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

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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 renders 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.

11.1. 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 of the aquatic environment has negative impacts on

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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 UNEP (UNEP, no date b), 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. 11.1).

Fig. 11.1. Schematic representation of examples of human activities and pollutant's sources of water contamination.

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, Working Group on the Global Metal Flows to the International Resource

Panel. van der Voet, E.; Salminen, R.; Eckelman, M.; Mudd, G.; Norgate, T.; Hischier, 2013). Once released, some metals such as cadmium, lead, copper, chromium, mercury, uranium, nickel, cobalt, zinc, arsenic, selenium, thallium, and antimony, tend to bioaccumulate (Akpor, 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, Mishra and Mamba, 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, Mishra and Mamba, 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, Kim and Brown, 2011; Sajid *et al.*, 2018). PAHs are highly toxic and some of them are mutagenic and carcinogenic (Scragg, 2005; Sajid *et al.*, 2018). PAHs 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, Potocki and Santodonato, 1992; Burgess, Ahrens and Hickey, 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, no date a).

Another commonly found type of pollutants, especially due to agriculture activities, are **pesticides,** which include herbicides, fungicides and insecticides (UNEP, no date 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, β-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 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).

11.2. 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, Birnbaum and Nilsson, 2007). The high demand for environmental monitoring is confirmed by the increasing number of reports along the years, as shown in Fig. 11.2. Around 2001, a boom of publications on this matter arouse, 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. 11.3. From these publications it is possible to ascertain the types of samples used, namely “water”, “soil” and “air”, being the water samples those that 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. 11.3).

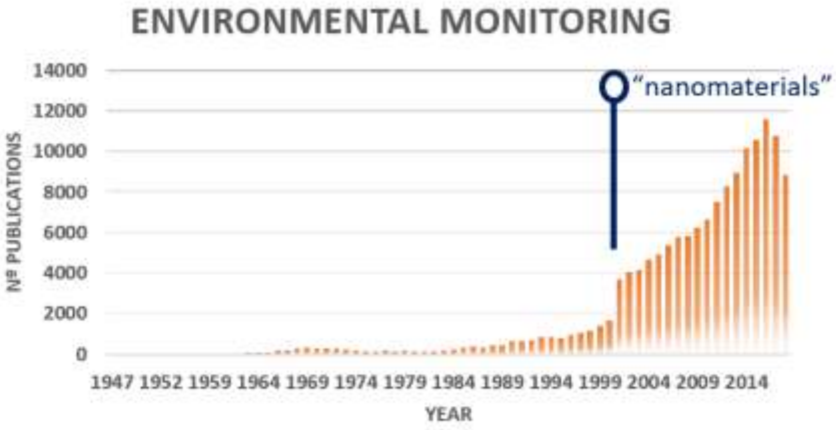

Fig. 11.2. Number of publications *per* year (from 1947 to 2018) focusing on environmental monitoring. The search was carried out in the PUBMED database in December 2018 using the keywords ''environmental monitoring''. The search was refined using the additional keyword "nanomaterials". Publications dealing with nanomaterials in environmental monitoring appeared after 2001.

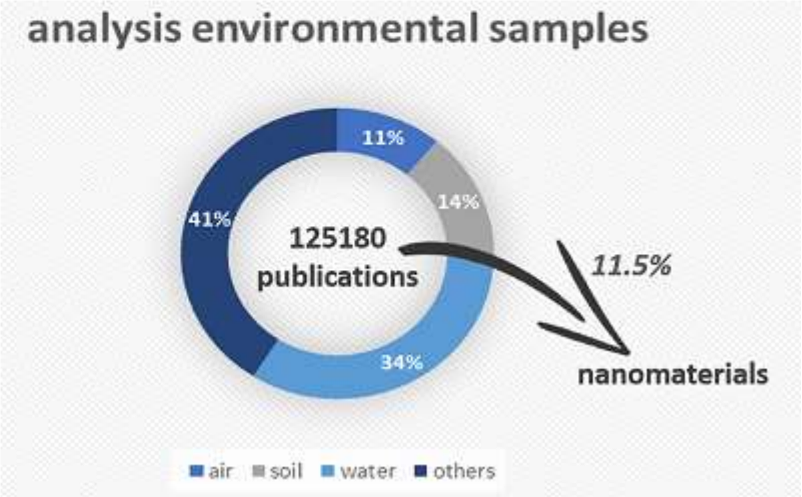

Fig. 11.3. Overview on publications (from 1947 to 2018) focusing on the analysis of environmental samples. The search was carried out in the PUBMED database using the keywords ''analysis", "environmental" and "samples''.

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. 11.4).

Fig. 11.4. General overview of the applications of nanomaterials in environmental samples analysis.

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. 11.5 (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 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.

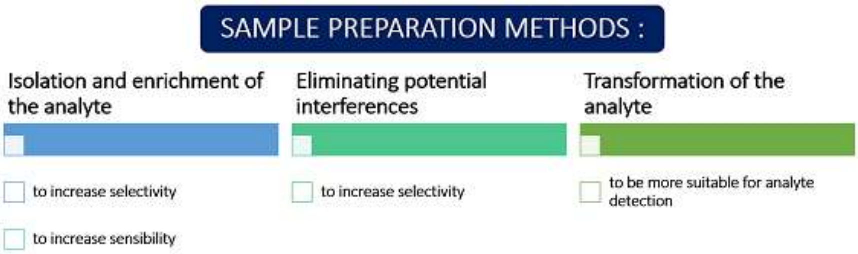

Fig. 11.5. Schematic representation of the main goals in the sample preparation step.

11.3. 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 methodologies, 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, Gupta and Das, 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, Gupta and Das, 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. 11.6). 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).

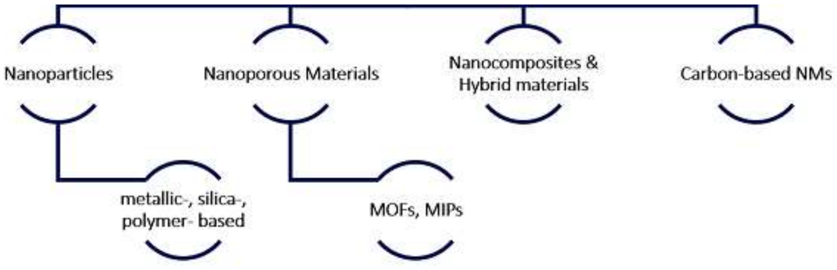

Fig. 11.6. Schematic representation of the different types of nanomaterials used in SPE for the analysis of environmental aqueous samples. MOFs: metal organic frame-work materials; MIPs: molecularly imprinted polymers.

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). 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.

11.3.1. 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, Lin and Tseng, 2012; Tian *et al.*, 2013; Hussain and Kharisov, 2016). In the past decade, Liu (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 ($-NH_2$) groups can adsorb spontaneously onto Au surfaces to form well-organized self-assembled monolayers (Liu, 2009). Accordingly, Wang and Campiglia (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. (Karimipour *et al.*, 2012) showed the applicability of Au NPs for the enrichment and preconcentration of trace amounts of metals, namely Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{2+}, Pb^{2+}, and 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. (Lo *et al.*, 2012) tested the affinity of mercury species for Au NPs, namely by mixing Au NPs with aluminium oxide (Al_2O_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-Al_2O_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 µg/mL) (Lo *et al.*, 2012).

Ag NPs have also been described as adsorbents with high affinity towards mercury. In this line, Wu et al. (Wu, Lin and Tseng, 2012) increased the selectivity (more than 1000-fold) of the analytical system for 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 (T_{33}–AgNPs) that specifically captures Hg^{2+} from tap water samples (LOD = 0.006 ng/mL) (Wu, Lin and Tseng, 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 TiO_2, Al_2O_3, ZnO, ZrO_2, MnO and 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). 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 11.1, several MONPs have been used to analyse metal ions in environmental aqueous samples (Afkhami *et al.*, 2011; Baytak, Zereen and Arslan, 2011; Erdogan, Yalçinkaya and Türker, 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. (Baytak, Zereen and Arslan, 2011) described the use of a minicolumn of a yeast (*Yamadazyma spartinae*) immobilized on TiO_2 nanoparticles for the determination of Cr, Cu, Fe, Mn, Ni and Zn in environmental water samples by ICP-MS. Alumina (Al_2O_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. (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).

Table 11.1. Summary on the use of metal oxide nanoparticles in SPE for metal ions detection (in the last 10 years). 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.

Metal oxide NPs	Modification	Sample matrix	Analyte	Analytical technique	LOD (ng/mL)	Ref.
TiO_2	-	Ground and waste waters	Cd(II)	ID-ICPMS	-	(García-ruiz *et al.*, 2011)
TiO_2	Coated with yeast (*Yamadazyma spartinae*)	Tap and lake waters	Cr(III), Cu(II), Fe(III), Mn(II), Ni(II) and Zn(II)	ICP-AES	0.1-0.45	(Baytak, Zereen and Arslan, 2011)
Al_2O_3	Coated with 2,4-dinitrophenylhydrazine	Tap, bottled mineral, waste waters, industrial effluents	Pb(II) and Cr(III)	FAAS	0.43-0.55	(Afkhami *et al.*, 2011)
ZrO_2-B_2O_3	-	Tap and hot spring waters	As(III) and As(V)	HGAAS	0.009	(Erdogan, Yalçinkaya and Türker, 2011)
ZrO_2-B_2O_3	-	Waste water	Al(III)	FAAS	7.71	(Yalçinkaya *et al.*, 2012)

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 (Fe_3O_4) and maghemite (Fe_2O_3) (Hussain and Kharisov, 2016). Since pure iron-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). Fig. 11.7 shows a scheme of the sol-gel process usually applied to synthetize silica-coated MNPs. Zhang et al. (Zhang *et al.*, 2011) described the use of a core-shell magnetic (Fe_3O_4/SiO_2) mesoporous silica sorbent functionalized with 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, Yamini and Rezaee, 2010) or antidepressant drugs (fluoxetine) (Bagheri, Zandi and Aghakhani, 2011). 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, Roohi and Jabbari, 2011), a copolymer of methyl methacrylate (MMA) and maleic anhydride (MA) (Masoumi, Ghaemy and Bakht, 2014), polydopamine (Iqbal *et al.*, 2011) and polypyrrole (Iqbal *et al.*, 2011; Meng *et al.*, 2011).

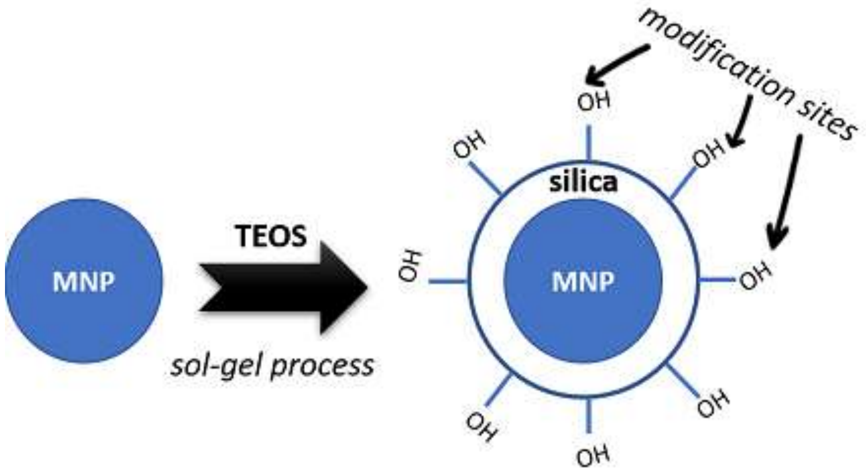

Fig. 11.7. Synthesis of silica-coated magnetic nanoparticles (MNPs), where hydroxyl groups could be then modified. TEOS: tetraethyl orthosilicate.

More recently, Tolmacheva et al. (Tolmacheva *et al.*, 2016) suggested the use of a new generation of highly porous polymers, the hypercrosslinked polystyrene (HCP), for the modification of Fe_3O_4 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 11.2 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. 11.8). 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.

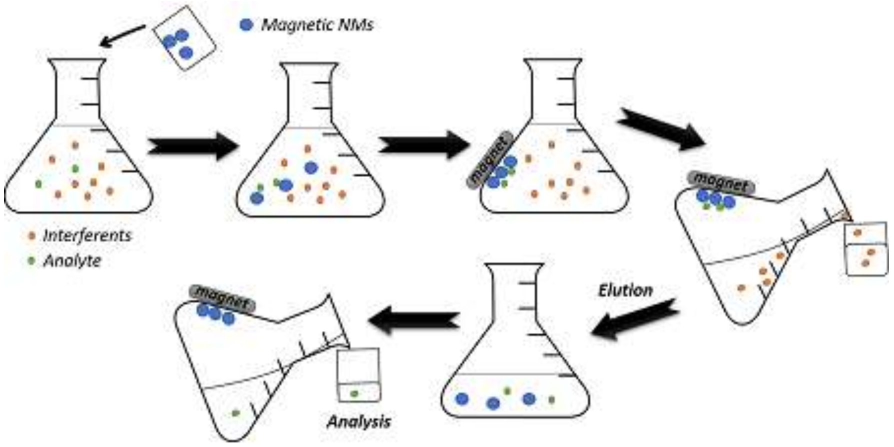

Fig. 11.8. Schematic representation of the MSPE procedure.

Table 11.2. Summary on the use of MSPE in the pretreatment of aqueous sample (in the last 10 years). 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.

Magnetic Core	**Covering layer**	**Sample matrix**	**Analyte**	**Analytical technique**	**LOD (ng/mL)**	**Ref.**
Fe_3O_4	SDS	Tap, well and mineral water	Hg(II)	ICP-OES	0.04	(Faraji, Yamini and Rezaee, 2010)
	SDS	Tap and river water	Fluoxetine	LC-FD	20	(Bagheri, Zandi and Aghakhani, 2011)

Magnetic Core	Covering layer	Sample matrix	Analyte	Analytical technique	LOD (ng/mL)	Ref.
	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	(Mehdinia, Roohi and Jabbari, 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, benzylbutyl 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^{2+}, Cr^{3+}, Zn^{2+}, and Cd^{2+}	-	-	(Masoumi, Ghaemy and Bakht, 2014)
	HCP	River water	Sulfamethoxypyridazine, sulfamethazine, sulfamethoxazole and sulfachloropyridazine	HPLC-PDA	0.6–1.0	(Tolmacheva *et al*., 2016)

Magnetic Core	Covering layer	Sample matrix	Analyte	Analytical technique	LOD (ng/mL)	Ref.
	Silica	Lake and waste waters	Maphthalene, 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(a)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^{2+}	FAAS	0.04	(Omidi *et al*., 2015)
	$Cu_3(BTC)_2$ MOF and functionalization with dithizone	Tap and lake water	Pb^{2+}	FAAS	0.0046	(Y. Wang *et al*., 2013)

11.3.2. 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 10000 m^2/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 (Tian *et al.*, 2013; Wen *et al.*, 2014; Hussain and Kharisov, 2016; Xu *et al.*, 2016; Hashemi *et al.*, 2017)

Hashemi et al. (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-NH2), 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. (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 π-π 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 $Cu_3(BTC)_2$ (BTC=benzene-1,3,5-tricarboxylate). Sohrabi (Sohrabi, 2014) reported a novel thiol-functionalized MOF, where thiol-functionalized silica NPs were incorporated in the $Cu_3(BTC)_2$ MOF, for the removal and preconcentration 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. 11.9. 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. (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).

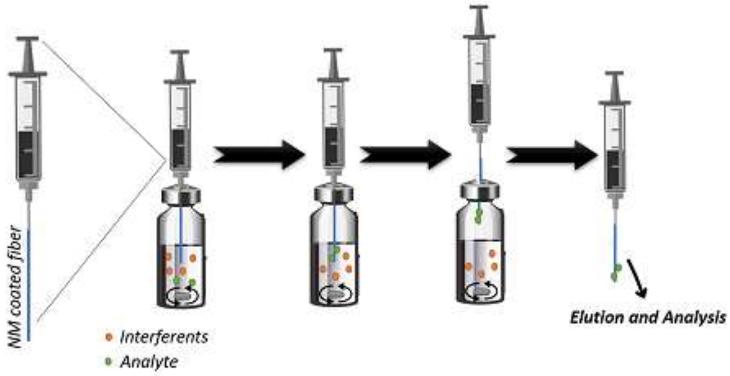

Fig. 11.9. Schematic representation of SPME by the direct immersion extraction mode.

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. (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).

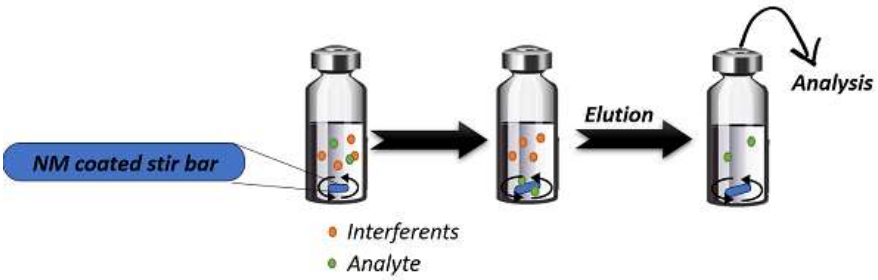

Fig. 11.10. Schematic representation of SBSE.

Recently, composites of MOFs with magnetic NPs have also been developed for the preconcentration of different analytes using the MSPE technique. Wang et al. (Y. 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 ($Fe_3O_4/Cu_3(BTC)_2$). 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 (Y. Wang *et al.*, 2013). Ma et al. (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 11.3. the use of MOFs for the preconcentration of different analytes in environmental aqueous samples are summarized (in the last decade).

Table 11.3. Application of MOFs in SPE, SPME, SBSE and MSPE in environmental monitoring (in the last 10 years). 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; CVAAS; cold vapor atomic absorption spectroscopy; FAAS: flame atomic absorption spectrophotometry; GC-MS: gas chromatography-mass spectrometry; ETAAS: electrothermal atomic absorption spectrometry.

MOFs	**Metal**	**Modification**	**Preconcentration technique**	**Sample matrix**	**Analyte**	**Analytical technique**	**LOD (ng/mL)**	**Ref.**
MOF-5	Zn	-	SPE	Tap, spring and river water	PAHs	HPLC-PDA	0.0004-0.004	(S. Yang *et al.*, 2013)
MIL-101	Cr		SPE	Lake water	Triazine herbicides	DART-MS	0.1-0.2	(Li *et al.*, 2014)
ZIF-8 (Zn(2-methylimidazole)2)	Zn	-	SPE	River water	1H-benzotriazole, 5-tolyltriazole	-	-	(Jiang, Yang and Yan, 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)

MOFs	Metal	Modification	Preconcentration technique	Sample matrix	Analyte	Analytical technique	LOD (ng/mL)	Ref.
[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 fish-pond waters	Estrogens	HPLC	-	(Hu *et al.*, 2013)
MOF-199	Zn						-	
IRMOF-3	Cu						0.15–0.35	
MIL-101	Cr	Addition of $Fe_3O_4@SiO_2$	MSPE	Lake and waste waters	PAHs	HPLC-PDA	0.0028-0.0272	(Huo and Yan, 2012)
MIL-101	Cr	Addition of $Fe_3O_4@SiO_2$	MSPE	Reservoir, river, and seawater	Pyrazole/ pyrrole pesticides	HPLC	0.3–1.5	(J. Ma *et al.*, 2016)
MOF-177	Zn	Addition of $Fe_3O_4@SiO_2$	MSPE	River, lake and waste waters	Phenols	GC-MS	0.0168-0.2083	(Wang, Lei and Song, 2014)
Magnetic MOF ($Fe_3O4/Cu_3(BTC)_2$)	Cu	Dithizone	MSPE	Tap and lake water	Pb(II)	ETAAS	0.0046	(Y. Wang *et al.*, 2013)
Magnetic MOF ($Fe_3O4/Cu_3(BTC)_2$)	Cu	Fe_3O_4 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 ($Fe_3O4/Cu_3(BTC)_2$)	Cu	Fe_3O_4 NPs with pyrine	MSPE	Tap, river and sea water	Cd(II) and Pb(II)	FAAS	0.2-1.1	(Sohrabi *et al.,* 2013)

MOFs	Metal	Modification	Preconcentration technique	Sample matrix	Analyte	Analytical technique	LOD (ng/mL)	Ref.
Magnetic MOF ($Fe_3O4/Cu_3(BTC)_2$)	Cu	Fe_3O_4 NPs with pyrine	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	(R. Ma *et al.*, 2016)

11.3.3. 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 that are sterically complementary to the target compounds (Lucena *et al.*, 2011; Hussain and Kharisov, 2016). Fig. 11.11 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).

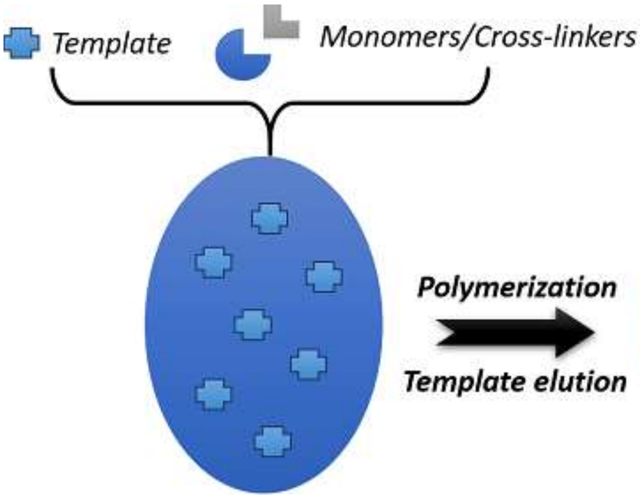

Fig. 11.11. Schematic representation for MIPs synthesis.

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 (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. (Canale *et al.*, 2010) reported a method to analyse bisphenol A (BPA), 17-b-estradiol (17β-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 synthetized imprinted polymer (poly-4-VP-co-TRIM) showed high affinity and selectivity for BPA, 17β-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. (Ji *et al.*, 2009) and Chen et al. (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. (Tan *et al.*, 2011) and Yang et al. (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 11.4 lists some applications of MIPs in sample preparation and extraction of toxic analytes from environmental water samples.

Table 11.4. Application of MIPs in SPE, SPME, and MSPE for environmental monitoring (in the last 10 years). 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□-E2: 17-b-estradiol; EE2: ethynylestradiol; MMA: Methacrylic acid; EGDMA: ethylene glycol dimethacrylate; 4-VP: 4-vinylpyridine; TRIM: trimethylolpropane trimethacrylate; γ-MPTMS: γ-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.

Template	Monomer/ cross-linker	Modification	Sample matrix	Analyte	Preconcentration technique	Analytical technique	LOD (ng/mL)	Ref.
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	γ-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, 17β-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)

Template	Monomer/ cross-linker	Modification	Sample matrix	Analyte	Preconcentration technique	Analytical technique	LOD (ng/mL)	Ref.
Ciprofloxacin	MAA/ EGDMA	Incorporated with Fe_3O_4 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 Fe3O4 NPs	River and waste water	BPA	MSPE	HPLC	0.014	(Ji *et al.*, 2009)
Prometryn	MAA/ 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_2-coated MWCNTs	River water	2,4-D	SPE	HPLC	100	(W. Yang *et al.*, 2013)

11.3.4. 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_{60} was firstly prepared by Smalley et al. (Kroto *et al.*, 1985). Nevertheless, only in 1994 Gallego et al. (Gallego, Pena and Valcarcel, 1994) fabricated a continuous-flow system using a C_{60} 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. (Jurado-sánchez, Ballesteros and Gallego, 2009) described the use of fullerenes for aromatic and non-aromatic N-nitrosamines separation. The authors compared the performance of C_{60} and C_{70} fullerenes and nanotubes, reporting that C_{60} fullerene is the best choice to selectively retain the aromatic fraction (sorption efficiency >99%). Fullerenes act as filters retaining only the aromatic fraction via π-π interactions (Jurado-sánchez, Ballesteros and Gallego, 2009). Thus, by using an automatic system containing two sequential sorbent columns coupled to GC-MS, the quantification at the low nanogram per litter 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, Ballesteros and Gallego, 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 large delocalized π-electron system, offering a strong affinity for π-π 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. (Luo *et al.*, 2014) and Wu et al. (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. (Z. 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. (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) (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. (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 11.5.

Table 11.5. Application of graphene nanomaterials in SPE for environmental monitoring (in the last 10 years). 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.

Carbon material	**Modification**	**Sample**	**Analyte**	**Operation mode**	**Analytical technique**	**LOD (ng/mL)**	**Ref.**
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	(Z. 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)

Carbon material	Modification	Sample	Analyte	Operation mode	Analytical technique	LOD (ng/mL)	Ref.
Graphene oxide	Oxidized with H_2SO_4	River, lake and sea water	Pb(II), Cd(II), Bi(III) and Sb(III)	SPE	AFS	0.002-0.01	(Deng *et al.*, 2014)

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 (MWCNs). Like other carbon-based compounds, CNTs also exhibit good performance for the adsorption of several organic compounds (Yu *et al.*, 2010; Hadjmohammadi, Peyrovi and Biparva, 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, Satiroglu and Soylak, 2010; El-sheikh *et al.*, 2011; López-garcía, Rivas and Hernández-córdoba, 2011; Soylak and Unsal, 2012; Cui *et al.*, 2012; Nabid *et al.*, 2012; Behbahani *et al.*, 2013; Soliman, Marwani and Albishri, 2013; Kocot *et al.*, 2013; Madadizadeh, Taher and Ashkenani, 2013; Soylak and Topalak, 2014; Sahmetlioglu *et al.*, 2014). Chen et al. (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. (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; Madadizadeh, Taher and Ashkenani, 2013; Soliman, Marwani and Albishri, 2013; Sahmetlioglu *et al.*, 2014; Soylak and Topalak, 2014). Cui et al. (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 11.6.

Table 11.6. Application of CNTs in SPE for environmental monitoring (in the last 10 years). LOD: limit of detection; ICP-MS: inductively coupled plasma-mass spectrometry; FAAS: flame atomic absorption spectrometry; RRLC-DAD: RRLC-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; ETAAS: 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.

CNTs	**Modification**	**Sample**	**Analyte**	**Analytical technique**	**LOD (ng/mL)**	**Ref.**
SWNTs	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, Satiroglu and Soylak, 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)
MWCNTs	-	Tap, well and river water	Chlorpyrifos and phosalone pesticides	HPLC	0.403-3.03	(Hadjmohammadi, Peyrovi and Biparva, 2010)
MWCNTs	-	Bottled mineral, tap, river and sea water	As (III, V) and Sb (III, V)	ETAAS	0.02-0.05	(López-garcía, Rivas and Hernández-córdoba, 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	(Madadizadeh, Taher and Ashkenani, 2013)
MWCNTs	Immobilization of 5-aminsalicylic acid	Distilled, tap, sea and waste water	Pb(II) ions	ICP-OES	0.25	(Soliman, Marwani and Al-bishri, 2013)

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	Diphenylcarbazide functionalized	Distilled, tap, river, and waste waters	Cd(II) ions	FAAS	0.05	(Behbahani *et al.*, 2013)
MWCNTs	Phenyl-iminodi-acetic-acid functionalized	Tap and river water	Fe (III), Cu(II) and Pb(II) ions	ICP-OES	0.15-0.26	(Cui *et al.*, 2012)

11.3.5. Silica-based nanomaterials

Silica-based nanomaterials for sample preparation include silica nanoparticles (SiO_2 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, Ayazi and Aghakhani, 2011; Zhang *et al.*, 2011; Zhu *et al.*, 2011; Liu *et al.*, 2011; Yang *et al.*, 2011; Song *et al.*, 2012; Yin *et al.*, 2012; W. Wang *et al.*, 2013; Mehdinia *et al.*, 2014; Sohrabi, 2014; Omidi *et al.*, 2015).

Rao et al. (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. (Leopold, Foulkes and Worsfold, 2009) reported the use of gold-coated silica as a preconcentration 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, Foulkes and Worsfold, 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, Foulkes and Worsfold, 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 (Liang and Peng, 2010) and Ayata et al. (Ayata, Bozkurt and Ocakoglu, 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, Bozkurt and Ocakoglu, 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, Bozkurt and Ocakoglu, 2011)). A summary of the materials and applications of silica-based nanomaterials in SPE in the last decade are listed in Table 11.7.

Table 11.7. Application of silica-based nanomaterials in SPE for environmental monitoring (in the last 10 years). LOD: limit of detection; GC-MS: gas chromatography-mass spectrometry; AFS: atomic fluorescence spectrometry; UPLC: ultra-performance liquid chromatography; FAAS: flame atomic absorption spectrometry.

Type of material	Functionalization	Sample matrix	Analyte	Analytical technique	LOD (ng/mL)	Ref.
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, Foulkes and Worsfold, 2009)
Silica gel	Hydrophobic IL (SG-1,10-PhenanNTf2)	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)

Type of material	Functionalization	Sample matrix	Analyte	Analytical technique	LOD (ng/mL)	Ref.
Silica gel	1-methyl-3-butylimidazolium bromide	River water	Pb(II)	FAAS	0.7	(Ayata, Bozkurt and Ocakoglu, 2011)
Mesoporous silica particles (UVM-7)	Triethanolamine	Tap, river and waste water	Cr(VI)	FAAS	1.2	(Shirkhanloo *et al.*, 2015)

11.4. 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 pretreatment 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 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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