Book: MAGNETIC NANOPARTICLE-BASED HYBRID MATERIALS

CHAPTER 24

Applications of hybrid nanoparticles to improve environmental monitoring

Sandra C. Bernardo[1], Márcia C. Neves[2], Mara G. Freire[2], Ana P. Tavares[2]*

[1]CICS-UBI – Health Sciences Research Centre, University of Beira Interior, Av. Infante D. Henrique, 6200-506 Covilhã, Portugal

[2]CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

*corresponding author: aptavares@ua.pt

Abstract

Environmental pollution has become a serious concern, nowadays requiring an adequate monitoring of hazard compounds, such as heavy metals, pesticides and other organic compounds, and pharmaceutical drugs. However, due to the low concentration of some of these pollutants in environmental aqueous samples and complexity of these samples, the major challenge in this field is the selective isolation of target pollutants and their identification and quantification by feasible analytical equipment. Among a wide array of SPE adsorbents that have been studied for this purpose, the application of hybrid magnetic nanoparticles (HMNPs) has been considered a hot topic and largely investigated in the past decade. In this chapter it is reviewed the literature of the past decade dealing with the application of HMNPs, namely MNPs combined with polymers and carbon materials, used in SPE with the goal of preconcentrating pollutants from aqueous environmental samples to improve their environmental monitoring.

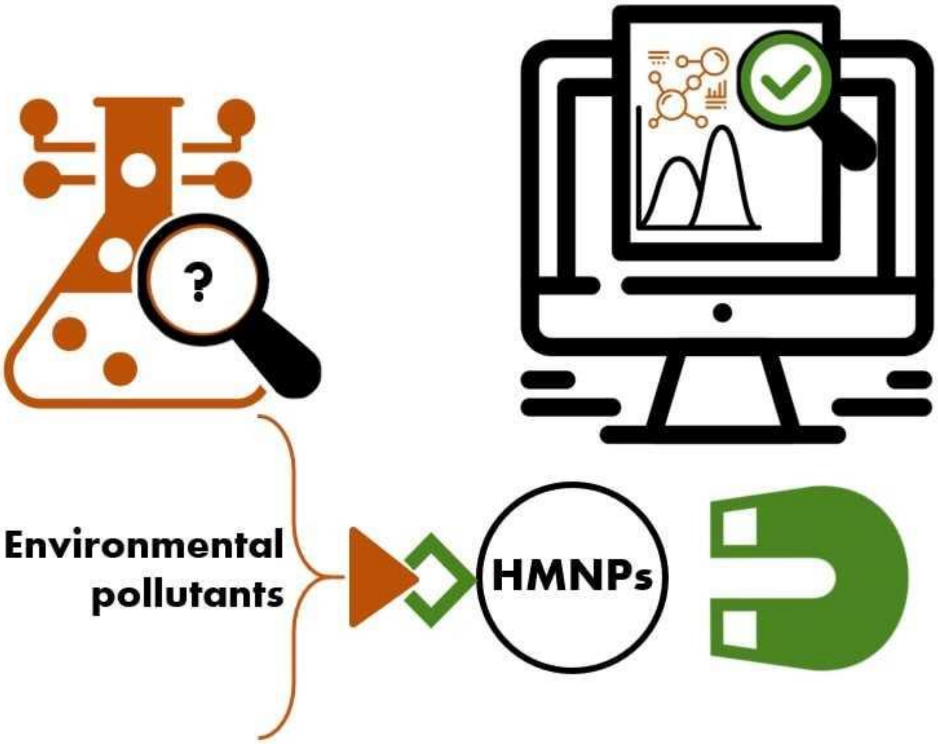
Key Words

Hybrid Magnetic Nanoparticles; Polymers; Carbon Nanotubes; Graphene Oxide; Magnetic Solid-Phase Extraction; Preconcentration; Metals; Pesticides; Organic Compounds; Pharmaceutical Drugs

Introduction

Due to growth of human activities, emergent environmental pollution has become a serious threat and health major concern, since pollutants and/or toxic compounds can enter and accumulate in human's food chain [1]. Environmental pollution is nowadays a critical issue that requires adequate regulation to ensure ecological sustainability and human health being [2, 3]. Therefore, both the development of effective nanomaterials that could be used in environmental remediation and the development of pretreatment strategies of environmental samples for an effective pollutants monitoring are fields of high relevance. Within the studied materials for these purposes, hybrid magnetic nanoparticles (HMNPs) have received significant attention due to their versatile nature [4].

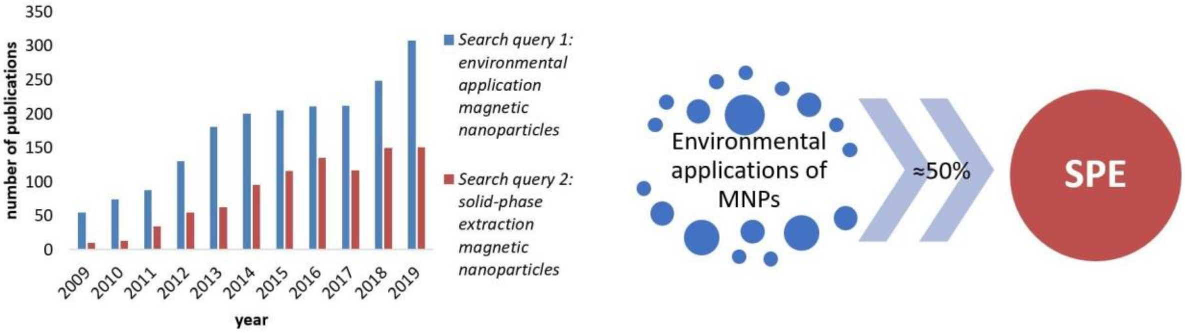
HMNPs combining optical, electronic and magnetic properties have attracted a large interest due to their wide-range applications in the environmental field, e.g. from photo-remediation to solar energy conversion [5]. For instance, noble metal-metal oxide nanohybrids are mostly used for solar energy conversion in photocatalysis and photovoltaic cells [6]. Other types of HMNPs, composed of both inorganic and organic components (like carbon or polymers), have recently been explored for separation and preconcentration purposes [7]. Moreover, this unique class of hybrid nanomaterials can hold valuable features of both the inorganic and organic parts of their components, and also provide the ability to tune the materials properties through the combination of suitable multi-functional components [7]. Despite their large range of possible applications, and since catalysis and sensors are going to be addressed in other chapters of this book, this chapter mainly reviews the use of HMNPs in the pre-treatment of environmental samples envisioning the improvement in the detection of hazardous trace compounds and/or pollutants and respective monitoring (as exemplified in Figure 24.1), fitting within solid-phase extraction (SPE) approaches.



Caption Fig. 24.1: Schematic representation of the subject addressed in this chapter: use of hybrid magnetic nanoparticles in the SPE pretreatment of environmental samples towards the improved detection of hazard trace compounds.

Solid-phase extraction in the pretreatment of environmental samples

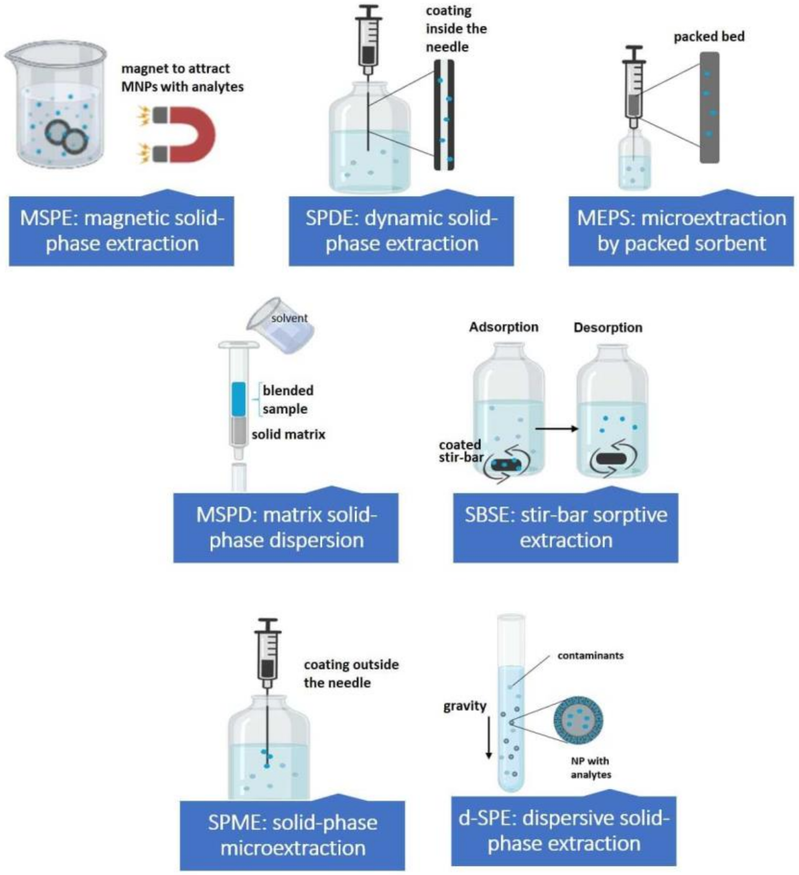
Sample preparation, prior to the analysis and detection of target pollutants, is one of the most crucial steps in a whole analytical process, accounting usually for over 60% of the total analytical time and influencing the reliability and accuracy of the outcome [1–3]. Recently, several environmentally friendly extractions based on SPE methods have gradually replaced conventional liquid-liquid extractions (that use large amounts of organic solvents) for sample pre-treatment [1, 2]. SPE has gained wide acceptance because of its simplicity, economy in terms of time and eco-friendly nature [1, 2]. Moreover, considering the principles of green analytical chemistry, finding novel techniques to preconcentrate analytes that are present in trace levels and that allow automation and miniaturization of the extraction steps, together with low solvent consumption or solventless procedures, has become a hot topic of research [2,8]. In this field, a relevant number of works focused on magnetic nanoparticles (MNPs) as alternatives to conventional SPE sorbents has been reported [1,8]. In the last 10 years, a boom of publications on this matter has emerged, as summarized in Figure 24.2. In addition to their large surface areas, the main advantage of MNPs is the rapid separation of adsorbent from solution by applying an external magnetic field [1,8].



Caption Fig. 24.2: Graphical representation of the number of publications per year (from 2009 to 2019) focusing on environmental applications of magnetic nanoparticles (MNPs). The search was performed in the PUBMED database in June 2020 using the following search queries: “environmental application magnetic nanoparticles” and “solid-phase extraction magnetic nanoparticles”. About half of the environmental application of MNPs are in solid-phase extraction (SPE).

Solid-phase extraction (SPE) is a technique used for the isolation of a target compound from a liquid phase to a solid phase by mechanisms of adsorption. Afterwards, the target compound or analyte can be adsorbed/eluted from the solid matrix with appropriate solvents/conditions, and further detected and quantified by several analytical techniques, such as gas chromatography (GC) or high-performance liquid chromatography (HPLC), coupled to several detectors such as mass spectrometer [1].

Nowadays, SPE is the most used isolation and enrichment technique for analytes in environmental samples [8]. Over the past few years, several modifications and improvements of SPE were discovered. Due to differences in the extraction process, the shape and size of the sorbent bed, and the type of adsorbent material, there are now many variations of this technique, most being based on the miniaturization and automation of various stages of the SPE [8], as summarized in Figure 24.3.



Caption Fig. 24.3: Several variations of the SPE technique applied in the pretreatment of environmental samples.

Many researchers have reported SPE as a simpler, more convenient and rapid technique that can be automated [1,8]. However, low detection limit, long extraction time and congestion of the column or disc have been described as major problems in SPE techniques [1]. In most of SPE methodologies, it is not always possible to obtain satisfactory recovery of the analytes, and the isolation and the enrichment of individual compounds can be laborious and time consuming. Hence, MNPs are an alternative to conventional SPE adsorbents, since they allow these limitations to be overcome [8]. Recently, Fe_3O_4 and Fe_2O_3 MNPs have been used for the adsorption of toxic metal ions and radioactive elements, capturing of microbial pathogens and organic dyes [1]. In magnetic SPE (MSPE) procedure, the adsorbed analytes onto the surface of MNPs are separated from the remaining environmental sample using an external magnetic field. The analytes can thus be eluted from the adsorbent and analyzed.

Due to cumulative functional properties, HMNPs can be designed to have high selectivity, in addition to the magnetic-derived advantages, high specific surface area and adsorption capacity [1,8]. Due to these advantages, several HMNPs have recently emerged to be used in environmental monitoring applications, showing promising performance in MSPE for the pretreatment of water samples, being resumed ahead in this chapter (Tables 1-4).

Adsorption mechanisms behind the SPE technique

Despite the obvious advantages of the magnetic effect, adsorption is the key mechanism ruling the effectiveness of a pollutant adsorption from a solution. In order to be a good sorbent, the material must have high adsorption capacity with a large surface area, high solution stability and mobility and enable a fast separation in a large sample amount [4]. However, to understand the adsorption mechanisms behind the adsorption of a certain pollutant from a sample, the concentration and the type of chemical species in solution must be well-known. Moreover, the nature of the bonding depends on the species involved, specifically on the strength of the interactions between an adsorbent and an adsorbate, being generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent or ionic bonding) [9]. While, the physisorption interaction is weak, in which the physiosorbed molecule does not disturb the structural environment near the adsorption site to any significant extent, the chemisorption is a strong interaction that changes the adsorbate chemical state and, in the case of chemisorption of molecules, this can cause their dissociation and formation of new adsorbate species [9]. A typical example of chemisorption is the adsorption of metal atoms on metal and semiconductor surfaces at elevated temperatures [9].

Countless factors may affect the mechanism and efficiency of adsorption, including solution pH, adsorbent concentrations and contact time. Hence, key features that characterize the performance of a nanoparticle (adsorbent) in adsorbing a certain pollutant (absorbate) from a sample solution are the so-called adsorption isotherms and kinetics [4]. Kinetics is the external manifestation of atomic-scale dynamic processes occurring at surface level; thus, the analysis of the kinetic data gives insights into the atomic mechanisms involved in the adsorption and desorption [10]. The kinetics analysis is important to characterize the performance of an adsorbent in removing a certain pollutant, and reveals information on its uptake rate and the adsorption mechanism [4].

To the kinetic experimental results obtained, the pseudo first-order and pseudo second-order kinetic models by Lagergren's [11] first-order rate equation (Equation I) and the Ho's [12] second-order rate equation (Equation II) are usually applied:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad \text{(I)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad \text{(II)}$$

where t is the time (min), q_e is the amount of target compound adsorbed (adsorbate) onto the adsorbent at equilibrium (mmol/g), q_t is the amount of adsorbate adsorbed onto the adsorbent at different times (mmol/g), k_1 (1/min) is the rate constant of the pseudo first-order adsorption, and k_2 (g/mmol.min) is the rate constant of the pseudo-second-order adsorption.

Isotherms relate the isothermal variation of the concentration of an analyte/absorbate at the surface of an adsorbent with its concentration in the solution [4]. Two models are commonly apply to describe adsorption isotherms, namely the Langmuir model [13] and the Freundlich model [14]:

$$q_e = \frac{q_{max} \times B \times C_e}{1 + B \times C_e} \qquad \text{(III)}$$

$$q_e = K_f \times C_e^{1/n} \qquad \text{(IV)}$$

where Ce is the equilibrium concentration of adsorbate (mmol/L), q_e is the equilibrium concentration of adsorbate in the solid phase (mmol/g), B (L/mmol) is the Langmuir isotherm constant, q_{max} (mmol/g) is the maximum capacity of monolayer coverage, and K_f (adsorption capacity) and n (adsorption intensity) are the constants of the Freundlich equation.

Langmuir model, given by equation III, is based on the following assumptions: (i) the adsorbent has adsorption sites, all with the same binding energy; (ii) the adsorption is limited by a monolayer coverage; and (iii) only one adsorbate can bind to each adsorption site [4,10]. In contrast, the Freundlich model, given by equation IV and where the K_f is a constant describing the adsorption capacity of the adsorbent in mmol/g and relates to the adsorption intensity, assumes reversible heterogeneous adsorption that takes place with the binding energies of each site not being necessarily the same [4].

In most cases, adsorption isotherm data are satisfactorily described by both models, though the Freundlich model more often leads to slightly better fittings, and which is particularly true for most of HMNPs rather than for simpler metal or metal oxide nanoparticles [4].

From the Langmuir model it is possible to proceed with the determination of the maximum adsorption capacity (q_{max}), characterized by the quantity of pollutant adsorbed (complete monolayer) as a function of the adsorbent mass. This value is commonly applied to describe the performance of a nanoparticle in adsorbing/removing a specific pollutant. The adsorption recovery efficiency is an additional parameter commonly used to address the materials adsorption performance, which is given by the ratio of the equilibrium concentrations of an absorbate before and after the adsorption onto the adsorbent; however, this value depends on the initial concentration of the absorbate and weight of the adsorbent [4]. Hence, for a better understanding of the performance and absorption behaviour of nanoparticles on adsorbing a pollutant, it is also helpful to compare the specific surface areas, which are usually determined by the Brunaer–Emmett–Teller (BET) analysis [4].

In addition to the adsorption kinetics and isotherms described above, two other concepts are also worth mention regarding the SPE technique for sample preparation, i.e. the enrichment/preconcentration factor and limit of detection (LOD). The enrichment/preconcentration factor is the number of times the analytical signal is enhanced through sample preparation relative to the analyte(s) signal without that enrichment, corresponding to the ratio between the analyte(s) concentrations before and after the preconcentration step. The LOD, often mistakenly confounded with the analytical sensitivity, is derived from the smallest concentration (x_L) of an analyte that can be distinguished from its absence (a blank value) in a given confidence level, in which x_L is given by the Equation V:

$$x_L = \bar{x}_{bi} + ks_{bi} \qquad \text{(V)}$$

where $\bar{x}_{bi}$ is the average of the blank measures, s_{bi} is the standard deviation of the blank measures, and k is a numerical factor chosen according to the confidence level desired (generally 99%) [15].

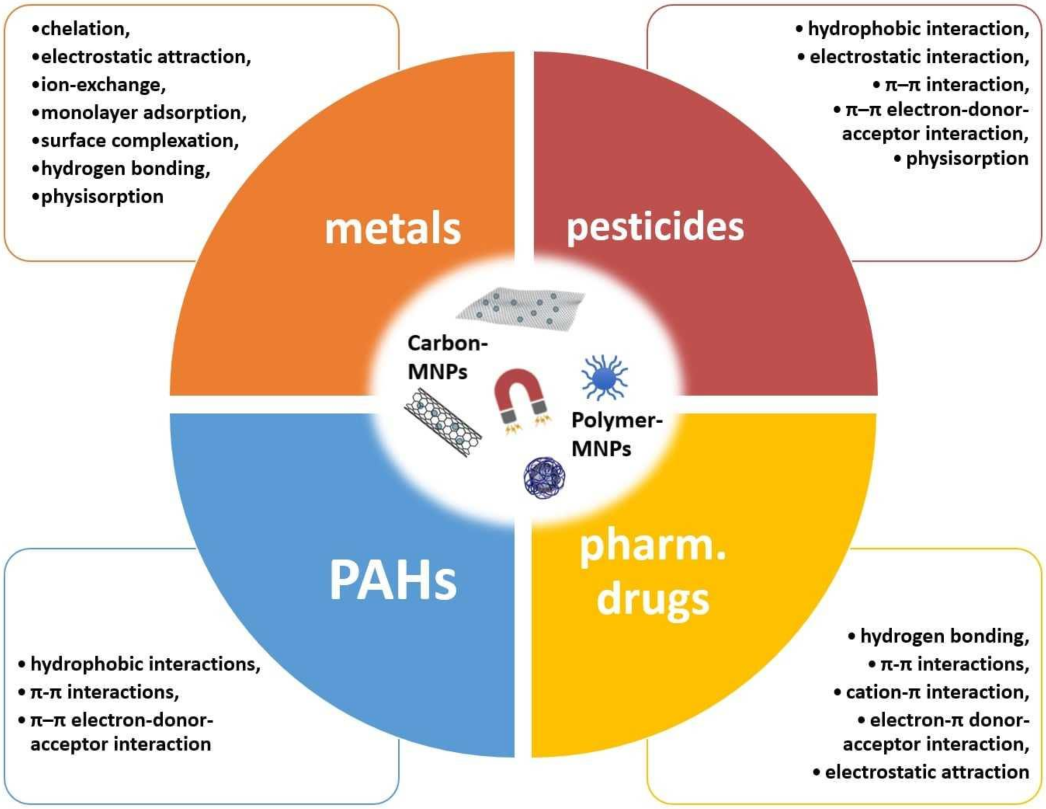
Types of materials used in HMNPs for SPE

Magnetic nanoparticles can be mixed or coated with different materials to improve their stability and/or introduce new surface properties and functionalities to promote selective adsorption. Among these materials, carbon-based materials are a versatile coating for MNPs due to their chemical stability, biocompatibility, possibility of surface modification and pore creation [16]. For instance, carbon nanotubes (CNTs) have been successfully used as sorbents in continuous on-column preconcentration systems, although there is a time limiting step due to the large volume of samples loaded [16]. Thus, an alternative to the column mode is the magnetic solid phase extraction (MSPE), using MNPs modified with CNTs as sorbents [16]. Additionally, graphene oxide (GO) has various functional groups (e.g., carboxyl, epoxy and hydroxyl groups) and good hydrophilicity, being proved to be a promising material for the adsorption and preconcentration of not only metal ions but also aromatic compounds such as polycyclic aromatic hydrocarbons (PAHs), aromatic pharmaceutical drugs, dyes, phenolic compounds and inorganic nanoparticles [17–19].

More recently, functional polymers attracted tremendous interest. The investigation of polymer-based HMNPs for MSPE applications has raised in the past years because polymer-MNPs have plentiful functional groups that allow a more selective adsorption. Many authors published on the synthesis of these polymer-MNPs, including polystyrene, polyaniline, polypyrrole and poly (N-isopropylacrylamide) [20–22]. Among these polymer-based materials, polypyrrole is one of the widely used polymers for the extraction of various types of compounds, such as aromatic compounds (e.g. PAHs), organometal compounds (e.g. organoarsenic) and anionic compounds (e.g. nitrite) with high efficiency [20–22]. This is probably because it has multifunctional adsorption sites, and therefore interactions among polar functional groups, π–π interactions and hydrogen-bonding can be established. Recently, it was shown that the polymer polyaniline (PANI) is quite efficient as an adsorbent in SPE, having many advantages over conventional sorbents [23,24]. This polymer is promising for separation applications due to its good stability, simple synthesis, relatively low cost, and adsorption capability of polar compounds, which is due to its polymeric skeleton and functional groups (enabling π-π interactions). Another functional polymer that has been proved to be a promising and effective bio-adsorbent is chitosan, a deacetylated natural product of chitin of low cost [25], which has high adsorption capacity towards many heavy metals due to the presence of multiple functional groups (e.g., NH_2 and OH) [26]. Moreover, polystyrene HMNPs (MNP/PSt) have been studied as adsorbents for pesticides [27]. Recently, a new generation of highly porous polymers, hyper cross-linked polystyrenes (HCPs), has been suggested as novel adsorbents [28]. By introducing magnetic properties into HCP it is possible to combine the high adsorption capacity of HCP and separation convenience of magnetic materials [28]. Moreover, several reports have shown that HCP-based magnetic materials (mHCP) are good adsorbents for some pharmaceutical drugs, such as tetracycline [29], chlorotetracycline [30], and carbamazepine [31], and pesticides such as atrazine [32].

Pretreatment of environmental samples using HMNPs

The most common pollutants found in the environment include inorganic metals, PAHs, persistent organic pollutants (POPs), pesticides, and pharmaceutical drugs [3, 33, 34]. In the following subsections, the applications of HMNPs for the adsorption and preconcentration of these environmental pollutants are presented, as well as the potential mechanisms that influence their adsorption onto HMNPs. A summary of the target pollutants and identified interactions ruling their adsorption onto HMNPs is given in Figure 24.4.



Caption Fig. 24.4: Schematic representation of the mechanisms that may be involved in the adsorption of several pollutants (metals, pesticides, PAHs and pharmaceutical drugs) onto HMNPs (mostly carbon- and polymer-based) (adapted from [35]).

Extraction and preconcentration of heavy metals

Heavy metals ions are a serious threat to human life, even in trace amounts. Toxic heavy metals such as mercury, copper, nickel, cadmium, zinc, cobalt, lead, and chromium are highly hazardous, nonbiodegradable and cause eminent health problems, such as skin irritations, vomiting, stomach cramps, kidney dysfunction, anemia and nausea [1, 36]. These compounds are excessively released to the environment by industrial effluents, posing a great concern towards the environmental protection agencies [36]. Even when present in ultra-trace levels, their presence in the environment poses great threat to human health [1].

Some heavy metals, such as mercury, pose a severe impact on the environment and human health. Mercury is able to bioconcentrate along the food chain and it can even cross the blood brain barrier [3]. Its high toxicity and bioavailability are also very depending on the chemical form (species) in which it is found, namely the organic species, the monomethylmercury (MMHg) and dimethylmercury (DMHg), are much more toxic than the inorganic ones [37]. Thus, special emphasis on the environmental risk assessment of MMHg has been found in the literature [37]. A large number of prevalently used techniques for the determination of trace amounts of mercury has been proposed for the detection and quantification of mercury species, such as gas chromatography (GC) coupled to atomic fluorescence spectroscopy (AFS) via thermal pyrolysis (GC-pyro-AFS), inductively coupled plasma mass spectrometry (ICP-MS) and cold vapor atomic absorption spectrometry (CVAAS) [38,39]. Despite significant developments in analytical techniques, the mercury speciation analysis in water samples is still very challenging, especially due to the fact that in these samples mercury species are found at trace levels and the concentration of MMHg is much lower than its inorganic form [40]. Thus, it is highly demanding to find effective techniques that enable not only their preconcentration before detection envisioning their monitoring but also to find novel adsorbents for their removal from the environment. Several types of SPE adsorbents have been applied for the extraction of heavy metals from water samples, e.g. activated carbon [41], carbon nanotubes [16], polymeric adsorbents [42], and natural-based adsorbents [43]. Table 24.1 summarizes recent reports on the preconcentration and removal of heavy metals using HMNPs in MSPE.

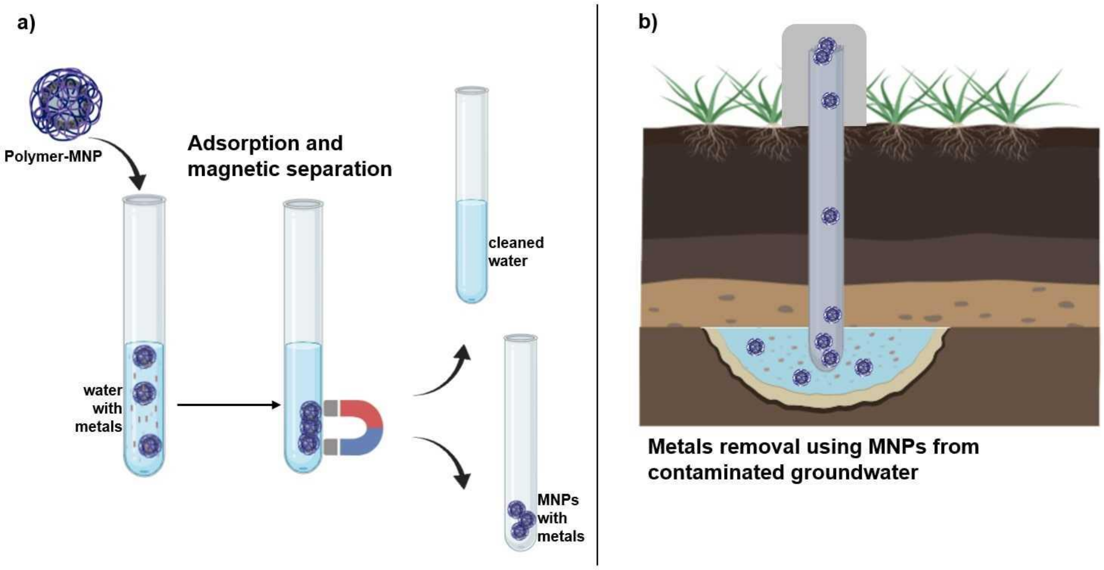
Table 24.1 - Application of HMNPs in MSPE for the preconcentration and removal of metal ions (in the last 10 years).

Magnetic Core	**Modifying layer**	**Carbon-/Polymer-HMNP**	**Sample matrix**	**Analytes**	**Analytical technique**	**LODs (µg/L)**	**Ref.**
Fe_3O_4	poly(MMA-co-MA)* coating w/ APTMS as surface modification	polymer	-	Co^{2+}, Cr^{3+}, Zn^{2+}, and Cd^{2+}	-	-	[36]
	PANI coating	polymer	seawater	MMHg	GC-MS	0.1	[44]
	graphene oxide-chitosan coating w/ MPTS as surface modification	carbon/ polymer	tap water, sea water from Iran	Hg^{2+}	FAAS	0.06	[45]
	CNTs coating	carbon	tap, dam and river waters.	MMHg	GC-pyro-AFS	0.0054	[40]

PEI coating mixed w/ monocationic sodium clay	polymer	-	Cr(VI)	-	-	[46]

**poly(MMA-co-MA): copolymer of methyl methacrylate (MMA) and maleic anhydride (MA); APTMS: 3-aminopropyltrimethoxysilane; PANI: polyaniline; MPTS: 3-mercaptopropyltrimethoxysilane; CNTs: carbon nanotubes; PEI: Polyethyleneimine; GC-MS: gas chromatography-mass spectrometry; FAAS: flame atomic absorption spectrophotometry; GC-pyro-AFS: gas chromatography coupled to atomic fluorescence spectroscopy via thermal pyrolysis.*

Magnetic Fe_3O_4 nanoparticles covered with a number of hydroxyl (−OH) groups were prepared by Masoumi et al. [36] through chemical coprecipitation method, and subsequently modified with 3-aminopropyltrimethoxysilane (APTMS) through a silanization reaction with −OH groups to yield amine-terminated APTMS- Fe_3O_4 nanoparticles. Afterwards, a hybrid formed by the copolymer of methyl methacrylate (MMA) and maleic anhydride (MA) at the surface of magnetite MNPs, the poly(MMA-co-MA)/APTMS-Fe_3O_4, was prepared via cross-link reactions between the amine groups and anhydride groups of the copolymer chains [36]. Then, this hybrid magnetic adsorbent was used to study the effect of different parameters, including pH, reaction time, adsorbent dosage, and initial metal ion concentration on the removal of Cr^{3+}, Cd^{2+}, Co^{2+}, and Zn^{2+} from aqueous solutions [36]. The prepared poly(MMA-co-MA)/APTMS-Fe_3O_4, was proven to be an excellent nanomagnetic adsorbent for the removal of heavy metal ions from aqueous solution, whereas the results showed that the highest removal of these metal ions occurs in approximately 1 h at pH 6.0 for 20 mg of adsorbent and for 20 mg/L of initial metal ion concentration [36]. Moreover, it was found that the adsorption rates followed the pseudo-second-order rate law, and adsorption of metal ions followed the Langmuir model, with a q_{max} ranging from 90.09 to 111.11 mg/g [36]. These features coupled to the facile removal of the MNPs through a magnetic field show that this type of HMNPs could be used as efficient adsorbents for heavy metals removal from aqueous solutions. The removal strategy followed by this work is summarized in Figure 24.5.a), whereas in Figure 24.5.b) it is presented an example of a strategy to metals removal using MNPs for groundwater remediation.



Caption Fig. 24.5: MSPE of toxic metals using polymer-MNPs in a preconcentration strategy (a) and in a groundwater remediation strategy (b) (adapted from [4]).

Mehdinia et al. [44] prepared new Fe_3O_4/PANI hybrid NPs as novel MSPE sorbents for further determination of monomethylmercury (MMHg) in seawater samples, *via* quantification by gas chromatography-mass spectrometry (GC-MS). The MSPE developed process involved the dispersion of the Fe_3O_4/PANI nanoparticles in water samples with sonication, followed by magnetic phishing of the metals, and desorption of the extracted MeHg for quantification. After the optimization of adsorption and desorption conditions, a detection limit of 0.1 ng/mL was obtained, in which these values were better than the commercial sorbent C18 (0.1 versus 3 ng/mL) [44]. Moreover, good recoveries (>98%) and an enrichment factor of 91 were obtained with real seawater samples [44].

Ziaei et al. [45] have functionalized graphene oxide-magnetic chitosan (GO–MC) hybrid materials with 3-mercaptopropyltrimethoxysilane (MPTS) for the preconcentration and determination of Hg^{2+}. MC, MC-MPTS and GO–MC-MPTS adsorbents were compared for the adsorption of Hg^{2+}, showing that the GO-MC-MPTS hybrid materials have a higher extraction efficiency than MC and MC-MPTS, whereas recoveries of the analyte higher than 95.6% and a preconcentration factor ca. 80 were obtained [45].

Hybrid nanocomposites based on Fe_3O_4 MNPs coated with different types of CNTs have been studied recently as adsorbents for MSPE of mercury in its speciation analysis [40]. The applied synthesis is very simple since it only involves the addition of either single-walled (SW-), double-walled (DW-) or multi-walled (MW-) CNTs to the mixture for the synthesis of magnetite MNPs, without any additional modification of the CNTs. The determination of MMHg was performed by GC-pyro-AFS after derivatization by ethylation. The overall procedure provided a preconcentration factor of MMHg of 150 and the obtained LOD was 5.4 pg/mL [40]. Finally, the methodology was validated with tap, dam and river water samples to evaluate the performance under real conditions, with recoveries from 79% to 97% of spiked MMHg [40].

Different HMNPs (polymer-based or carbon-based) proven to be suitable for both the removal and preconcentration of toxic metal ions from environmental water solutions (shown in Table 24.1). It was concluded that the adsorption mechanism of metals is highly dependent on the pH value since the coatings/modifications at the HMNPs surface leads to the speciation of several functional groups (hydroxyl, carboxylic or amine). At appropriate pH values, these materials can act as chelating sites for the metal cations or can be involved in electrostatic attraction or ion-exchange mechanisms. In general, chelation, ion-exchange, electrostatic attraction, surface complexation, monolayer adsorption, hydrogen bonding and physisorption are the main mechanisms involved in metals adsorption [35]. Besides the HMNPs containing functional groups, layers of functional particles (e.g. SiO_2) or other functional nanomaterials (e.g. zeolite, chitosan, cellulose, CNTs, graphene) can be used to improve adsorption [35,47–49]. Moreover, it was proven that the presence of GO in the hybrid chitosan-based material shows the valuable applicability of using not only the polymer coating but also conjugating with carbon-based materials in extracting mercury for water samples [45].

Preconcentration of pesticides and organic pollutants

A consequence of the intensification of agriculture activities are the severe use of pesticides to increase crops productivity, including herbicides, fungicides and insecticides, which leads to their accumulation in the food chain [1,50]. Moreover, the slow degradation of these pesticides, along with the extensive or inappropriate use by farmers across the last decades, led to a general environmental contamination by these compounds. Pesticides are a wide-ranging group of chemical compounds, including organochlorines, organophosphates, carbamates, chloroacetanilide, pyrethroids and neonicotinoids [1,50].

Organophosphates are the base chemistry of many pesticides, being a class of chemicals that generally act as cholinesterase inhibitors and thus are highly neurotoxic compounds

[51]. Most of these compounds can be found in surface water and groundwater; therefore, the detection and extraction of these compounds in environmental water samples has attracted increasing attention in recent years. Another widely used pesticide is glyphosate (N-(phosphonomethyl)glycine), a broad-spectrum and foliar-applied herbicide for controlling unwanted weeds and vegetation. Its biodegradation in the environment yields the aminomethylphosphonic acid (AMPA) as major metabolite [52]. Glyphosate (GLY) has become one of the most generally used herbicide due to its relatively low mammal toxicity; however, its indiscriminate application worldwide has generated some concerns regarding the possible health hazard and environmental impact [52]. The US Environmental Protection Agency (EPA) has set a maximum contaminant level of GLY in drinking water at 0.7 ppm [53]. Accordingly, the monitoring of glyphosate in environmental samples and tracing at residue levels in several agricultural products has attracted substantial attention lately [52]. Another class of pesticides widely used in agriculture in the last decades comprises pyrethroids, a large group of synthetic insecticides. These compounds possess noteworthy advantages such as high killing activity, rapid knockdown activity and high photostability [54]. Due to this extensive usage, pyrethroids can easily enter into environmental water systems from irrigation, laundry, rain, etc [27,54]. Furthermore, health issues have emerged due to their widespread and inevitable adverse effects, such as being able of inducing teratogenicity, carcinogenicity and mutagenicity [27]. Hence, promising sample pretreatment techniques to monitor pyrethroids based on MSPE have lately received significant attention.

Not only pesticides pose big concerns to the environment and human health, but also a certain group of manmade chemicals that are persistent, toxic and widely distributed, known as the persistent organic pollutants (POPs). POPs include different classes of chemicals, such as polychlorinated biphenyls (PCBs), perfluorinated compounds (PFCs), dioxins and furans, and organochlorine pesticides [3]. Most of them are currently banned from usage since their harmful consequences include cancer, neurotoxicity, immunotoxicity and endocrine disruption [3,55]. Within the group of perfluorinated compounds (PFCs), the perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), are widely used as anionic surfactants in several industries. Their use poses major concerns since they are extremely persistent in the environment, highly resistant to typical environmental degradation processes and have higher capacity for bioaccumulation in animals and biomagnification in higher organisms throughout the food chain [56,57].

Thus, numerous HMNPs have been synthesized and applied to the extraction/adsorption of different organic pollutants, pesticides and also endocrine disruptors, from diverse environmental complex matrices. Table 24.2 summarizes recent reports on the preconcentration of pesticides and organic pollutants using HMNPs in MSPE.

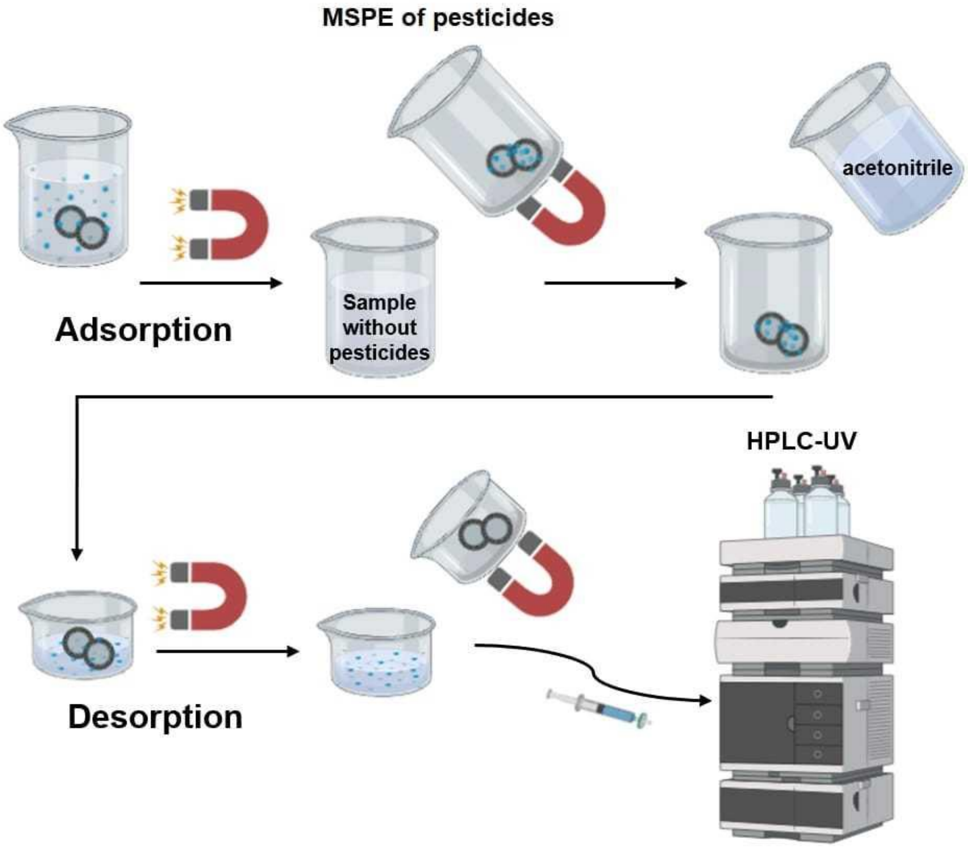
Table 24.2 - Summary of the use of HMNPs in MSPE for preconcentration of pesticides and other organic compounds (from the last 10 years).

Magnetic Core	**Modifying layer**	**Carbon-/Polymer-HMNP**	**Sample matrix**	**Analytes**	**Analytical technique**	**LODs (µg/L)**	**Ref.**
Fe_3O_4	carbon coating	carbon	well, tap, river and mineral	organophosphorus pesticides	HPLC-UV	0.0043-0.0474	[51]
	alumina coating	-	water extract of the guava fruit	glyphosate	CE-ECL	0.01 (µg/g)	[52]

PSt* coating	polymer	river water, lake water, tap water, melted snow and reservoir water	pyrethroids	UFLC-UV	0.012-0.026	[27]
C18-functionalized chitosan coating	polymer	tap water, rainwater, wastewater, and river	PFOA, PFOS, and other PFCs	HPLC-MS/MS	0.000075-0.00024	[55]
PPy coating	polymer	tap water	phthalates	GC-MS	0.006-0.068	[20]
PDA or PPy coating	polymer	-	organic compounds: bisphenol A, proflavine, naphthalene acetic acid	CE-UV	-	[58]
deposition on graphene sheets	carbon	river and pond water	phthalate acid esters	GC-MS	0.010-0.056	[59]

**PSt: polystyrene; C18: octadecyl; PPy: polypyrrole; PDA: Polydopamine; PFOA: Perfluorooctanoic acid; PFOS: Perfluorooctanesulfonic acid; PFCs: perfluorinated compounds; HPLC-UV: high performance liquid chromatography with ultraviolet detection; CE-ECL: capillary electrophoresis with electrochemiluminescence detection; UFLC-UV: ultra-fast liquid chromatography with ultraviolet detection; HPLC-MS/MS: HPLC-tandem mass spectrometry system; GC-MS: gas chromatography-mass spectrometry; CE-UV: capillary electrophoresis with ultraviolet detection.*

Heidari and Razmi reported the application of carbon coated Fe_3O_4 (Fe_3O_4/C) HMNPs as adsorbents for MSPE of trace amounts of organophosphorus pesticides from several environmental water samples and their determination using high performance liquid chromatography with ultraviolet detection (HPLC–UV) [51]. The magnetite MNPs were synthesized by the chemical coprecipitation technique and then modified with carbon coating by a simple hydrothermal reaction [51]. After proper characterization of the prepared HMNPs, the MSPE procedure was performed as exemplified in Figure 24.6. Under the optimal conditions (pH of 9.16, 97.4 mg Fe_3O_4/C and 10 mmol/L NaCl), the proposed MSPE-HPLC-UV method was then evaluated and applied in the extraction and quantification of several organophosphates from environmental water samples (well, tap, river and mineral). High enrichment factors were achieved, ranging from 330-1200, and the analytical method displayed a wide linear range (0.05-400 ng/mL) with low detection limits (4.3-47.4 pg/mL) [51].



Caption Fig. 24.6: Schematic representation of the MSPE procedure for pesticides preconcentration followed by HPLC analysis and UV detection.

Due to its high solubility in water, glyphosate often represents an analytical detection challenge. To overcome this drawback, alumina-coated iron oxide MNPs ($Fe_3O_4@Al_2O_3$ MNPs) were proposed as affinity probes to selectively concentrate phosphopeptides from complex sample matrices [52]. Since glyphosate is structurally similar to amino acids and both glyphosate and its metabolite (AMPA) contain a phosphate group, and alumina has been shown to have high specificity for analytes containing phosphate groups [60], one of the main advantages of using these HMNPs is their high selectivity towards GLY and AMPA. By conjugating these dual interesting properties, $Fe_3O_4@Al_2O_3$ HMNPs can be used as a magnetic affinity probe to enrich glyphosate and AMPA from aqueous samples, and readily isolated them from sample solution by simply employing an external magnetic field. Hsu et al. [52] reported a simple and rapid microscale MSPE procedure for glyphophate in water using these $Fe_3O_4@Al_2O_3$ HMNPs as affinity adsorbents. The MSPE technique applied follows the same principles described in Figure 24.6, whereas the desorption solution was a $Na_4P_2O_7$ solution instead of acetonitrile, and the analytical method applied was capillary electrophoresis with electrochemiluminescence detection (CE-ECL) [52]. The applicability of this method was demonstrated by analyzing GLY in water extract of the guava fruit, whereas the LOD of GLY in guava was found to be 0.01 μg/g, which is 20-fold lower than the maximum contaminant level allowed in guava [52]. Yu et al. [27] prepared polystyrene-coated MNPs (MNPs/PSt) to be used as MSPE adsorbents for extracting pyrethroids from water samples. A simple, green, economical, time saving and effective method for pyrethroids analysis in environmental water samples was established, whereas the MNPs/PSt can be reused afterwards and the whole extraction process is completed in less than one hour [27]. The MSPE procedure was performed as exemplified in the Figure 24.6, and the determination of the pyrethroids was carried out by ultra-fast liquid chromatography-ultraviolet spectrometry (UFLC–UV) [27]. A high enrichment factor of 500 was achieved and the limits of detection for several pyrethroids ranged from 0.012 ng/mL to 0.026 ng/mL, while recoveries were found to be between 78.97% and 96.05% [27]. The developed method was then applied to five kinds of environmental water samples, including river water, lake water, tap water, melted snow and reservoir water, and no pyrethroids residues were detectable in all these real water samples [27].

Zhang et al. [55] reported the preparation of chitosan-coated octadecyl-functionalized MNPs (Fe_3O_4-C18-chitosan MNPs) and its potential application in the preconcentration of these PFCs from environmental water samples. The porous hydrophilic chitosan polymer nature allows not only the adsorption of PFCs at low pH, but most importantly, it allows analyte molecules to pass through and enter the interior hydrophobic layer (with octadecyl groups), while preventing the natural organic matter macromolecules from passing through the coating by the size exclusion effect and electrostatic repulsion. This behavior enhances the anti-interference ability of this hybrid adsorbent [55]. To this end, MNPs were modified with an octadecyl group by silylation reaction. Then, the surface of the obtained Fe_3O_4-C18 MNPs was coated with a layer of hydrophilic chitosan-tripolyphosphate polymer by ionotropic gelation to form this novel HMNP [55]. Afterwards, PFCs were extracted from real environmental water samples (wastewater, river water, tap water, surface water and rainwater) using these Fe_3O_4-C18-chitosan MNPs at pH 3, and then determined by HPLC-tandem mass spectrometry (HPLC-MS/MS) [55]. Recoveries of PFOA and PFOS were in the ranges of 88-108% and 63-112% for the four water samples, with detection limits of 0.19 and 0.036 ng/L, respectively. These values correspond to an increase by 10-50-fold relative to what obtained with the RP-C18 cartridge [55].

The different properties of HMNPs contribute to several mechanisms of reaction with different pesticides/POPs, in which these mechanisms of adsorption are due to diverse types of interactions, such as electrostatic, π-π, electron-donor-acceptor and hydrophobic interactions, as well as by physisorption mechanisms [35]. Both polymer-MNPs and carbon-based MNPs are very attractive adsorbents for several POPs and pesticides. Since some of the functionalized polymers possess a hydrophobic character they display a high performance to adsorb less polar organic compounds (e.g. pesticides and POPs), whereas other polymers with aromatic groups such as polypyrrole favor π–π interactions with aromatic pollutants [20]. Carbon-based materials have the advantage of increasing significantly the surface area of MNPs, being a factor also responsible in the improved adsorption of pesticides by physisorption mechanisms [35,50].

Preconcentration of polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are hydrocarbons with two or more fused aromatic rings, which are obtained from the incomplete combustion or pyrolysis of carbonaceous and organic matter (coal, diesel, gas, wood, etc.) by some industrial processes, vehicle exhausts, energy producing plants, waste incineration, and domestic heating emissions [3,61]. PAHs are highly toxic and some of them are mutagenic and carcinogenic; they also are ubiquitous in the environment, being detected in all compartments (air, soils and water) [3,61]. In what concerns aquatic systems, PAHs have been detected in river, lakes, oceans and also in groundwater and drinking water, being thus very important the monitoring of these PAHs in environmental water samples

[3,62,63]. Table 24.3 summarizes recent reports on the applications of HMNPs in MSPE for sample preparation and preconcentration of PAHs in environmental samples.

Table 24.3 - Summary on the use of HMNPs in MSPE for preconcentration of polycyclic aromatic hydrocarbons (in the last 10 years).

Magnetic Core	**Modifying layer**	**Carbon- /Polymer- HMNP**	**Sample matrix**	**Analytes**	**Analytical technique**	**LODs (µg/L)**	**Ref.**
Fe_3O_4	C18*-functionalized mesoporous silica coating	-	ultra-pure water spiked with various targets	fluoranthene, pyrene, etc.	HPLC-FLD	-	[64]
	silica coating and mixing w/ MOF MIL-101(Cr)	-	lake water and wastewater samples	naphthalene, anthracene, fluoranthene, pyrene, etc.	HPLC-UV	0.0028-0.0272	[65]
	deposition on graphene sheets	carbon	reservoir water, tap water, sea water	fluorene, anthracene, fluoranthene, pyrene, etc.	HPLC-FLD	0.0005-0.005	[66]
	carbon coating	carbon	spiked and lake water	naphthalene, fluorene, anthracene, pyrene, etc.	GC-MS	0.015-0.335	[67]

**C18: octadecyl; MOF: metal-organic framework; MIL-101(Cr): [$Cr_3(O)X(bdc)_3(H_2O)_2$] (bdc = benzene-1,4-dicarboxylate, X = OH or F); HPLC-FLD: high performance liquid chromatography with fluorescence spectrometry; HPLC-UV: high performance liquid chromatography with ultraviolet detection; GC-MS: gas chromatography-mass spectrometry.*

Zhang et al. [64] have successfully functionalized C18-mesoporous silica shell onto the surface of a Fe_3O_4 magnetic core to obtain Fe_3O_4/SiO_2-C18 HMNPs aiming their application in extraction of trace levels of PAHs from water solution. The prepared

HMNPs exhibited high extraction performance towards PAHs, while showing strong anti-interference ability to natural organic matter present in solution [64]. It was found that the recoveries of PAHs remained almost constant in a broad pH range, which is due to the fact of having the adsorption being ruled by hydrophobic interactions [64]. Moreover, and also for the same reason, high ionic strength and equilibrium time have negligible influence in the extraction parameters, whereas under the optimal conditions recoveries of most targets up to 90% were found [64].

Huo and Yan [65] reported the use of metal-organic framework (MOF)-based MSPE, in combination with HPLC, for PAHs extraction from environmental water samples. Fe_3O_4 MNPs were coated with silica, according to the Stöber method, and the MOF MIL-101(Cr) was synthetized; these compounds were mixed to react and form the hybrid Fe_3O_4@SiO_2–MIL-101 MNPs [65]. By using these Fe_3O_4@SiO_2–MIL-101 HMNPs it was possible to achieve enrichment factors of PAHs up to 180 [65]. Comparing to previously reported SPE methods, using several sorbents for HPLC determination of PAHs, the developed method required smaller amounts of the adsorbent and smaller volumes of sample, while providing lower LODs for UV detection [65]. These remarkable results showed that not only hydrophobic interactions occur, but also π-π interactions between PAHs and the terephthalic acid molecules in the framework of MIL-101, whereas the π-complexation between PAHs and the Lewis acid sites in the pores of the MOF play a significant role in the adsorption of PAHs [65].

Carbon-based HMNPs have a vast application on the extraction of PAHs from aqueous samples [67]; in this lined, several authors demonstrated the usefulness of having two layers with different properties added to the MNPs. These consist of one more hydrophobic sublayer, to allow efficient extraction of nonpolar compounds, and one more hydrophilic layer at the surface to provide suitable compatibility with the aqueous solution and efficient MNPs dispersion [8,67]. Overall, by the previously described works it is possible to conclude that carbon-based HMNPs that allow hydrophobic interactions are the most promising for the adsorption of PAHs.

Preconcentration of antibiotics and other pharmaceuticals

Despite the important role of pharmaceuticals in modern life, their excessive and prolonged use presents major environmental and health safety concerns. Some pharmaceuticals are not completely metabolized, being mainly cleared by urine and reaching the environment [3,68]. Additionally, their bioactive metabolites could be more reactive and dangerous to the aquatic environment [68]. Hence, several pharmaceutical drugs are nowadays of high concern due to their large consumption and release into the environment. The relative contributions of the various emission sources are not precisely known, however, effluents from WWTPs and untreated wastewater are definitely the most significant sources for the unexpended pharmaceuticals [69]. Most relevant pharmaceuticals that are nowadays present in the environment are antibiotics, non-steroidal anti-inflammatory drugs (NSAIDs), analgesics, β-blockers, lipid regulators and psychiatric drugs [3]. The use of antibiotics began in the early of 20th century with the discovery of synthetic antibiotics derived from dyes, and later with the discovery of penicillin-derived or β-lactam antibiotics. Antibiotics are thus amongst the pharmaceutical drugs posing a higher health hazard, since they can, in a long-term, contribute to the growth of antibiotic resistant bacteria [35]. Sulfonamide, tetracycline and fluoroquinolone antibiotics are different classes of antibiotics, all presenting aromatic rings, thus allowing multi-interaction sites for adsorption by different types of HMNPs (summarized in Table 24.4).

Table 24.4 - Summary on the use of HMNPs in MSPE for preconcentration of antibiotics (from the last 10 years).

Magnetic Core	**Modifying layer**	**Carbon- /Polymer- HMNP**	**Sample matrix**	**Analytes**	**Analytical technique**	**LODs (µg/L)**	**Ref.**
Fe_3O_4	HCP*	polymer	river water	sulfonamides	HPLC-AD	0.6-1.0	[28]
	deposition on GO sheets	carbon	mineral water and river water	tetracycline, oxytetracycline, chlortetracycline, and doxycycline	CLC-UV	-	[17]
	MIP coating	polymer	lake water, river water, sewage effluent waters	ciprofloxacin, enrofloxacin, lomefloxacin, levofloxacin, etc.	HPLC-MS/MS	0.0032-0.0062	[70]

**HCP: hypercrosslinked polystyrene; GO: graphene oxide; MIP: molecularly imprinted polymer; HPLC-AD: high-performance liquid chromatography with amperometric detection; CLC-UV: capillary liquid chromatography with ultraviolet detection; HPLC-MS/MS: HPLC-tandem mass spectrometry system; GC-MS: gas chromatography-mass spectrometry.*

Tolmacheva et al. [28] reported a novel MSPE adsorbent, HCP-Fe_3O_4, for the preconcentration of four sulfonamide antibiotics (sulfamethoxypyridazine, sulfamethazine, sulfamethoxazole and sulfachloropyridazine) from natural water samples. This material was prepared by adsorption of pre-synthesized Fe_3O_4 MNPs onto

HCP and the developed MSPE method was performed by combining it with HPLC analysis and amperometric detection [28]. The results showed that the recoveries of these compounds were in the range of 84–105%, with LODs ranging between 0.21 and 0.33 ng/mL for river water samples [28].

Lin et al. [17] prepared graphene oxide functionalized MNPs (GO-MPs) and applied these materials as adsorbents of four tetracycline antibiotics (tetracycline, oxytetracycline, chlortetracycline, and doxycycline) from aqueous solution with the goal of developing a preconcentration technique. Several factors that could affect the adsorption process were studied, such as contact time, volume of sample, solution pH and ionic strength. It was found that the adsorption process is fast, highly efficient, and both the pH value and ionic strength had insignificant effects on tetracyclines adsorption [17]. The adsorption of tetracyclines onto GO-MPs was attributed to strong π–π interactions that may be established.

A magnetic molecularly imprinted polymer (MMIP) has been developed as a novel adsorbent for the selective extraction of fluoroquinolone antibiotics (FQs) from environmental water samples, followed by HPLC-MS/MS for analysis [70]. MIPs are synthetic cross-linked polymers that hold tailored hollows, which are suitable for target template molecule or similar compounds [70]. This hybrid MMIP was prepared by Chen et al. [70] using ciprofloxacin as the template molecule, methacrylic acid as the functional monomer, ethylene glycol dimethacrylate as the cross-linking agent and Fe_3O_4 magnetite as the magnetic component. The detection limits of FQs were in the range of 3.2–6.2 ng/L, and the recoveries of FQs were found to be in the range of 76.3–94.2% [70]. The proposed method was then applied to determine FQs (ciprofloxacin, enrofloxacin, lomefloxacin, levofloxacin, fleroxacin and sparfloxacin) in real environmental water samples, such as lake water, river water, and primary and final sewage effluent, whereas ciprofloxacin and fleroxacin were found in the sewage effluent samples with contents in the range of 26-87 ng/L [70].

Like many other pharmaceutical drugs, most antibiotics such as sulfonamides, tetracyclines, cephalosporins, fluoroquinolones, carbapenems and some other β-lactams, present aromatic rings and π–π interaction sites. This possibility of π–π interactions has been described has the most relevant factors in the adsorption of antibiotics onto MNPs. However, hydrogen bonding, cation-π, electron-π donor-acceptor, and electrostatic interactions can also play a role in defining these materials adsorption performance [35].

Conclusions and Future Perspectives

In the last decades, emergent environmental pollution has become a serious health threat and major concern; therefore, both the removal and monitoring of hazardous compounds from environmental samples have been a priority. However, due to the low concentration of pollutants in some of these samples, the major challenge is the isolation of trace amounts of analytes from complex matrices and their identification and quantification by feasible analytical equipment. Among a wide array of SPE adsorbents that have been studied, the application of hybrid magnetic materials has been considered a hot topic and largely investigated in the past decade. In this context, this chapter reviews the literature of the past decade dealing with the application of hybrid magnetic materials, i.e. MNPs combined with other materials (e.g., polymers and carbon materials), used in SPE with the goal of preconcentrating pollutants from aqueous environmental samples to improve their monitoring.

The use of MNPs in SPE significantly reduces the duration of the analysis and number of stages in the extraction process, particularly due to the use of an external magnetic field. Also, in accordance with the principles of green chemistry, MSPE can reduce the usage of organic solvents, and thus the formation of toxic and dangerous waste. Besides their magnetic characteristic, MNPs can be mixed or coated with layers of different materials to improve their stability as well as to introduce new surface properties and functionalities. These materials, known as hybrid MNPs, are much more target selective and suitable for the pretreatment of complex samples, such as environmental samples. In this sense, MNPs have several advantages, such as higher adsorption capabilities and faster adsorption rates, in comparison to conventional SPE materials for the adsorption of several organic pollutants (pesticides, antibiotic and PAHs) and toxic inorganic metals.

In this chapter it is overviewed the application of hybrid MNPs in SPE to improve environmental monitoring over the past decade. Both polymer- and carbon-based materials are versatile coatings for MNPs, being suitable adsorbents for extracting and preconcentrating many different pollutants due to a multitude of interactions. In particular, the investigation of functional polymers has attracted tremendous interest in the past years, namely the polystyrene (PSt), polyaniline (PANI), and polypyrrole (PPy). For instance, it was shown that the PANI is quite efficient as an adsorbent in SPE towards MeHg, having many advantages over conventional sorbents. Additionally, a carbon-based material, GO, has various functional groups, being proved to be a promising material when applied in HMNPs for the adsorption and preconcentration of not only metal ions but also aromatic compounds, such as PAHs, pharmaceutical drugs, and phenolic compounds. Overall, it has been shown in the literature that both polymer- and carbon-based HMNPs are promising adsorbents for a wide range of pollutants from environmental samples, allowing their preconcentration and improved environmental monitoring.

Despite the promising potential of HMNPs in SPE for environmental monitoring, uncertainties over the knowledge on their environmental fate, bioavailability and health impacts need however to be addressed before their widespread application. Thus, in order to turn these materials feasible for large-scale applications, significant research is still needed in this field.

Acknowledgements

This work was developed within the scope of the project CICECO - Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Portuguese Foundation for Science and Technology/MCTES. This work was financially supported by the project POCI-01-0145- FEDER-031106 (IonCytDevice) funded by FEDER, through COMPETE2020—Programa Operacional Competitividade e Internacionalização (POCI), and by national funds (OE), through FCT/MCTES, and developed in the scope of the “Smart Green Homes” Project [POCI-01-0247-FEDER-007678], a co-promotion between Bosch Termotecnologia S.A. and the University of Aveiro. It is financed by Portugal 2020 under the Competitiveness an Internationalization Operational Program, and by the European Regional Development Fund. Márcia C. Neves acknowledges FCT, I.P. for the research contract CEECIND/00383/2017 under the

CEEC Individual 2017; Sandra C. Bernardo acknowledges FCT for the research contract under the project POCI-01-0145-FEDER-029496; and Ana P. Tavares acknowledges the FCT Investigator Programme and Exploratory Project (IF/01634/2015) with financing from the European Social Fund and the Human Potential Operational Programme.

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