeared after 2001

reports along the years, as shown in Fig. 2. Around 2001, a boom of publications on this matter arose, especially due to the introduction of nanomaterials in environmental monitoring. Accordingly, more than 10% of the total of publications concerning the analysis of environmental samples are related with the use of nanomaterials, as summarized in Fig. 3. From these publications it is possible to ascertain the types of samples used, namely “water”, “soil” and “air”, being the water samples those that



**Fig. 3** Overview on publications (from 1947 to 2018) focusing on the analysis of environmental samples. The search was carried out in the PUBMED database using the keywords “analysis”, “environmental” and “samples”

correspond to a higher number of publications (34%). Moreover, 11.5% of the total publications comprise the use of “nanomaterials” for the analysis of environmental samples (Fig. 3).

Nanomaterials could have different applications in environmental analysis. For instance, they can be used as sorbent materials in solid-phase extraction (SPE) for sample pretreatment prior to the analysis (Savage and Diallo 2005; Liang and Guo 2009), as supports for the fabrication of sensors (Liang and Guo 2009), or as stationary or pseudostationary phases in several analytical techniques (Zhang et al. 2006; Liang and Guo 2009) (Fig. 4).

The low concentration of target analytes, the high content of potential interferents and the incompatibility of the sample matrix with the instrumental techniques are the main reasons behind the need of improving the sample preparation step, envisioning the enhancement of speed, reliability and sensitivity. The goals of sample preparation methods are summarized in Fig. 5 (Xu et al. 2016). **Solid-phase extraction (SPE)** is one of the most attractive procedures for sample preparation since it can be easily implemented, can be combined with different detection techniques and it holds high ability for preconcentration (Hussain and Kharisov 2016). In SPE, nanomaterials, which will be discussed below, usually display a high performance for the adsorption

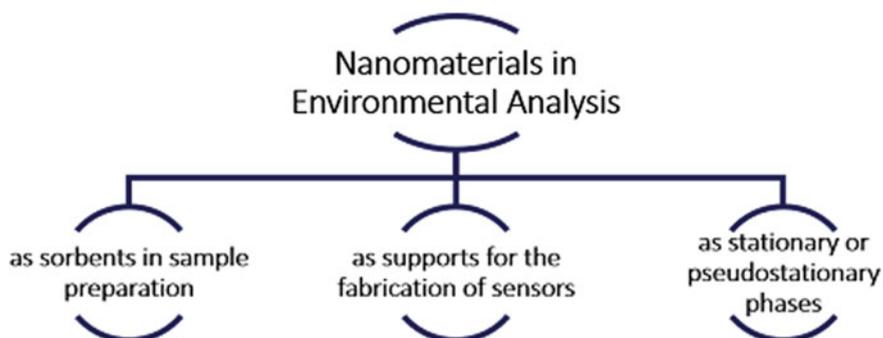


Fig. 4 General overview of the applications of nanomaterials in environmental samples analysis

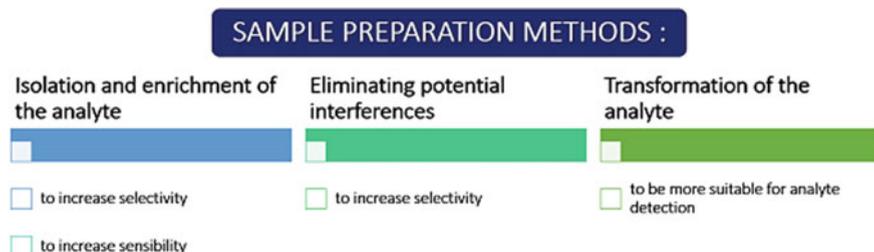


Fig. 5 Schematic representation of the main goals in the sample preparation step

of a wide range of analytes due to their high surface area and possibility of modifying their chemical nature and chemical groups at the surface.

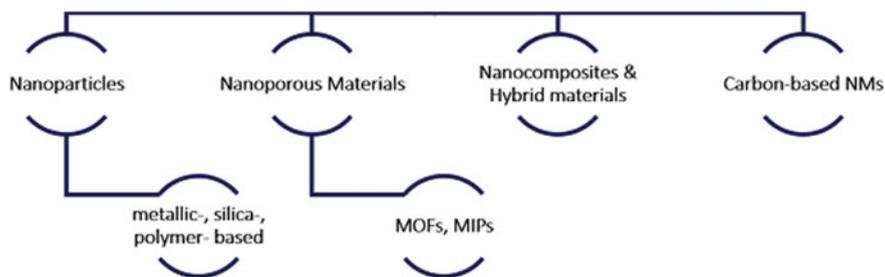
### 3 Nanomaterials in Solid-Phase Extraction

As highlighted before, sample preparation is a crucial step in the analysis of aquatic environmental samples since these matrices tend to be highly complex, presenting most of the times trace level analytes (Ribeiro et al. 2014; Wierucka and Biziuk 2014). Sample preparation is essential to improve the analytes concentration and to remove interfering species (Tian et al. 2013), contributing to the enhancement of both accuracy and sensitivity (Xu et al. 2016). In sample preparation procedures, the most common difficulties are related with the use of time-consuming techniques, complete recovery of the target analytes, removal or isolation of impurities, and high associated costs (Wierucka and Biziuk 2014). It is highly desirable to improve the adsorption efficiency and selectivity, as well as the miniaturization and automation of various stages of sample preparation (Ribeiro et al. 2014; Wen et al. 2014; Wierucka and Biziuk 2014).

Amongst the different preconcentration techniques for sample preparation, SPE is advantageous over other pretreatment techniques, like liquid-liquid extraction, precipitation, co-precipitation, etc. (Das et al. 2012). SPE is a simple and fast operation, it allows high enrichment factors and recovery, may be of low cost, and can avoid the consumption of organic solvents (Das et al. 2012). Some classic materials, such as C8 and C18, mixed-mode/cationic-exchange (MCX), mixed-mode/anion-exchange (MAX) and weak anion-exchange (WAX), are commonly used in SPE (Wen et al. 2014). More recently, novel solid-phase sorbents based mainly on nanomaterials have been studied and applied for water samples pretreatment in environmental analysis. Although several sample preparation methods using nanomaterials have been proposed, in this chapter the use of nanomaterials in SPE for monitoring of environmental aqueous samples and drinking water samples is reviewed.

The term “nanomaterials” (NMs) usually refers to materials with nanometric size (typically 1–100 nm), at least in one dimension (length, width or thickness) (Tian et al. 2013; Xu et al. 2016). Therefore, nanomaterials may include nanometer sized particles and materials with porous size in the nanometer range or even nanometer sized particles dispersed within a porous matrix (Tian et al. 2013) (Fig. 6). These NMs present exceptional physical and chemical properties, such as high specific areas, and the possibility of displaying unique optical, electrical, thermal and magnetic characteristics. They can also be functionalized with various chemical groups to increase their affinity toward target compounds and present various morphologies, being tuneable according to the type of analyte and analytical technique (Tian et al. 2013; Xu et al. 2016).

During the past two decades, nanomaterials have been extensively employed to design novel pretreatment techniques focused on isolation and/or preconcentration of target analytes from different types of samples (Hussain and Kharisov 2016).



**Fig. 6** Schematic representation of the different types of nanomaterials used in SPE for the analysis of environmental aqueous samples. *MOFs* metal organic frame-work materials; *MIPs* molecularly imprinted polymers

Herein, we summarize and discuss some of the latest (from 2009 to 2018) and most significant applications of nanomaterials in SPE for sample preparation, namely for environmental aqueous sample analysis. These NMs include metallic nanoparticles (MNPs), metal organic frame-work (MOF) materials, molecularly imprinted polymers (MIPs), carbonaceous nanomaterials and silica-based nanoparticles, which are described below in detail.

### 3.1 *Metallic Nanoparticles (MNPs) in SPE*

Metallic nanoparticles involve a wide range of different inorganic and inorganic/organic hybrid nanoparticles, such as **metal nanoparticles**, **metal oxide nanoparticles** and **magnetic nanoparticles** (Lucena et al. 2011; Tian et al. 2013).

Among **metal nanoparticles**, gold nanoparticles (Au NPs) and silver nanoparticles (Ag NPs) are the most well-known nanosorbents for metal ions and organic pollutants, such as PAHs (Wang and Campiglia 2010; Lo et al. 2012; Wu et al. 2012; Tian et al. 2013; Hussain and Kharisov 2016). In the past decade, Liu (2009) provided an overview on the characterization and applications of Au NPs, highlighting the incorporation of Au NPs in analytical systems, namely in the preparation and concentration of samples.

Au NPs are highly relevant in the field of environmental monitoring and analysis since organic molecules containing thiol (–SH) or amino (–NH<sub>2</sub>) groups can adsorb spontaneously onto Au surfaces to form well-organized self-assembled monolayers (Liu 2009). Accordingly, Wang and Campiglia (2010) described the use of a gold nanoparticle-based SPE method for benzo[a]pyrene (PAH) determination in spiked tap water samples. The methodology was combined to laser-excited time-resolved Shpol'skii spectrometry (LETRSS), being able to improve the limit of detection (LOD) of the technique by an order of magnitude (LOD = 0.001 ng/mL) (Wang and Campiglia 2010). In addition to organic compounds, Karimipour et al. (2012) showed the applicability of Au NPs for the enrichment and preconcentration of trace amounts

of metals, namely  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$ , from real samples. By using a new sorbent based on Au NPs loaded in activated carbon (Au-NP-AC) and modified by bis(4-methoxy salicylaldehyde)-1,2-phenylenediamine (BMSAPD), a preconcentration factor of 200 was reported for all the metal ions under study, with detection limits ranging from 1.4 to 2.6 ng/mL (Karimipour et al. 2012). Also, Lo et al. (2012) tested the affinity of mercury species for Au NPs, namely by mixing Au NPs with aluminium oxide ( $\text{Al}_2\text{O}_3$ ) particles. The authors reported removal efficiencies higher than 97% for the four mercury species, from spiked lake water, groundwater, and seawater samples (Lo et al. 2012). Moreover, by using this Au NP- $\text{Al}_2\text{O}_3$  adsorbent it was found that the LODs for the mercury species were in the sub-ppq level, which is about 24-fold lower than those obtained without preconcentration (LOD = 0.028  $\mu\text{g/mL}$ ) (Lo et al. 2012).

Ag NPs have also been described as adsorbents with high affinity towards mercury. In this line, Wu et al. (2012) increased the selectivity (more than 1000-fold) of the analytical system for  $\text{Hg}^{2+}$  over other metal ions, by combining nanoparticle extraction, fluorescent dye labelling, and flow injection analysis (FIA) detection. Silver nanoparticles were functionalized with an oligonucleotide composed of repeated 33 thymine nucleotides ( $\text{T}_{33}$ -AgNPs) that specifically captures  $\text{Hg}^{2+}$  from tap water samples (LOD = 0.006 ng/mL) (Wu et al. 2012). Not only surface modification with functional groups in Ag NPs provided extra selectivity, but also it prevents the prepared Ag NPs from aggregating (Tian et al. 2013).

**Metal oxide nanoparticles** (MONPs), such as  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{MnO}$  and  $\text{CeO}_2$ , have been reported in the literature as major inorganic nanoadsorbents for the enrichment and separation of metal trace elements (Lucena et al. 2011; Wen et al. 2014; Hussain and Kharisov 2016).  $\text{TiO}_2$  NPs were used for Cd determination from groundwater and wastewater samples at the nanogram *per* kilogram level with high preconcentration factors (>10) (García-ruiz et al. 2011). As summarized in Table 1, several MONPs have been used to analyse metal ions in environmental aqueous samples (Afkhami et al. 2011; Baytak et al. 2011; Erdogan et al. 2011; García-ruiz et al. 2011; Yalçinkaya et al. 2012). Most of the times these MONPs are modified with functional coatings to increase their selectivity (Lucena et al. 2011); for instance, Baytak et al. (2011) described the use of a minicolumn of a yeast (*Yamadazyma spartinae*) immobilized on  $\text{TiO}_2$  nanoparticles for the determination of Cr, Cu, Fe, Mn, Ni and Zn in environmental water samples by ICP-MS. Alumina ( $\text{Al}_2\text{O}_3$ ) nanoparticles were also successfully used for the determination of trace amounts of Pb(II) and Cr(III) in environmental water samples (Afkhami et al. 2011). Afkhami et al. (2011) prepared modified MONPs by the immobilization of 2,4-dinitrophenylhydrazine on nano-alumina coated with sodium dodecyl sulphate, with recoveries of the metals ranging from 98 to 104% and a maximum preconcentration factor of 267 (Afkhami et al. 2011).

**Magnetic nanoparticles** (MNPs) are constituted by a core and a supported layer, in which the magnetic core is mainly composed of iron, nickel, cobalt, and their corresponding oxides (Wierucka and Biziuk 2014; Hussain and Kharisov 2016). The most common magnetic cores are composed of iron oxides, including magnetite ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\text{Fe}_2\text{O}_3$ ) (Hussain and Kharisov 2016). Since pure iron-

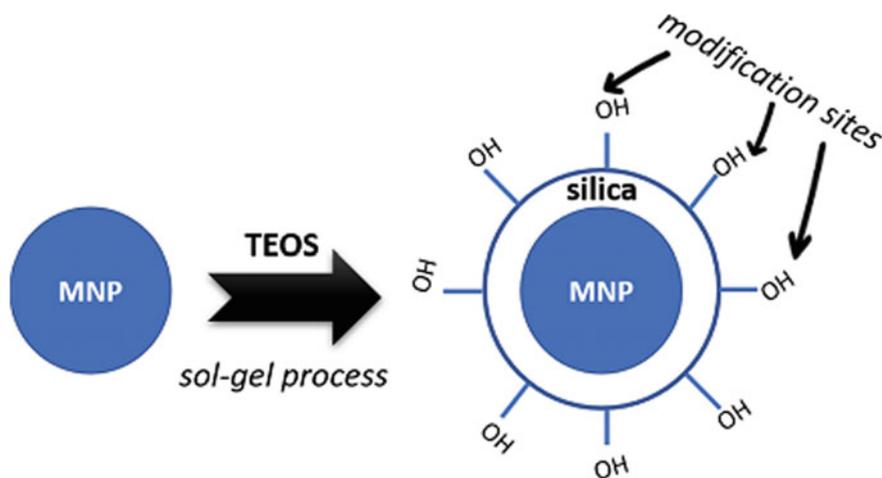
**Table 1** Summary on the use of metal oxide nanoparticles in SPE for metal ions detection (in the last 10 years)

Metal oxide NPs	Modification	Sample matrix	Analyte	Analytical technique	LOD (ng/mL)	References
TiO <sub>2</sub>	–	Ground and waste waters	Cd(II)	ID-ICPMS	–	García-ruiz et al. (2011)
TiO <sub>2</sub>	Coated with yeast ( <i>Yamadazyma spartinae</i> )	Tap and lake waters	Cr(III), Cu(II), Fe(III), Mn(II), Ni(II) and Zn(II)	ICP-AES	0.1–0.45	Baylak et al. (2011)
Al <sub>2</sub> O <sub>3</sub>	Coated with 2,4-dinitrophenylhydrazine	Tap, bottled mineral, waste waters, industrial effluents	Pb(II) and Cr(III)	FAAS	0.43–0.55	Alkhami et al. (2011)
ZrO <sub>2</sub> –B <sub>2</sub> O <sub>3</sub>	–	Tap and hot spring waters	As(III) and As(V)	HGAAS	0.009	Erdogan et al. (2011)
ZrO <sub>2</sub> –B <sub>2</sub> O <sub>3</sub>	–	Waste water	Al(III)	FAAS	7.71	Yalçinkaya et al. (2012)

LOD limit of detection: ID-ICPMS inductively coupled plasma mass spectrometry; ICP-AES inductively coupled plasma atomic emission spectrometry; FAAS flame atomic absorption spectrometry; HGAAS hydride generation atomic absorption spectrometry

oxide NPs easily form aggregates, which may alter their magnetic properties, the surface of the magnetic core is usually modified with a suitable coating (Wen et al. 2014; Wierucka and Biziuk 2014). The modifying layer can be either constituted by inorganic substances (e.g. silica, alumina, manganese oxide (IV), or graphene), organic substances (e.g. molecularly imprinted polymers, chitosan, divinylbenzene, polyamidoamines), or surfactants (Wierucka and Biziuk 2014; Hussain and Kharisov 2016). This coating layer protects not only the magnetic core from aggregation but also from oxidation and, if properly selected, may enhance the interaction between analytes and the adsorbent material.

Due to its several advantages, silica is the most commonly used material for coating MNPs. Silica carries silane groups that can be easily modified (Wierucka and Biziuk 2014). Figure 7 shows a scheme of the sol-gel process usually applied to synthesize silica-coated MNPs. Zhang et al. (2011) described the use of a core-shell magnetic ( $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ) mesoporous silica sorbent functionalized with  $\text{C}_{18}$  (octadecyltriethoxysilane) groups for the removal of PAHs from water samples. Also, surfactants such as sodium dodecyl sulphate (SDS) can be functionalized on the surface of MNPs, being suitable either for the adsorption of metal ions (mercury) (Faraji et al. 2010) or antidepressant drugs (fluoxetine) (Bagheri et al. 2011b). Moreover, some polymers and copolymers were described as coating agents of MNPs for the removal of toxic metal ions and organic compounds from environmental water samples and their pretreatment, such as polyaniline (Mehdinia et al. 2011), a copolymer of methyl methacrylate (MMA) and maleic anhydride (MA) (Masoumi et al. 2014), polydopamine (Iqbal et al. 2011) and polypyrrole (Iqbal et al. 2011; Meng et al. 2011).



**Fig. 7** Synthesis of silica-coated magnetic nanoparticles (MNPs), where hydroxyl groups could be then modified. *TEOS* tetraethyl orthosilicate

More recently, Tolmacheva et al. (2016) suggested the use of a new generation of highly porous polymers, the hypercrosslinked polystyrene (HCP), for the modification of Fe<sub>3</sub>O<sub>4</sub> NPs. This absorbent was used for the preconcentration of four sulphonamide antibiotics from river water samples. The compounds were quantified by high-performance liquid chromatography with amperometric detection, with recoveries varying between 84 and 97% and the detection limit ranging between 0.6 and 1.0 ng/mL (Tolmacheva et al. 2016). Ionic liquids (ILs) such as 3-chloropropyl-N-methylimidazolium (Yang et al. 2011) and 1-hexadecyl-3-methylimidazolium bromide have also been successfully used to functionalize MNPs (Cheng et al. 2012), both works envisaging the preconcentration of chlorophenols in environmental water samples prior to HPLC-UV analysis. Table 2 compiles the latest uses of MNPs with different surface modifications in the preconcentration of several analytes in environmental water samples.

The latest described works correspond to magnetic solid-phase extraction (MSPE). This method presents a clear advantage over simple SPE, explaining the increased interest of researchers in such an approach. With MNPs, the sorbent with the adsorbed analytes can be easily separated from the aqueous solution using an external magnetic field (magnet) without the need for sample centrifugation or filtration, thus contributing to a faster separation process (Fig. 8). Due to these benefits, other types of magnetic absorbents have been reported for sample preparation in environmental analysis of water samples, such as the magnetic metal-organic frameworks (MMOFs), magnetic molecularly imprinted polymers (MMIP) and carbon-based magnetic hybrid nanocomposites, which will be discussed further ahead in this chapter.

### 3.2 *Metal Organic Frameworks (MOFs)*

In the last decade, a class of organic-inorganic hybrid microporous materials have emerged as improved absorbent materials in separation science, namely metal organic frameworks (MOFs) (Wen et al. 2014; Xu et al. 2016; Hashemi et al. 2017). MOFs are self-assembled materials composed of metal ions (or clusters) with organic linkers via coordination bonds (Tian et al. 2013; Wen et al. 2014; Hussain and Kharisov 2016; Xu et al. 2016; Hashemi et al. 2017). Their inorganic moieties act as the nodes of 3-D frameworks with ligands as linkers that create a porous structure with stable and well-defined cavities (Hussain and Kharisov 2016). Provided with a super large surface area, in the range between 1000 and 10,000 m<sup>2</sup>/g, MOFs can be a promising material in sample preparation (Xu et al. 2016). Moreover, by changing the structure or size of guests, these materials can exhibit different pore size and diverse topology, and their surfaces can be also easily functionalized (Tian et al. 2013). The diversity of either metal ions or organic linkers allows the design and preparation of new and different types of MOFs in terms of topology, structure, and porosity (Hashemi et al. 2017). In summary, MOFs are remarkable porous materials as they possess the robustness of their inorganic metal structure and the tuneability of polymer materials

**Table 2** Summary on the use of MSPE in the pretreatment of aqueous sample (in the last 10 years)

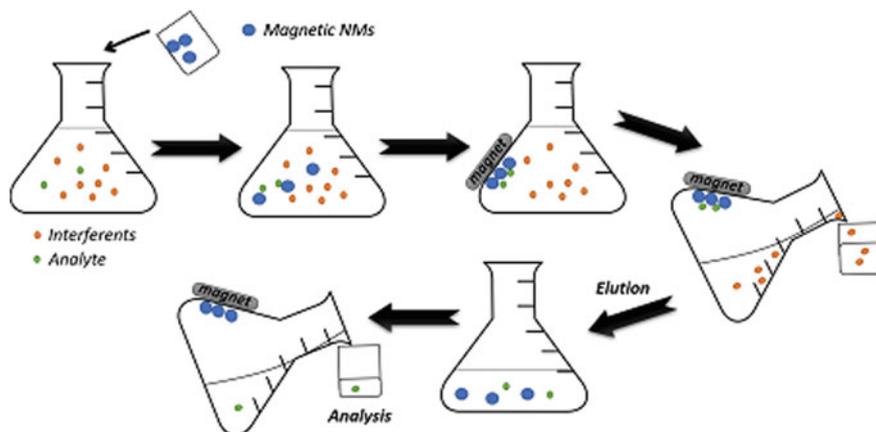
Magnetic core	Covering layer	Sample matrix	Analyte	Analytical technique	LOD (ng/mL)	References
Fe <sub>3</sub> O <sub>4</sub>	SDS	Tap, well and mineral water	Hg(II)	ICP-OES	0.04	Faraji et al. (2010)
	SDS	Tap and river water	Fluoxetine	LC-FD	20	Bagheri et al. (2011)
	Alkyl (C10-C18) carboxylates	River, reservoir and sea water	Benzo(a)pyrene, benzo(b)-fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene and indene(1,2,3-cd)pyrene (PAHs)	LC-FD	0.0002–0.0005	Ballesteros-Gomez and Rubio (2009)
	Polyaniline	Seawater	Methylmercury	GC-MS	0.1	Mehdima et al. (2011)
	Polydopamine or Polypyrrole	–	Bisphenol A, proflavine, naphthalene acetic acid	CE-UV	–	Iqbal et al. (2011)
	Polypyrrole	Spiked water	Dimethyl phthalate, diethylphthalate, di-iso-butyl phthalate, di-n-butyl phthalate, benzybutyl phthalate, di-(2-ethylhexyl) phthalate and di-n-octyl phthalate	GC-MS	0.006–0.068	Meng et al. (2011)
	APTMS and poly(MMA-co-MA)	–	Co <sup>2+</sup> , Cr <sup>3+</sup> , Zn <sup>2+</sup> , and Cd <sup>2+</sup>	–	–	Masoumi et al. (2014)
	HCP	River water	Sulfamethoxy-pyridazine, sulfamethazine, sulfamethoxazole and sulfachloropyridazine	HPLC-PDA	0.6–1.0	Tolmacheva et al. (2016)

(continued)

Table 2 (continued)

Magnetic core	Covering layer	Sample matrix	Analyte	Analytical technique	LOD (ng/mL)	References
	Silica	Lake and waste waters	Naphthalene, acenaphthene, anthracene, fluoranthene, and pyrene, benz[a]anthracene (PAHs)	HPLC-PDA	0.0028–0.0272	Huo and Yan (2012)
	Silica and 3-chloropropyl-N-methylimidazolium	River, spring and tap waters	3-chlorophenol, 2,4-dichlorophenol, pentachlorophenol	HPLC	0.20–0.35	Yang et al. (2011)
	1-hexadecyl-3-methylimidazolium bromide	River and tap water	2,4-dichlorophenol and 2,4,6-trichlorophenol	HPLC	0.12–0.13	Cheng et al. (2012)
	C18-functionalized mesoporous silica	Spiked ultra-pure water	Fluoranthene, pyrene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[e]pyrene, benzo[g,h,i]perylene (PAHs)	HPLC-FD	–	Zhang et al. (2011)
	Mesoporous silica (MCM-41) and functionalization with pyridine	Tap, river and sea water	Cd <sup>2+</sup>	FAAS	0.04	Omid et al. (2015)
	Cu <sub>3</sub> (BTC) <sub>2</sub> MOF and functionalization with dithizone	Tap and lake water	Pb <sup>2+</sup>	FAAS	0.0046	Wang et al. (2013)

LOD limits of detection; SDS sodium dodecyl sulphate; APTMS 3-aminopropyltrimethoxysilane; HCP hypercrosslinked polystyrene; ICP-OES inductively coupled plasma optical emission spectrometry; LC-FD liquid chromatography with fluorescence detection; GC-MS gas chromatography-mass spectrometry; CE-UV capillary electrophoresis with UV-detection; HPLC high-performance liquid chromatography; HPLC-PAD HPLC with pulsed amperometric detection; HPLC-FD HPLC with fluorescence detection; FAAS flame atomic absorption spectrophotometry

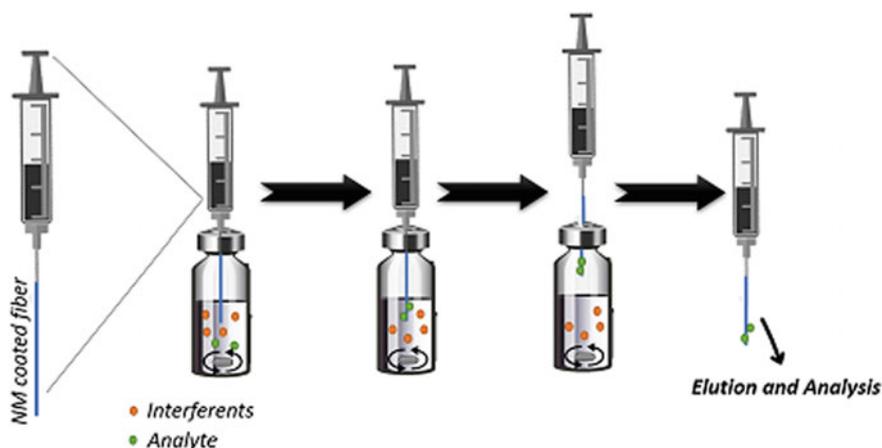


**Fig. 8** Schematic representation of the MSPE procedure

(Tian et al. 2013; Wen et al. 2014; Hussain and Kharisov 2016; Xu et al. 2016; Hashemi et al. 2017)

Hashemi et al. (2017) reviewed the available data on the use of MOFs for the separation of diverse organic and inorganic pollutants from several types of samples. The authors also described the chemical and physical features responsible for the high performance of this class of materials; metal ions are linked to organic ligands or organic secondary building units (SBU) by strong bonds, whereas the common inorganic secondary building units include metal clusters (e.g. metal-carboxylate clusters and metal-azolate clusters), metal atoms, or rod-shaped clusters, and the common used organic linkers contains oxygen or nitrogen donors (e.g. carboxylates, azoles, nitriles, etc.) to offer linkage sites with inorganic SBU (Hashemi et al. 2017).

When dealing with water-based matrices, water-stable MOFs have to be considered, such as the “Material Institute Lavoisier” (MIL)-series MOFs (e.g. MIL-101(Cr), MIL-100(Fe), and MIL-53(M) (M: Fe, Al, and Cr), Zr-MOFs (e.g. UiO-66 and UiO-66-NH<sub>2</sub>), and zeolite imidazolate frameworks (ZIFs: e.g. ZIF-8) (Hashemi et al. 2017). Due to its excellent thermal and chemical stability, MIL-101(Cr) was widely used in diverse fields, such as in chromatography, catalysis, gas adsorption and in SPE (Li et al. 2014). Li et al. (2014) used MIL-101(Cr) as a SPE sorbent material combined with fast detection analysis in real time mass spectrometry (DART-MS) for the analysis of triazine herbicides from lake water samples. LODs for the five studied herbicides were below the ng/mL level, meeting the regulatory requirements of the European Union (Li et al. 2014). Moreover, the recoveries were in the range of 85–110%. The obtained high adsorption capacity is probably due to the  $\pi$ - $\pi$  interactions between the organic ligand network of the MOF and the phenyl ring of the target molecules (Li et al. 2014). Another commonly used MOF, especially for metals recovery, is Cu<sub>3</sub>(BTC)<sub>2</sub> (BTC = benzene-1,3,5-tricarboxylate). Sohrabi (2014) reported a novel thiol-functionalized MOF, where thiol-functionalized silica NPs were incorporated in the Cu<sub>3</sub>(BTC)<sub>2</sub> MOF, for the removal and preconcentra-

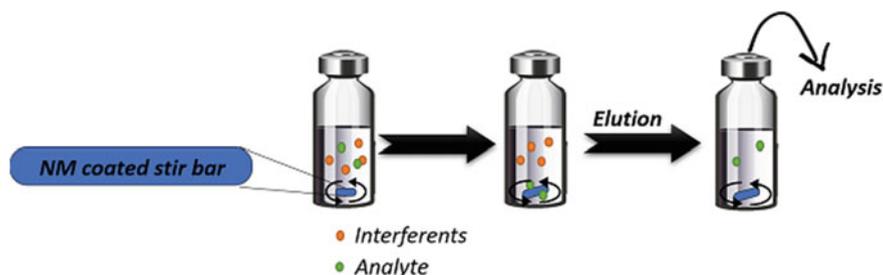


**Fig. 9** Schematic representation of SPME by the direct immersion extraction mode

tion of Hg(II) ions from environmental water samples. When compared with other solid-phases, this MOF sorbent allowed higher enrichment factors and lower LODs, reaching 20 pg/mL (Sohrabi 2014).

MOFs can be used not only in SPE but also in the coating of fibers for solid-phase microextraction (SPME), as summarized in Fig. 9. Solid-phase microextraction (SPME) was proposed in 1990 (Arthur and Pawliszyn 1990), integrating sampling and sample preparation in one step (Lucena et al. 2011; Ribeiro et al. 2014). SPME consists in the exposure of a small fused-silica fiber coated with an appropriate sorbent layer to a gas or liquid sample that can be easily coupled with chromatographic and electrophoretic techniques (Lucena et al. 2011; Ribeiro et al. 2014). Chen et al. (2012) explored the application of MIL-53(Al, Cr, Fe) as fiber coatings for the SPME-GC-MS/MS of 16 PAHs in environmental water samples. It was found that MIL-53(Al) showed the highest adsorption efficiency towards PAHs, where very low detection limits (0.10 pg/mL) were achieved. These materials were compared with commercial fibers, showing that the MIL-53(Al) coatings provide better results in terms of adsorption efficiency of PAHs, while being of lower cost and higher robustness (Chen et al. 2012).

Similar to SPME, stir bar sorptive extraction (SBSE) is an additional equilibrium technique, possessing significant advantages, such as high sensitivity and good reproducibility. Contrastingly, the coating amount on the stir bar is 50–250 times higher than that on SPME fibers, resulting in an increase in the adsorption and recovery values (Frank and Pat 2007). Hu et al. (2013) reported the synthesis of three novel PDMS/MOFs (MOF-5, MOF-199 and IRMOF-3) coatings by the sol-gel technique for the extraction of 7 estrogens from environmental water samples by SBSE. Under the optimal experimental conditions, LODs were found to be in the range of 0.15–0.35 ng/mL using the best-found material (PDMS/IRMOF-3), with enrichment factors ranging from 30.3 to 55.6-fold (Hu et al. 2013) (Fig. 10).



**Fig. 10** Schematic representation of the SBSE process

Recently, composites of MOFs with magnetic NPs have also been developed for the preconcentration of different analytes using the MSPE technique. Wang et al. (2013) used dithizone (H2Dz, 1,5-diphenylcarbazone), a commonly used chelating reagent that can form a stable complex with lead, to functionalize a magnetic MOF ( $\text{Fe}_3\text{O}_4/\text{Cu}_3(\text{BTC})_2$ ). The developed method was applied for the preconcentration and determination of lead in environmental water samples, with recoveries in the range of 97–102% from real samples, and a detection limit as low as 0.0046 ng/mL (Wang et al. 2013). Ma et al. (2016) developed different kinds of magnetic MOFs for MSPE; for instance, they have reported a SPE procedure based on a magnetic porous carbon derived from an MOF for the preconcentration of steroid hormones from wastewater samples. In this approach, MIL-53-C was prepared through the direct carbonization of MIL-53, and the recoveries of the analytes for this novel methodology ranged from 96.2 to 98.7%. This method was also compared with other reported ones for the determination of steroid hormones, being found that it had a similar or even better performance in terms of LOD (0.005–0.01 ng/mL) and recovery. In Table 3 the use of MOFs for the preconcentration of different analytes in environmental aqueous samples are summarized (in the last decade).

### 3.3 Molecularly Imprinted Polymers (MIPs)

Molecularly imprinted polymers (MIPs) are a specific class of synthetic polymers that have been used as selective sorbents for SPE since 1994 (Sellergren 1994), which can be tailor-made for target analytes (Lucena et al. 2011; Hussain and Kharisov 2016; Xu et al. 2016). These selective sorbent materials are built by the introduction of templates in order to form specific nanosized cavities or surface binding sites (Lucena et al. 2011; Xu et al. 2016). The main components for MIPs synthesis include a functional monomer, a cross-linking agent, a template, a reaction initiator and an appropriate solvent (Hussain and Kharisov 2016). A reaction of copolymerization occurs, where the functional monomer forms a stable complex with the template, resulting in a three-dimensional crosslinked polymer (Hussain and Kharisov 2016). After the template elution, imprinted pores/cavities are left in the polymer network

**Table 3** Application of MOFs in SPE, SPME, SBSE and MSPE in environmental monitoring (in the last 10 years)

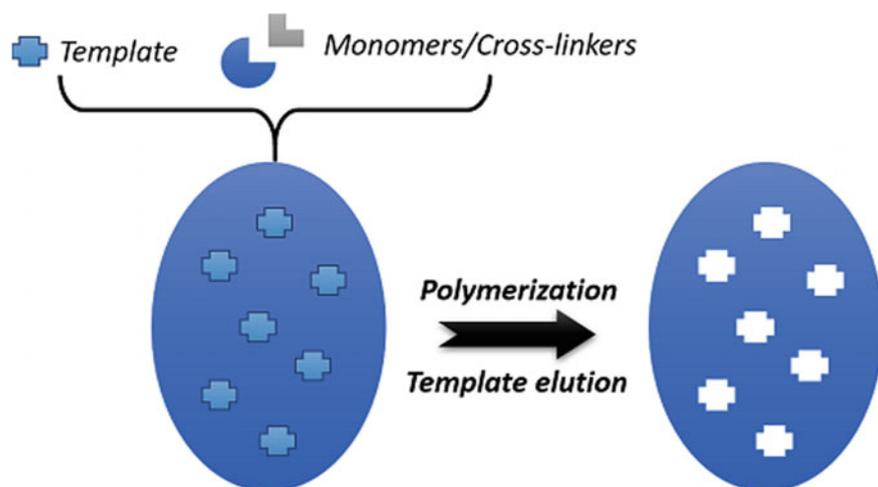
MOFs	Metal	Modification	Preconcentration technique	Sample matrix	Analyte	Analytical technique	LOD (ng/mL)	References
MOF-5	Zn	–	SPE	Tap, spring and river water	PAHs	HPLC-PDA	0.0004–0.004	Yang et al. (2013)
MIL-101	Cr	–	SPE	Lake water	Triazine herbicides	DART-MS	0.1–0.2	Li et al. (2014)
ZIF-8 (Zn2-methylimidazole)2	Zn	–	SPE	River water	1H-benzotriazole, 5-tolyltriazole	–	–	Jiang et al. (2013)
Cu3(BTC)2	Cu	Thiol-modified silica NPs	SPE	River, tap, waste water and sea water	Hg(II)	CV-AAS	0.02	Sohrabi (2014)
[Ag12 (MA)8(mal)6,18 H2O]n MOF	Ag	–	SPE	Distilled, tap, river, lake, waste and sea water	Pb(II)	FAAS	0.5	Salarian et al. (2014)
MIL-53	Al	–	SPME	Waste water	PAHs	GC-MS/MS	0.0001–0.00073	Chen et al. (2012)
MOF-5	Zn	Polydimethylsiloxane	SBSE	Lake, river and fishpond waters	Estrogens	HPLC	–	Hu et al. (2013)
MOF-199	Zn	–	–	–	–	–	–	–
IRMOF-3	Cu	–	–	–	–	–	0.15–0.35	–
MIL-101	Cr	Addition of Fe3O4 @SiO2	MSPE	Lake and waste waters	PAHs	HPLC-PDA	0.0028–0.0272	Huo and Yan (2012)
MIL-101	Cr	Addition of Fe3O4 @SiO2	MSPE	Reservoir, river, and seawater	Pyrazole/pymrole pesticides	HPLC	0.3–1.5	Ma et al. (2016)

(continued)

**Table 3** (continued)

MOFs	Metal	Modification	Preconcentration technique	Sample matrix	Analyte	Analytical technique	LOD (ng/mL)	References
MOF-177	Zn	Addition of Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	MSPE	River, lake and waste waters	Phenols	GC-MS	0.0168-0.2083	Wang et al. (2014)
Magnetic MOF (Fe <sub>3</sub> O <sub>4</sub> /Cu <sub>3</sub> (BTC) <sub>2</sub> )	Cu	Dithizone	MSPE	Tap and lake water	Pb(II)	ETAAS	0.0046	Wang et al. (2013)
Magnetic MOF (Fe <sub>3</sub> O <sub>4</sub> /Cu <sub>3</sub> (BTC) <sub>2</sub> )	Cu	Fe <sub>3</sub> O <sub>4</sub> NPs with Dithizone	MSPE	Distilled, tap, river, sea and mineral water	Cd(II), Pb(II), Ni(II) and Zn(II)	FAAS	0.12-1.2	Taghizadeh et al. (2013)
Magnetic MOF (Fe <sub>3</sub> O <sub>4</sub> /Cu <sub>3</sub> (BTC) <sub>2</sub> )	Cu	Fe <sub>3</sub> O <sub>4</sub> NPs with pyrene	MSPE	Tap, river and sea water	Cd(II) and Pb(II)	FAAS	0.2-1.1	Sohrabi et al. (2013)
Magnetic MOF (Fe <sub>3</sub> O <sub>4</sub> /Cu <sub>3</sub> (BTC) <sub>2</sub> )	Cu	Fe <sub>3</sub> O <sub>4</sub> NPs with pyrene	MSPE	Distilled, tap, River, and mineral water	Pd(II)	FAAS	0.37	Bagheri et al. (2012)
MIL-53-C	Fe	Carbonization of the MIL-53	MSPE	Waste water	Hormones	HPLC	0.005-0.01	Ma et al. (2016)

LOD limit of detection; HPLC high-performance liquid chromatography; HPLC-PAD HPLC with pulsed amperometric detection; DART-MS direct analysis in real time-mass spectrometry; CV-AAS cold vapor atomic absorption spectroscopy; FAAS flame atomic absorption spectrophotometry; GC-MS gas chromatography-mass spectrometry; ETAAS electrothermal atomic absorption spectrometry



**Fig. 11** Schematic representation for MIPs synthesis

that are sterically complementary to the target compounds (Lucena et al. 2011; Husain and Kharisov 2016). Figure 11 shows a schematic representation of the MIPs synthesis. Regarding the templates, neutral organic molecules, ionic compounds and epitopes have been employed (Lucena et al. 2011).

Due to the high specificity and selectivity of the molecular recognition mechanism of molecular imprinting, several studies regarding the applicability of MIPs for sample preparation have been carried out. Lian and Wang (2016) reported a molecularly imprinted solid-phase extraction step followed by high-performance liquid chromatography with fluorescence detection for the clean-up, preconcentration and further analysis of ciprofloxacin, a fluoroquinolone antibiotic, in natural seawater samples. Ciprofloxacin was used as a template molecule and methacrylic acid was selected as the functional monomer because it was favourable for hydrogen bond recognition between the monomer and the target pollutant (Lian and Wang 2016). The recoveries of spiked seawater on the prepared MIP-based cartridges ranged from 75.2 to 112.4% and the obtained LOD was 0.2 ng/mL (Lian and Wang 2016). Canale et al. (2010) reported a method to analyse bisphenol A (BPA), 17 $\beta$ -estradiol (17 $\beta$ -E2,) and ethynylestradiol (EE2) at ultratrace levels, with the goal of developing a screening procedure to monitor these endocrine-disrupting chemicals (EDCs) in environmental water samples. In their study, the fluorinated BPA derivative (4,40-(hexafluoroisopropylidene)-diphenol) was used as a mimic template, where the synthesized imprinted polymer (poly-4-VP-co-TRIM) showed high affinity and selectivity for BPA, 17 $\beta$ -E2 and EE2, providing recoveries close to 100% and low LOD (0.010 pg/mL) for BPA in real drinking water samples (Canale et al. 2010).

Traditionally, the use of MIPs involves the loading of MIPs into SPE cartridges; however, more recently, MSPE became a popular extraction mode based on the use of MIPs that are grafted onto magnetic NPs. Ji et al. (2009) and Chen et al.

(2010) prepared magnetic MIPs for the preconcentration and detection of BPA and fluoroquinolone antibiotics in environmental water samples. Additionally, both silica particles (Zhu et al. 2011; Song et al. 2012; Yin et al. 2012) and carbon nanotubes (Tan et al. 2011; Yang et al. 2013) can be an excellent support material of MIPs, especially MWCNTs due to their extremely large surface area (Wen et al. 2014). Accordingly, Tan et al. (2011) and Yang et al. (2013) described the preparation of MIPs on the surface of MWCNTs for the determination of several herbicides in environmental water samples.

Table 4 lists some applications of MIPs in sample preparation and extraction of toxic analytes from environmental water samples.

### 3.4 Carbon-Based Nanomaterials

Carbon-based nanomaterials have been described in the literature as one of the most important trends in SPE technology (Wen et al. 2014). Carbon exists in various allotropes, such as fullerenes, carbon nanocones, carbon nanodisks, carbon nanofibers, carbon nanohorns, diamond, **graphene (G) and graphene oxide (GO)**, and **carbon nanotubes (CNTs)**, including single-walled CNTs (SWCNTs) and multi-wall CNTs (MWCNTs) (Tian et al. 2013; Wen et al. 2014; Xu et al. 2016). However, applications in environmental analysis, namely regarding sample preparation, have been mainly focused on the use of fullerenes, CNTs and G/GO (Tian et al. 2013; Wen et al. 2014).

The earliest report on carbon-based nanomaterials dates from 1985, when fullerene C<sub>60</sub> was firstly prepared by Smalley et al. (Kroto et al. 1985). Nevertheless, only in 1994 Gallego et al. (1994) fabricated a continuous-flow system using a C<sub>60</sub> fullerene mini-column for the preconcentration of lead for environmental analysis (Wen et al. 2014; Xu et al. 2016). Fullerenes are polyhedral nanostructures, in a spherical arrangement, in which carbons are bonded to form five-to-six-membered rings (Lucena et al. 2011). They present a low tendency to form aggregates, and thus fullerenes are promising alternatives to be used as sorbents in SPE procedures based on continuous flow devices. In this perspective, Jurado-Sanchez et al. (2009) described the use of fullerenes for aromatic and non-aromatic N-nitrosamines separation. The authors compared the performance of C<sub>60</sub> and C<sub>70</sub> fullerenes and nanotubes, reporting that C<sub>60</sub> fullerene is the best choice to selectively retain the aromatic fraction (sorption efficiency >99%). Fullerenes act as filters retaining only the aromatic fraction via  $\pi$ - $\pi$  interactions (Jurado-sánchez et al. 2009). Thus, by using an automatic system containing two sequential sorbent columns coupled to GC-MS, the quantification at the low nanogram per liter level of non-aromatic amines in drinking water and wastewater samples was possible, in which LODs of 0.004–0.012 ng/mL were reached (Jurado-sánchez et al. 2009).

**Graphene** is a single-atom-thick honeycomb two-dimensional lattice carbon nano-scaled material (Tian et al. 2013; Wen et al. 2014). Graphene exhibits a nanosheet structure with a large specific theoretical surface area and possesses a

**Table 4** Application of MIPs in SPE, SPME, and MSPE for environmental monitoring (in the last 10 years)

Template	Monomer/cross-linker	Modification	Sample matrix	Analyte	Preconcentration technique	Analytical technique	LOD (ng/mL)	References
Ciprofloxacin	MAA/EGDMA		Seawater	Ciprofloxacin	SPE	HPLC-FD	0.2	Lian and Wang (2016)
BPA	4-VP/TRIM		Tap, waste and river waters	BPA	SPE	CE-UV	3.0-6.9	Mei et al. (2011)
TMB	$\gamma$ -MPTMS/TMOS	Grafted on the silica gel surface	Tap, lake and sea water	Biphenyls	SPE	GC-ECD	1	Zhu et al. (2011)
Fluorinated BPA derivative	4-VP/TRIM		Potable water	BPA, 17 $\beta$ -E2, EE2	SPE	GC-MS	0.00001	Canale et al. (2010)
PAHs	PTMS/TEOS	Grafted on the silica gel surface	Seawater	PAHs	SPE	GC-MS	0.0052-0.0126	Song et al. (2012)
DPA or BPA	APTES/TEOS	Grafted on the silica gel surface	Tap, river and lake water	TBBPA	SPE	RRLC-DAD	2	Yin et al. (2012)
Ciprofloxacin	MAA/EGDMA	Incorporated with Fe <sub>3</sub> O <sub>4</sub> NPs	Lake, river, waste waters	Fluoroquinolone antibiotics	MSPE	HPLC-MS/MS	0.0032-0.0062	Chen et al. (2010)
BPA	2-VP/EGDMA	Incorporated with Fe <sub>3</sub> O <sub>4</sub> NPs	River and waste water	BPA	MSPE	HPLC	0.014	Ji et al. (2009)

(continued)

**Table 4** (continued)

Template	Monomer/cross-linker	Modification	Sample matrix	Analyte	Preconcentration technique	Analytical technique	LOD (ng/mL)	References
Prometryn	MAAA/TRIM	Polymerized on MWCNTs	River and waste water	Triazine herbicides	SPME	HPLC	0.08–0.38	Tan et al. (2011)
2,4-D	Acrylamide and styrene/EGDMA	Polymerized on SiO <sub>2</sub> -coated MWCNTs	River water	2,4-D	SPE	HPLC	100	Yang et al. (2013)

LOD limit of detection; BPA bisphenol A; TMB 3,3',5,5'-tetramethylbenzidine; DPA diphenolic Acid; TBBPA tetrabromobisphenol A; 2,4-D 2,4-dichlorophenoxyacetic acid; 17 $\beta$ -E2 17 $\beta$ -estradiol; EE2 ethynylestradiol; MMA Methacrylic acid; EGDMA ethylene glycol dimethacrylate; 4VP 4-vinylpyridine; TRIM trimethylolpropane trimethacrylate;  $\gamma$ -MPTMS  $\gamma$ -mercaptopropyltrimethoxysilane; TMOS tetramethoxysilane; PTMS propyltrimethoxysilane; TEOS tetraethyl orthosilicate; APTES (3-aminopropyl)triethoxysilane; HPLC high-performance liquid chromatography; HPLC-FD HPLC with fluorescence detection; CE-UV capillary electrophoresis with UV-detection; GC-ECD gas chromatography with electron capture detection; GC-MS gas chromatography-mass spectrometry; RRLC-DAD reversed-phase rapid-resolution liquid-chromatography with photodiode array detection; HPLC-MS/MS HPLC coupled with tandem mass spectrometry

large delocalized  $\pi$ -electron system, offering a strong affinity for  $\pi$ - $\pi$  interactions with aromatic analytes. Due to these characteristics, it is a very popular option for use as an adsorbent material in SPE (Tian et al. 2013; Wen et al. 2014). Since many types of organic pollutants, such as PAHs, organophosphorus pesticides (OPPs), and phthalic acid esters (PAEs) hold aromatic residues, there are several available studies reported in the literature describing graphene as a good sorbent in SPE. For instance, Luo et al. (2014) and Wu et al. (2013) reported the use of graphene as a SPE sorbent for the determination of PAEs in environmental water samples, while Wang et al. (2013) used graphene in a SPE disks-based column for a fast separation and preconcentration of trace PAHs from environmental water samples. Different types of SPE approaches and analytical techniques were used in these studies. In the first study (Luo et al. 2014), graphene nanoplatelets were used as a novel sorbent material for a SPE cartridge to analyse PAEs by HPLC, showing that this method was highly effective for the extraction of target analytes with recoveries ranging from 87.7 to 100.9%, being superior to other sorbents (C18 silica, HLB Oasis, activated carbon, and MWCNTs) (Luo et al. 2014). A simple and inexpensive method of dispersive solid-phase extraction (DSPE) combined GC-MS was used by Wu et al. (2013), where graphene was dispersed into water samples in a centrifuge tube to adsorb PAEs; graphene was then isolated from the solution by centrifugation (recoveries between 71 and 117%). Sun et al. (2014) proposed a miniaturized self-assembly pipette tip graphene SPE cartridge (PT-G-SPE) coupled with liquid chromatography with fluorescence detection (LC-FD) for the preconcentration and determination of three sulphonamides in environmental water samples, allowing to reach detection limits in the range of pg/mL.

**Graphene oxide (GO)** is a monolayer of two-dimensional carbon-based materials, containing multi-functional groups, such as carboxyl, epoxy, ketone and hydroxyl groups, which can easily offer functionalized sites to enhance the selectivity for certain analytes (Tian et al. 2013; Wen et al. 2014). However, the direct use of graphene or GO as SPE adsorbents may rise several concerns, regarding aggregation or the leakage of the G or GO sheets from the SPE cartridges/columns (Liu et al. 2011). Therefore, new types of SPE sorbents produced by graphene bounded silica and graphene oxide bounded silica were introduced by Liu et al. (2011), with this new material yielding excellent performance with recoveries of chlorophenols from water samples approaching 100%. Recent applications of graphene in environmental sample preparation are summarized in Table 5.

**Carbon nanotubes (CNTs)** are amongst the most currently used nanomaterials for sample preparation in environmental analysis. CNTs can be described as a graphene sheet derived from the scrolling up into a nanoscale-tube (Tian et al. 2013; Wen et al. 2014). CNTs can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Like other carbon-based compounds, CNTs also exhibit good performance for the adsorption of several organic compounds (Yu et al. 2010; Hadjmohammadi et al. 2010; Katsumata et al. 2010; Ma et al. 2010; See et al. 2010; Wu et al. 2010; Guo et al. 2011; Herrera-herrera et al. 2011; Gao et al. 2012; Gonzalez-Curbelo et al. 2013; Lasarte-aragonés et al. 2013) and metal ions with or without chelating agents (Chen et al. 2009; Ozcan et al.

**Table 5** Application of graphene nanomaterials in SPE for environmental monitoring (in the last 10 years)

Carbon material	Modification	Sample	Analyte	Operation mode	Analytical technique	LOD (ng/mL)	References
Graphene nanoplatelets (GN)		Tap and commercial bottled water	PAEs	SPE cartridge	HPLC	0.09–0.33	Luo et al. (2014)
Graphene		Tap, sea, river, and waste waters	Pb(II)	SPE column	FAAS	0.61	Wang et al. (2012)
Graphene		Ultrapure, river and sea water	PAEs	DSPE	GC-MS	2.0–6.0	Wu et al. (2013)
Graphene		Lake, river, waste water	Sulfonamide antibiotics	SPE cartridge	HPLC-FD	0.0005–0.0017	Sun et al. (2014)
Graphene		Tap and river water	PAHs	SPE column	GC-MS	0.00084–0.013	Wang et al. (2013)
Graphene/Graphene oxide	Bound to silica		Chlorophenols	SPE cartridge	MS		Liu et al. (2011)
Graphene oxide		River and sea water	Chlorophenoxy acid herbicides	SPE cartridge	CE	0.3–0.5	Tabani et al. (2013)
Graphene oxide	Oxidized with H <sub>2</sub> SO <sub>4</sub>	River, lake and sea water	Pb(II), Cd(II), Bi(III) and Sb(III)	SPE	AFS	0.002–0.01	Deng et al. (2013)

*LOD* limit of detection; *PAEs* phthalate esters; *HPLC* high-performance liquid chromatography; *FAAS* flame atomic absorption spectrometry; *GC-MS* gas chromatography-mass spectrometry; *HPLC-FD* HPLC with fluorescence detection; *CE* capillary electrophoresis; *AFS* atomic fluorescence spectrometry

2010; El-sheikh et al. 2011; López-garcía et al. 2011; Soylak and Unsal 2012; Cui et al. 2012; Nabid et al. 2012; Behbahani et al. 2013; Soliman et al. 2013; Kocot et al. 2013; Madadzadeh et al. 2013; Soylak and Topalak 2014; Sahmetlioglu et al. 2014). Chen et al. (2009) described the use of a microcolumn packed with SWCNTs as a new adsorption material for the preconcentration of trace metal ions in environmental samples. SWCNTs were first oxidized with nitric acid and filled into a PTFE microcolumn for the sample pretreatment, in which lake water samples were used. The levels of Cu, Co and Pb ions present in the samples were determined by ICP-MS, reaching LOD values as low as 1.2 pg/mL (Chen et al. 2009).

The modification of CNTs with specific functional groups has been also adopted for sample preparation (Tian et al. 2013; Xu et al. 2016). Gao et al. (2012) shown the applicability of cyano-functionalized MWCNTs for the preconcentration of phenolic compounds from river water and seawater samples. By using SPE cartridges filled with this cyano-functionalized MWCNTs adsorbent material, it was found that the limits of detection of the method were 0.45, 0.09, 0.08, and 3.00 ng/mL for *p*-chlorophenol, 1-naphthol, 2-naphthol, and 2,4-dichlorophenol, respectively (Gao et al. 2012). Furthermore, the functionalization of CNTs is also very valuable for metal ion analysis since several chelating reagents can be coupled to the surfaces of CNTs (Cui et al. 2012; Nabid et al. 2012; Behbahani et al. 2013; Madadzadeh et al. 2013; Soliman et al. 2013; Sahmetlioglu et al. 2014; Soylak and Topalak 2014). Cui et al. (2012) covalently grafted phenyl-iminodiacetic acid groups onto MWCNTs for the preconcentration of trace quantities of several metal ions (Fe (III), Cu(II) and Pb(II) ions) from tap and river water samples prior to their determination by ICP-OES. When compared with pristine (unmodified) MWCNTs, the functionalized PIAD-MWCNTs show better dispersibility in water and also higher sorption affinities for the tested metals (Cui et al. 2012). The recent applications of CNTs in SPE for the analysis of environmental water samples are summarized in Table 6.

### 3.5 Silica-Based Nanomaterials

Silica-based nanomaterials for sample preparation include silica nanoparticles (SiO<sub>2</sub> NPs), and mesoporous silica materials (e.g. MCM-41 and SBA-15). These silica-based materials are characterized by high surface areas and high adsorption capacity (Lucena et al. 2011; Tian et al. 2013). Moreover, compared with other materials, silica-based NMs provide good biocompatibility (Xu et al. 2016) and are also easy to synthesize. Because they display intrinsic surface reactivity, it is possible to easily introduce functional groups on the surface (Lucena et al. 2011; Tian et al. 2013). Most of the silica-based materials are chemically modified when used as SPE sorbents or used as a support in other nanomaterials to form composites/hybrid materials (Gao et al. 2010; Bagheri et al. 2011a; Zhang et al. 2011; Zhu et al. 2011; Liu et al. 2011; Yang et al. 2011; Song et al. 2012; Yin et al. 2012; Wang et al. 2013; Mehdinia et al. 2014; Sohrabi 2014; Omidia et al. 2015).

**Table 6** Application of CNTs in SPE for environmental monitoring (in the last 10 years)

CNTs	Modification	Sample	Analyte	Analytical technique	LOD (ng/mL)	References
SWCNTs	Oxidized with nitric acid	Lake water	Cu(II), Co(II) and Pb(II)	ICP-MS	0.0012–0.039	Chen et al. (2009)
MWCNTs	–	Fortified lake, tap, and bottled mineral water	Fe(III), Cu(II), Mn(II) and Pb(II)	FAAS	3.5–8.0	Ozcan et al. (2010)
MWCNTs	–	River water	Triazine herbicides	RRLC-MS/MS	0.0001	Yu et al. (2010)
MWCNTs	–	Sea, river and waste water	Cd(II) and Pb(II)	TXRF	1.0–2.1	Kocot et al. (2013)
MWCNTs	–	Run-off, mineral and tap water	Organophosphorus pesticides	GC-NPD	0.00116–0.0936	Gonzalez-Curbelo et al. (2013)
MWCNTs	–	Tap, river and sea water	Triazine herbicides	GC-MS	0.0025–0.005	Katsumata et al. (2010)
MWCNTs	–	River, tap and sea waters	PAHs	GC-MS	0.002–0.0085	Ma et al. (2010)
MWCNTs	–	River water	Triazine herbicides	Micro-LC	0.2–0.5	See et al. (2010)
MWCNTs	–	River water	PAHs	GC-MS	0.001–0.15	Wu et al. (2010)
MWCNTs	–	Fortified lake, well and waste water	Fe(III) and Pb(II)	FAAS	1.3–2.9	Soylak and Unsal (2012)

(continued)

Table 6 (continued)

CNTs	Modification	Sample	Analyte	Analytical technique	LOD (ng/mL)	References
MWCNTs	–	Tap, well and river water	Chlorpyrifos and phosalone pesticides	HPLC	0.403–3.03	Hadjohammadi et al. (2010)
MWCNTs	–	Bottled mineral, tap, river and sea water	As (III, V) and Sb (III, V)	ETAAS	0.02–0.05	López-garcía et al. (2011)
MWCNTs	–	Tap and river water	Linear alkylbenzene sulfonates	HPLC	0.02–0.03	Guo et al. (2011)
MWCNTs	–	River, well and tap water	Triazine herbicides	UPLC	0.15–0.40	Lasarte-aragonés et al. (2013)
MWCNTs	Oxidized with nitric acid	Commercial mineral, tap and waste water	Quinolone antibiotics	CE-DAD	0.028–0.094	Herrera-herrera et al. (2011)
MWCNTs	Oxidized with nitric acid	Tap, reservoir and mineral waters	Hg(II) ions	–	–	El-sheikh et al. (2011)
MWCNTs	Oxidized with nitric acid and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol modification	River, waste and sea waters	Cd(II) ions	ETAAS	0.00014	Madadzadeh et al. (2013)
MWCNTs	Immobilization of 5-aminoisocyclic acid	Distilled, tap, sea and waste water	Pb(II) ions	ICP-OES	0.25	Soliman et al. (2013)

(continued)

Table 6 (continued)

CNTs	Modification	Sample	Analyte	Analytical technique	LOD (ng/mL)	References
MWCNTs	Tartrazine impregnated	Tap, mineral and lake water	Cd(II) and Pb(II) ions	FAAS	0.8-6.6	Soylak and Topalak (2014)
MWCNTs	Polypyrrole coating	Well and wastewater	Pb(II) ions	FAAS	1.1	Sahmetlioglu et al. (2014)
MWCNTs	Poly(2-amino thiophenol) coating	Distilled, tap, river, lake and waste waters	Cd(II) and Pb(II) ions	FAAS	0.3-10	Nabid et al. (2012)
MWCNTs	Cyano-functionalized	River and sea waters	Phenolic compounds	HPLC	0.08-3.00	Gao et al. (2012)
MWCNTs	Diphenylcarbazine functionalized	Distilled, tap, river, and waste waters	Cd(II) ions	FAAS	0.05	Behbahani et al. (2013)
MWCNTs	Phenyl-iminodiacetic acid functionalized	Tap and river water	Fe (III), Cu(II) and Pb(II) ions	ICP-OES	0.15-0.26	Cui et al. (2012)

LOD limit of detection; ICP-MS inductively coupled plasma-mass spectrometry; FAAS flame atomic absorption spectrometry; RRLLC-DAD: RRLLC-MS/MS reversed-phase rapid-resolution liquid-chromatography coupled with tandem mass spectrometry; TRXF total reflection X-ray fluorescence; CG-NPD gas chromatography with nitrogen phosphorous detection; GC-MS gas chromatography-mass spectrometry; Micro-LC micro liquid-chromatography; HPLC high-performance liquid chromatography; ETAAAS electrothermal atomic absorption spectrometry; UPLC ultra-performance liquid chromatography; CE-DAD capillary electrophoresis with photodiode array detection; ICP-OES inductively coupled plasma optical emission spectrometry

Rao et al. (2016) tested the adsorption capacity of silica NPs in the pre-concentration of residues of pyrethroid pesticides in water samples. Spiked water samples were passed through silica NPs-filled cartridges for the simultaneous determination of the pesticide residues using GC-EI-MS (Rao et al. 2016). It was then found that silica NPs-based cartridges exhibit higher capacity to trap pesticides when compared with conventional C18 cartridges, leading also to a low LOD value of 0.05 ng/mL (Rao et al. 2016). Additionally, silica gel was used as a support material in SPE to extract and preconcentrate metal ions from environmental water samples. In particular, Leopold et al. (2009) reported the use of gold-coated silica as a pre-concentration method for the determination of mercury in river water samples. Due to the high potential of nanogold surfaces for the adsorption of mercury species from aqueous solutions, the gold-coated silica nanomaterials proved to be highly efficient for the adsorption of different mercury species from acidified waters without using chelating agents, with recoveries higher than 90% (Leopold et al. 2009). The microcolumn filled with gold-coated silica was then coupled to atomic fluorescence spectrometry (AFS), resulting in a low detection limit, of 0.18 pg/mL (Leopold et al. 2009). The application of silica-supported ionic liquids (ILs) in SPE has also been reported, namely in the preconcentration of trace metal ions from water samples. Liang and Peng (2010) and Ayata et al. (2011) described the preparation of a microcolumn packed with IL-modified silica combined with flame atomic absorption spectrometry (FAAS) for the determination of trace amounts of cadmium and lead in environmental water samples. The 1-butyl-3-methylimidazolium hexafluorophosphate (Liang and Peng 2010) and the 1-methyl-3-butylimidazolium bromide (Ayata et al. 2011) ILs were used to modify the silica surface for the determination of trace amount of metal ions in lake, tap water and river water samples with satisfactory results (LOD = 0.6 ng/mL (Liang and Peng 2010) and 0.7 ng/mL (Ayata et al. 2011)). A summary of the materials and applications of silica-based nanomaterials in SPE in the last decade are listed in Table 7.

## 4 Conclusions

The contamination of the aquatic environment is a serious concern, which has negative impacts on the ecosystem and human health. To better address this concern, environmental monitoring is mandatory. However, most of the ubiquitous pollutants are close or under the detection limits of the currently available analytical techniques. There is thus a crucial need on improving the sample preparation step, envisioning the enhancement of speed, reliability and sensitivity of analysis. In this chapter, the most recent applications of nanomaterials in SPE for environmental water samples pre-treatment were described and discussed. These NMs include metallic and magnetic nanoparticles, MOFs, MIPs, and carbonaceous- and silica-based nanomaterials.

In general, nanomaterials exhibit relevant physical and chemical properties, making of them superior candidates as sorbents in sample preparation techniques. Furthermore, the ability of nanomaterials for surface modification with a wide variety

**Table 7** Application of silica-based nanomaterials in SPE for environmental monitoring (in the last 10 years)

Type of material	Functionalization	Sample matrix	Analyte	Analytical technique	LOD (ng/mL)	References
Silica NPs	–	Water samples	Pyrethroid pesticides	GC-MS	0.05	Rao et al. (2016)
Silica NPs	Resacetophenone	River water	Pb(II)	UV	0.58	Kaur and Gupta (2009)
Silica gel	Gold deposition	Estuary and river water	Hg(II)	AFS	0.00018	Leopold et al. (2009)
Silica gel	Hydrophobic IL (SG-1, 10-PhenantiT2)	Ground, lake and waste water	Coumarin	HPLC		Marwani and Bakhsh (2013)
Silica gel	1-butyl-3-methylimidazolium hexafluorophosphate	Lake and tap water	Cd(II)	FAAS	0.6	Liang and Peng (2010)
Silica gel	1-methyl-3-butylimidazolium bromide	River water	Pb(II)	FAAS	0.7	Ayata et al. (2011)
Mesoporous silica particles (UVM-7)	Triethanolamine	Tap, river and waste water	Cr(VI)	FAAS	1.2	Shirkhanloo et al. (2015)

LOD limit of detection; GC-MS gas chromatography-mass spectrometry; AFS atomic fluorescence spectrometry; UPPLC ultra-performance liquid chromatography; FAAS flame atomic absorption spectrometry

of functional groups promotes higher adsorption efficiencies and selectivity, while decreasing the limits of detection of the analytical techniques. All these features turn possible the analysis of several toxic compounds that are found in ultratrace levels in water samples.

In addition to the described NMs, in the future it is expected that new nanomaterials emerge in sample preparation techniques. It is also expected that an increasing number of novel nanocomposites and/or hybrid nanomaterials will appear by combining advantageous properties of the different types of nanomaterials. For instance, the use of composite/hybrid materials containing MNPs combined with MIPs, MOFs, CNTs, graphene, among others, are an example of such new solutions, further allowing an easy recovery by an external magnetic field without the need of centrifugation or filtration steps.

Among the most recent functional groups in NMs, ionic liquids (ILs) have emerged as a new class of sorbents coatings in SPE, named as supported ionic-liquid phases (SILPs). ILs are described as designer solvents, and can be widely modulated by altering their cation/anion chemical structures, thus allowing the establishment of specific interactions with the target analyte and the improvement on analysis. Although their numerous advantages, the use of SILPs in the pretreatment of samples for environmental monitoring is still in its infancy.

A new trend in analytical chemistry and environmental monitoring is focused on the development of more sustainable pretreatment methods and analysis. To this end, it is necessary to eliminate, or at least to reduce, the amounts of organic solvents used in sample preparation techniques. Moreover, the recovery and reuse of solvents and/or nanomaterials, and the techniques automatization and miniaturization, are also major issues to improve.

Presently, most of the applications of nanomaterials for sample preparation in water environmental analysis are focused on metal ions, toxic organic compounds and pesticides. Nonetheless, due to their current serious concerns, pharmaceutical drugs and endocrine disrupting chemicals need to be more deeply addressed in the future.

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