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Chapter

Silica Based Mesoporous Materials as Sorbents for Solid-Phase Extraction of Organic Pollutants in Water

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Abstract

Since the first applications of solids with adsorbent properties in water treatment, Solid-Phase Extraction (SPE) has been the most suitable sample preparation technique for the determination of organic pollutants in water. In the last decades, numerous articles have appeared in the literature describing a wide variety of SPE sorbents. Attention in this field has focused on the search for new SPE materials capable of extracting a wide variety of pollutants from water. However, each sorbent has advantages for certain compounds, but not when it is used with others. Thus, conventional sorbents showed poor performance for most high polarity analytes. Recently, mesoporous materials are attracting increasing interest in sample preparation due to their desirable characteristics. They present unique advantages as highly ordered and size-controlled mesoporous structures, high surface areas and large pore volumes, good performance in thermal and chemical stability, compositional controllability and flexibility for functionalization.

Keywords: solid-phase extraction, mesoporous materials, organic pollutants, water, mesoporous functionalized silica-based mesoporous

1. Introduction

The rate of growth of the world's population [1] has led to an increase in demand for products and, consequently, to an increase in the production of chemicals in the framework of sustainable development of industry, agriculture and the welfare state. Thus, the pursuit of short-term high productivity over ecological sustainability has led to high environmental pollution. Unfortunately, water and pollution are two words that are closely related, mainly due to human activity. The main sources of water pollution [2] are agricultural, industrial and domestic and hospital wastewater discharges (**Figure 1**). As a result, water quality and quantity have deteriorated, affecting not only the aquatic ecosystem, but also the availability of drinking water for human consumption.

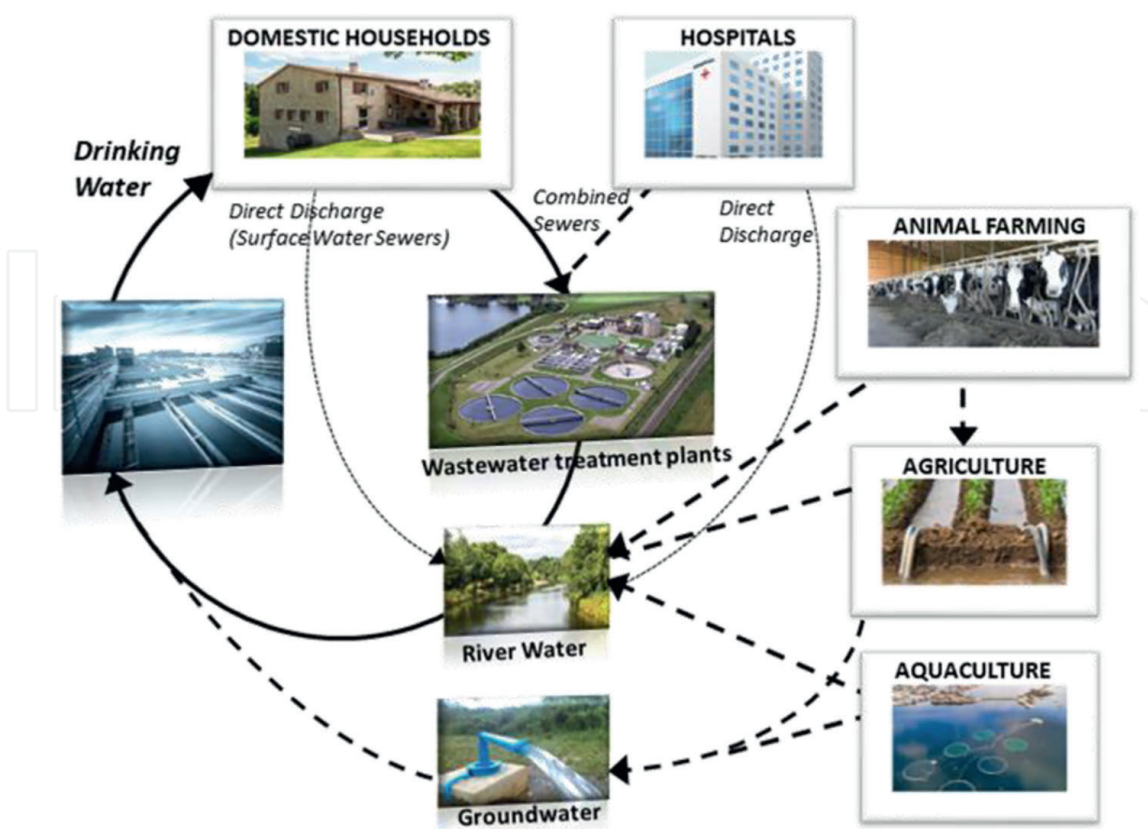


Figure 1.
Sources and pathways of PPCPs in the urban water cycle [3].

The occurrence of pesticides [2, 4] and fertilizers [5–7] in environmental waters is mainly due to their use in agriculture. According to FAO, the agricultural land has more than doubled in recent decades, which has increased the use of pesticides and eventually affected ground/underground water quality.

Currently, more than 1200 pesticides are used worldwide, posing a potential risk to human health and the environment [4]. Most of them are highly persistent and have been associated with mutagenic, teratogenic and carcinogenic effects [8]. International organizations have established strict standards for the control of “priority” contaminants in waters such as pesticides, metals, Polycyclic Aromatic Hydrocarbons (PAHs) and organochlorine compounds among other organic substances.

In recent years, research on pollutants has focused on a new generation of organic compounds, called “Emerging Contaminants” (CECs), which include pharmaceuticals and Personal Care Products (PCPs), among others. CECs are not commonly monitored in the environment but have the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effect at very low environmental concentrations [9]. CECs have been applied for years, but only recently have been found in domestic and hospital wastewater, in surface and groundwater and even in drinking water [10].

For this reason, the priority objectives are to control water pollution by conventional “priority” (pesticides and metals) and “emerging” (pharmaceuticals and personal hygiene products) contaminants in environmental water. Some of these anthropogenic organic chemical pollutants are highly persistent in the environment and, therefore, they are called Persistent Organic Pollutants (POPs).

To control water quality, the European Union (EU) has implemented controls on specific substances through a series of directives and regulatory laws. The first directive (Directive 75/440/EEC) on the quality of surface water intended for human consumption was adopted in 1975 [11], establishing a list of physical, chemical and microbiological parameters that are characteristics of drinking water. In 1998, EU Directive 98/83/EC [12] set the legal framework to protect human health from the adverse effects of any contamination of water intended for human consumption by ensuring that it is wholesome and clean. At the beginning of the twenty-first century, the EU adopted the Water Framework Directive (WFD) 2000/60/EC [13], which aims to improve, protect and prevent further deterioration of water quality by controlling 33 priority substances in surface waters, and the list of contaminants is updated with new hazardous priority substances, every 2 years. In this sense, the Stockholm Convention recognizes that POPs possess toxic properties, resist degradation, bioaccumulate and are transported, through air, water and migratory species, across international boundaries and deposited far from their site of release, where they accumulate in terrestrial and aquatic ecosystems, establishing the need to drastically reduce or eliminate the release of these pollutants into the environment [14].

Furthermore, Directive 2015/1787/EC recommended the monitoring study of three CECs (diclofenac and two hormones) and, furthermore, other CECs were considered [15] in a watch list (WL). In 2018, Directive 2018/8402/EU concluded that the substances diclofenac, oxadiazon, 2,6-di-tert-butyl-4-methylphenol, triallate and 2-ethylhexyl-4-methoxycinnamate should be removed from the WL, while the insecticide metaflumizone and the antibiotics amoxicillin and ciprofloxacin were identified as suitable candidates and then included [16]. Currently, in the last directive approved by the EU (Directive 2020/2184/EC) the third WL has been established [17].

2. Occurrence of organic pollutants in water

In the last years, some reviews have focused on the study of the presence of organic pollutants in water such as pesticides [10, 18–20] and pharmaceuticals, personal care products (PCPs) and Endocrine Disrupting Compounds (EDCs) [20]. River and groundwater are the main sources for human consumption, hence in recent years there has been an increase in the number of articles to detect the presence of organic pollutants in them although the number of studies on surface water is particularly predominant compared to groundwater. For this reason, this section focuses mainly on the presence of pesticides in surface water.

The pesticide pollution of surface waters has been extensively investigated. Thus, RM de Souza et al. [18] have reviewed the literature published in the period 2012–2019 related to the occurrence of pesticides in surface water, with the USA, China and Spain being the countries with the largest number of studies. Atrazine and its metabolites, metalochlor, chlorpyrifos, tebuconazole, diuron, dimethoate and carbendazim were the most detected pesticides in surface water. The highest concentrations were found for dimethoate (61,000 ng/L) and diuron (22,770 ng/L) in Guanacaste (Cosa Rica) and for metalochlor (10,500 ng/L) and diazinon (9000 ng/L) in Georgia (USA). **Table 1** summarizes the surface waters with the highest concentrations of pesticides.

In the same sense, E. Pereira de Araujo et al. [19] have reviewed articles investigating the presence of pesticides in surface waters. A total of 46 articles published between 1976 and 2021 were included of which 127 studies used grab sampling, 10

Country	Site	Pesticide	Concentration (ng/L)	Ref.
Costa Rica	Guacanaste	Dimethoathe	61,200	[21]
		Diuron	22,700	
		Terbutryin	4760	
		Carbendazim	2239	
USA	Tifton	Metolachlor	10,500	[22]
		Metalaxyl	5760	
		Alachlor	1400	
Bangladesh	Jamalpur	Diazinon	9000	[23]
		Chlorpyrifos	3100	
		Malathion	1800	
India	Ganga	Heptachlor	2138	[24]
China	Yangtze	Imidacloprid	1887	[25]
		Atrazina	1726	
Canada	Ontario	2,4-D	1678	[26]
Portugal	Alqueva	Bentazone	1769	[27]

Table 1.
Sites in the world with the highest levels of pesticides in surface waters.

passive sampling and 9 both sampling techniques, the most detected pesticides were atrazine (43%), simazine (29%), metolachlor (28%) and imidacloprid (28%) using grab sampling and for passive sampling (68%), simazine (42%), chlorpyrifos (42%), p,p'-DDDD (42%) and p,p'-DDE (42%) were the most detected.

In the last decade, the concern of researchers has focused on the study of other pollutants in water, mainly pharmaceuticals and personal care products due to their high consumption. Wastewater from sources like hospitals and households often contains a significant amount of pharmaceutical and personal care products (PPCP) and they are not entirely degraded in the wastewater treatment plants (WWTPs) and, therefore, they enter into the aquatic environment (particularly surface water).

Recently, a review of the occurrence of Emerging Organic Contaminants (EOCs) in drinking water has been published [20], including studies of the presence of pesticides, pharmaceuticals, personal care products and other organic contaminants in surface and groundwater. Several antihypertensives, analgesics, antibiotics, psychoactives, among other pharmaceuticals, have been detected in natural waters around the world, with carbamazepine being the most frequently detected antibiotic in surface waters, with the highest concentrations recorded in Germany (11,581 ng/L). Detailed information on the number of ECOs detected and their concentrations can be consulted in this review [20].

In order to assess the ultra-trace levels of organic contaminants in drinking water set by EU Directives, reliable and relevant data are needed and, for this purpose, rapid, sensitive and selective analytical methods need to be developed. In this respect, chromatographic techniques coupled to mass spectrometry have enabled the detection of a large number of organic contaminants in water [28–30]. Generally, this methodology involves a pre-concentration stage of the sample in order to detect the

target analytes at the required ultra-trace levels, with solid-phase extraction (SPE) being the most widely used pre-concentration technique for the analysis of organic pollutants in water.

3. Solid-phase extraction for organic pollutants in water

SPE is a sample treatment technique used to isolate and pre-concentrate analytes from a flowing sample stream of gas, fluid or liquid by transferring and retaining them onto a disposable solid-phase cartridge (disk, membrane, etc.), followed by the elution of the analytes with a suitable solvent [31, 32].

The first SPE work was carried out 70 years ago [33] using an iron cylinder filled with 1200–1500 g of Granular Activated Carbon (GAC) for the concentration of organic compounds from surface water by a group in the US Public Health Service [34]. After a volume of surface water pass through, GAC filter was removed, air-dried and the retained compounds were extracted with diethyl ether in a Soxhlet extractor. Next, the organic residue obtained was separated into five groups according to a modification of a method previously published by Shriner and Fuson [35]. A qualitative test for the elements nitrogen, sulfur and chlorine was made for each fraction. Since this pioneering work, thousands of articles applying SPE methodology with different solid sorbents have been published. In this sense, SPE has become the most suitable sample preparation technique in the analysis of organic contaminants in water [31].

The SPE technique can be performed by offline or online procedures. In recent years, advances in the automation of the sample SPE treatment have provided significant advantages over offline SPE, including fast analysis, reducing solvent consumption and avoiding human errors that they entail analyst chemical exposure [36]. Currently, the main limitation of online SPE methodology is the availability of commercial sorbent devices. Therefore, most of the published literature refers to the development of offline SPE methods in which a wide variety of sorbents in commercial formats can be purchased or it can be hand-made in the laboratory.

3.1 Solid-phase extraction steps

The most commonly used SPE device (**Figure 2a**) for off line pre-concentration of pollutants in water is a polypropylene syringe (1–25 mL volume capacity) that contains an amount of solid sorbent (50–200 mg or more) between two polypropylene frits, ensuring material compaction and preventing any loss of solid material during the SPE procedure.

Regardless of the SPE device used for pre-concentration and the type of methodology (offline or online), SPE procedures include the following four basic steps (**Figure 2b**):

1. *Sorbent conditioning.* Generally, a volume (2 to 4 times the sorbent volume) of suitable solvent or solvents mixture is passed through the cartridge to wet the SPE sorbent and to activate their functional groups. Usually, methanol is used as conditioning solvent for hydrophobic sorbents, and next, a similar volume of ultrapure water is passed through the cartridge to remove methanol [37]. In this step, care must be taken that the sorbent does not dry, as the retention capacity of the sorbent decreases and the analytes are poorly retained. Moreover, it has

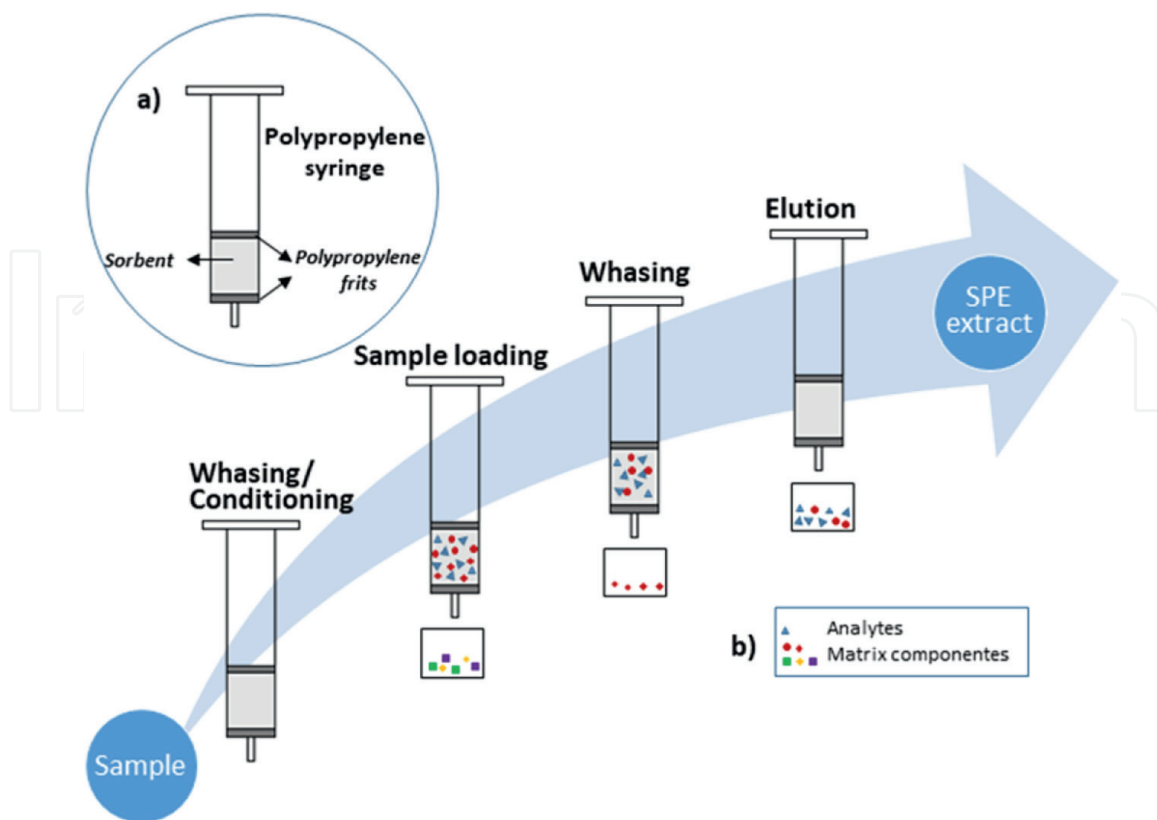


Figure 2.
(a) Components of a SPE syringe and (b) SPE operational steps.

been observed that this fact makes difficult the next step of the sample passing. Therefore, if the sorbent dries it must be reconditioned again. In some cases, the solid sorbent is washed with water or elution solvent before the conditioning step to remove impurities.

2. *Sample loading into the cartridge.* Usually, a volume of sample is passed through the cartridge using a semi-automated extraction manifold connected to a vacuum pump or using an automatic SPE extractor coupled on line with the chromatographic system [38].

To avoid losses of poorly retained analytes during the pre-concentration process, the sample volume to be pre-concentrated is a crucial parameter that must be optimized according to the retention capacity of the sorbent selected and the amount sorbent packed in the cartridge in order to avoid losses of poorly retained analytes (breakthrough volume). In addition, the sample flow rate selected should be low enough to allow efficient retention of the analytes, and high enough to avoid excessive duration of this step [37], with a range of 5 to 10 mL/min for pre-concentration of contaminants in water samples. In this step, both target analytes and some matrix compounds are retained on the sorbent, while other matrix interferences are eluted, allowing a partial purification of the sample.

3. *Sorbent washing.* To reduce Matrix Effect (ME) the sorbent can be washed (optional step) with a suitable solvent to remove most of the matrix components from the sorbent without loss of the target analytes [38, 39]. Normally, the sorbent is washed with a small volume of ultrapure water after the sample loading

step to remove the residual water sample remaining in the sorbent [40–43]. In order to reduce matrix effects, the washing solvent can contain a small percentage of organic solvent to remove matrix components [42, 44]. For aqueous matrices, the sorbent is then dried with air and/or N₂ stream to remove the washing aqueous solvent, which, in some cases, may hinder the subsequent concentration of the final extract [37].

4. *Elution of the analytes from the sorbent.* To quantify the target analytes in the chromatographic system, the analytes are eluted from the sorbent with a suitable solvent or several solvents, without eluting matrix interferences. In offline SPE procedures, the elution solvent is added to the cartridge and passed through by applying pressure. It is recommended to fractionate the solvent volume into several aliquots and allow it to soak the solid sorbent before elution [37].

To ensure their complete elution from the cartridge, the selection of the elution solvent depends on the nature of the analytes and the interactions between analytes and sorbent. For example, a polar solvent such as methanol, acetonitrile or ethyl acetate allows the elution of highly polar analytes while the best solvent for the elution of less polar analytes is hexane.

Figure 3 shows the experimental data obtained for the selection of the elution solvent for the SPE pre-concentration of 218 multiclass pesticides in water [45]. It can be observed that the most polar pesticides (pK_{ow} <4) were completely eluted with acetonitrile, whereas for the less polar pesticides (pK_{ow} >4) hexane was the best elution solvent.

Another parameter to take into account is the elution volume, which must be sufficient to completely elute the analytes, so elution volumes between 1 and 10 mL are usually applied for organic contaminants in water. Thus, larger volumes are not recommended to avoid dilution of the analytes for online SPE of direct injection into the chromatographic system and for offline SPE the solvent should be removed to dryness with a stream of nitrogen for subsequent redissolution in the injection solvent. Moreover, the elution flow rate of the solvent must be correctly adjusted to ensure interaction between the solvent and analytes and, therefore, their efficient elution.

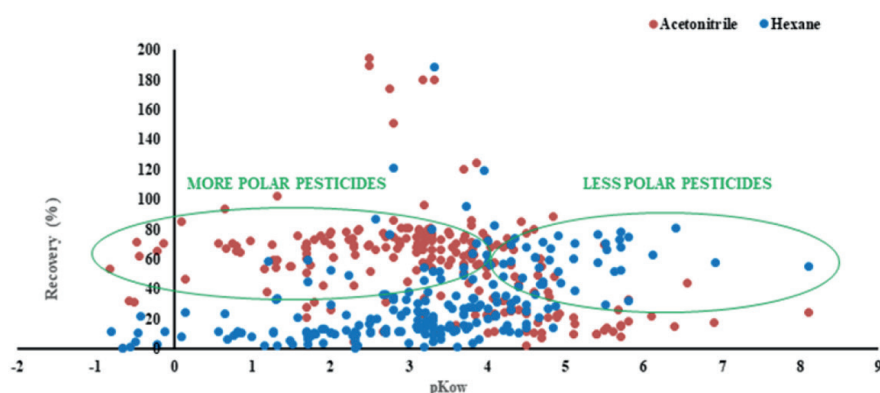


Figure 3. Relationship between the recoveries and the polarity of pesticides using acetonitrile and hexane solvents for elution [45].

3.2 Solid-phase extraction optimization

Water pollution encompasses multiclass analytes with different chemical properties, including solubility, polarity and acid-basic characteristics. The main goal for the researchers is to develop a simple, efficient and fast method, which requires small amounts of chemicals as SPE sorbent and organic solvents, according to the requirements of green chemistry. In addition, the analytical method can achieve the pre-concentration of a large number of analytes with one sorbent in a short treatment time.

Usually, the development of a SPE procedure for the pre-concentration of analytes in water samples requires the study of the effect of several parameters on the retention/elution of these analytes on the SPE sorbent. Optimization of these parameters can be performed using step-by-step and/or multifactorial experimental design methodologies, being the last approach particularly useful for the pre-concentration of multiclass analytes [45–48]. In general, step-by-step optimization approach is employed to determine the optimal conditions for independent parameters (e.g. sample pH, elution solvent and salt content). On the other hand, for variables that are interdependent (sorbent amount, sample volume and solvent elution volume), experimental design is the best option [45, 48].

The main parameters affecting the effectiveness of a SPE procedure are described:

1. *Elution solvent.* The selection of the solvent for elution of the retained analytes on the SPE sorbent is the first parameter to be optimized. There are two options, a small volume of ultrapure water spiked with the analytes is passed through the cartridge and then the retained analytes are eluted with the organic solvent [49] or a small volume of the organic solvent for elution spiked with the analytes is passed through the cartridge [32].
2. *Sample pH, salinity and matrix components.* The pH of the sample is one of the most important parameters that need to be adjusted to achieve efficient retention of the analytes on the SPE sorbent. Its influence depends on the nature of both the solid sorbent and the analytes, mainly for those containing acidic and basic functional groups in their structures. The pH of the sample defines the molecular state of the target compounds (ionic or neutral state) and therefore, their adsorption onto the SPE sorbent. Hao et al. [50] founded a greater extraction of acidic drugs using Oasis HLB when the water sample was adjusted to a pH value of 2, prior to extraction (recoveries higher than 100%). However, under basic and neutral pH conditions the SPE extraction still provided some degree of selectivity for acidic compounds and better recoveries were obtained for all analytes (near 100%). For that, the pH of the water sample was adjusted to pH 7 in agreement with similar studies [44, 51].

In a recent study [49] using Multi-Walled Carbon Nanotubes (MWCNTs) as SPE sorbent for the pre-concentration of drugs with acid-base properties in river and wastewater, it was found that the pH of the sample affected the recovery and the best recoveries for most analytes were obtained at a pH value of 8 (**Figure 4**). In other similar work [52] we also used MWCNTs as SPE sorbent for the pre-concentration of pesticides in surface water, and similar recoveries were obtained in the pH range 3 to 7, except for methomyl which showed better recoveries at pH 5. Therefore, pH 5 was selected as the optimum pH to adjust the water sample.

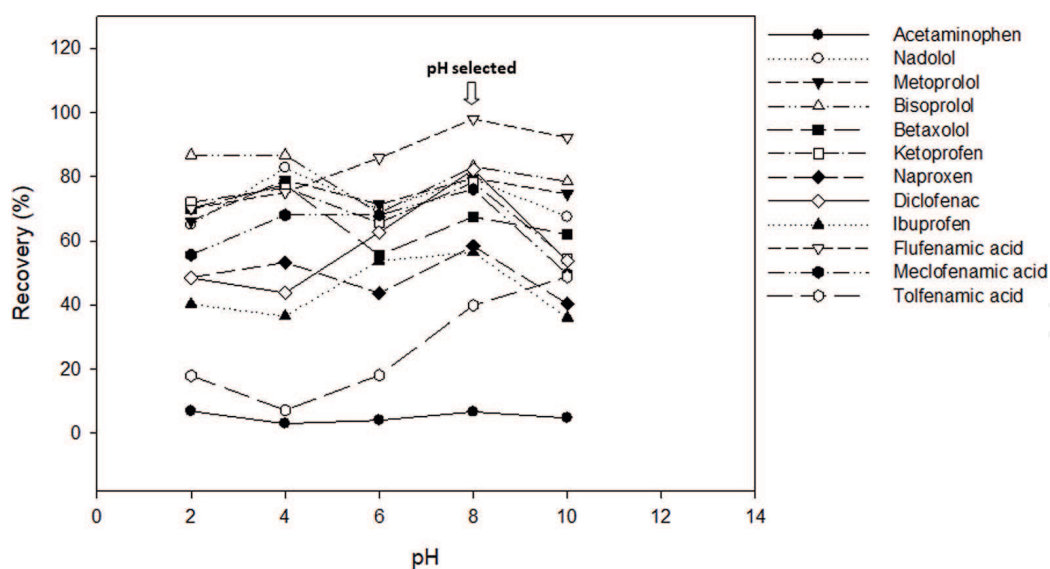


Figure 4. Influence of the sample pH on the retention of the pharmaceuticals in the MWCNT sorbent [49].

On the other hand, environmental waters contain different amounts of salts depending on their origin. In this sense, the salt content can modify the retention of the target analytes in the SPE sorbent and it can also affect its analytical signal (matrix effect). Generally, the water solubility of hydrophobic organic compounds decreases with increasing salt concentration, which is likely to increase their retention on the SPE sorbent [53]. This effect is called “salting out” and it can be explained by the engagement of water molecules in the hydration spheres around the ionic salt and hence in the reduction of the water concentration available to dissolve the analytes [52, 54].

For this reason, the effect of salt content should be assessed using water samples with different amounts of salt, NaCl and KCl being the most commonly used for this purpose. Zhang and Zhou [53] studied the effect of salinity on the retention of 11 pharmaceuticals in environmental water using several conventional SPE sorbents and they found that the recovery enhanced for six of them with increasing salt content in the water. However, the presence of salt can also negatively affect the recovery of some analytes, and therefore, strategies to reduce or compensate for this effect are required, such as the standard addition calibration [45]. On the other hand, addition of Na_2EDTA to water samples is recommended to improve extraction efficiency of the analytes, e.g. for the SPE extraction of pharmaceuticals [55, 56], because the analytes can interact with metals present in natural water and/or glass containers. Thus, soluble metals bind to the chelating agent, increasing the extraction efficiency of these pollutants.

3. *Sample volume (breakthrough volume), sorbent amount and elution volume.* In general, environmental waters (tap water, surface water and groundwater) may contain organic contaminants at concentrations below the detection limits achievable with current analytical instruments. Therefore, a trace enrichment step (SPE) is necessary prior to instrumental analysis. Thus, the amount of water needed for this task depends on the instrumental sensibility of the analytical technique and the legal requirements for the target compounds (e.g. the maximum residue level for one pesticide in ground water by EU Directive is $0.1 \mu\text{L}$),

the recommended water volume being between 100 mL and 1 L. Therefore, one of the most important parameters that requires optimization for the pre-concentration of organic contaminants in water is the sample volume that can be passed through the SPE sorbent, known as the *breakthrough* volume.

The *breakthrough* volume represents the maximum sample volume, which can be pre-concentrated with a theoretical 100% recovery of the analytes. This means that no loss of analytes by elution occurs during the loading step.

The estimation of breakthrough can be achieved using different approaches [38]:

1. The water sample spiked with the analytes is continuously passed through the sorbent and the analyte signals in the water at the outlet of the SPE cartridge are monitored. This approach is particularly convenient for online SPE-LC procedure [57].
2. Different volumes of water sample spiked with the same amount of analytes are pre-concentrated and their concentration in the SPE extracts is analyzed after elution.
3. Various sample volumes spiked with different amounts of analytes are pre-concentrated and the analytes are determined in the SPE extracts, and finally curves representing peak areas versus sample volume are constructed.

Although the experimental determination of the breakthrough volume is time-consuming, it is necessary to optimize it, especially for the analysis of organic contaminants in environmental water requiring large sample volumes to achieve adequate sensitivity. However, losses of highly polar pesticides and pharmaceuticals have been observed with increasing sample volume resulting in very low recoveries [58, 59].

One strategy to avoid the elution of highly polar analytes when using the required sample water volumes is to increase the amount of sorbent [39, 59]. However, increasing the amount of sorbent can have drawbacks such as large volumes of organic solvent being required for the elution of less polar analytes that are strongly retained on the sorbent.

In the light of these evidences, the three parameters (sorbent amount, sample volume and elution volume) are related and experimental design is the best option for their optimization. Recently, we have applied step-by-step (elution solvent, sample pH and salt content) and multi-response surface (sorbent amount, water volume and elution volume) methodologies to optimize a SPE method for the pre-concentration of 218 multiclass pesticides in environmental waters [45]. The statistical significance of the three SPE variables was evaluated by ANOVA test. According to the obtained results, it can be concluded that the most polar pesticides were more retained as the amount of sorbent increased, but eluted during the pre-concentration step if the sample volume was larger. In contrast, the most significant factor affecting negatively the recovery of less polar pesticides was the amount of sorbent because they are strongly retained, making the subsequent elution step more difficult and larger volumes of elution solvent are needed.

Once the parameters described above have been optimized, if the recoveries or sensibilities are not satisfactory for some of them, the most appropriate alternative is to change the SPE sorbent and replace it with another one that has a higher affinity and more selective for these analytes.

In this sense, one of the main advantages of offline SPE is the wide variety of commercially available SPE sorbents and devices that are recommended for the pre-concentration of organic contaminants in water (C18, Oasis HLB, Oasis MAX, among others). In addition, there are both commercially available (Oasis HLB, Oasis MCX,..) and new synthesized sorbents (MCM-41) that can be packed in different SPE devices in the laboratory and they can be used for this purpose. A variety of literature has been published about the types of sorbents and devices used for SPE, including conventional and new sorbents [37, 60].

This chapter focuses on the recent application of silica-based mesoporous materials as sorbents for the pre-concentration of organic pollutants in water.

4. Silica-based mesoporous materials as sorbents for SPE of organic pollutants in water

The development of new mesoporous materials with large surface area is a field of extensive research, particularly with a view to potential applications in sectors such as adsorption of inorganic and organic pollutants, separation, catalysis, sensors and gas storage [61–66].

In the late of 1980s, a team of researchers of the Mobil Research and Development Corporation [67] discovered a family of nanostructured mesoporous materials known as M41S by hydrothermal reactions of aluminosilicate gels in the presence of quaternary ammonium surfactants as template, MCM-41 with hexagonal form being the most widely studied [68]. Other mesoporous silica materials of the MS41 family are MCM-48 with cubic form and MCM-50 with lamellar form [65, 68–70]. The discovery of the M41S family attracted the interest of researchers and other mesoporous silica materials were synthesized following similar procedures to the MS41 series such as SBA (University of California), MSU (Michigan State University material) and KIT (Korea Adv. Inst. of Science and Technology).

There are two kinds of templates to obtain mesoporous materials: (1) supramolecular aggregates such as surfactant micelle assemblies (soft-templating route) and (2) preformed rigid mesoporous solids such as ordered mesoporous silica, carbon and colloidal crystal (hard-templating route) [71]. Generally, mesoporous silica materials are prepared using soft-templating strategies [65] under hydrothermal conditions using basic or acidic media (sol-gel process).

The sol-gel process for the syntheses of mesoporous silica materials consists of the following steps [72]:

1. The surfactant is dissolved in an aqueous medium, resulting in the formation of the template via self-assembly also named Cooperative Template (CTM) or via “True” Liquid Crystal Template (TLCT) mechanisms.
2. The silica precursor is added to the surfactant solution, which is hydrolyzed under acidic or basic conditions, resulting in the formation of a silicate oligomer.
3. The oligomers are then condensed with the surfactant micelles by cooperative assembly and aggregated to form an inorganic-organic hybrid, which finally precipitates as a gel.
4. The gel is hydrothermally treated over a period of time.

- The product obtained is cooled, filtered, washed and dried and, finally, the surfactant is removed by calcination or solvent extraction, resulting in a solid powder with an array of regular pores.

Figure 5 shows schematically the different steps of the MCM-41 synthesis procedure published by Grün et al. [73].

The morphological characteristics of mesoporous silica-based materials are influenced by different factors, such as the type of surfactant, silica source, concentration of both reagents, and synthesis conditions (medium pH, reaction time, temperature, among them) [66, 72].

Three kinds of surfactants can be used to obtain the template: cationic surfactants (hexadecyltrimethylammonium bromide, CTAB); anionic surfactants (sodium dodecyl sulphate, SDS) and non-ionic surfactants (Pluronic P123) and TEOS (tetraethyl orthosilicate), TMOS (tetramethyl orthosilicate) or inorganic sodium silicate are frequently used as silica sources.

Most mesoporous silica materials were developed in laboratory using six different synthesis pathways depending on the nature of the surfactant, the pH and the temperature [74] (**Table 2**). These mesoporous materials possess fascinating properties including regular, uniform and interpenetrating mesopores, tunable pore sizes and good chemical stability and biocompatibility. In addition, the properties of mesoporous materials can be easily modified by incorporation of different elements or organic groups to these silica structures, in order to improve their selectivity. For that, the number of published articles applying silica-based mesoporous materials as SPE sorbents for the pre-concentration of organic pollutants has increased in the recent years [71].

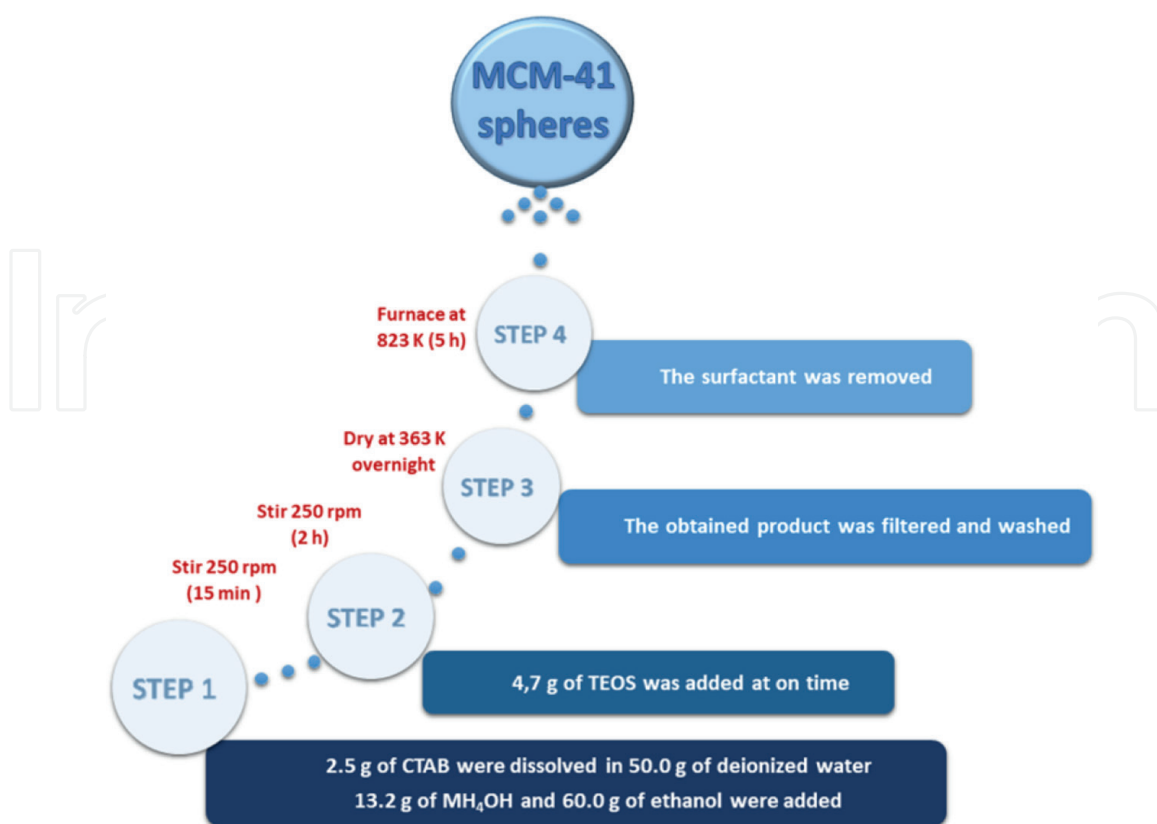


Figure 5.
Synthesis procedure of MCM-41.

Surfactant type	Interaction pathway	Interaction type	Examples
Cationic S ⁺	Electrostatic interaction	S ⁺ I ⁻	Tungsten oxide, MCM41
		S ⁺ X ⁻ I ⁺	Lamellar zinc phosphate, cubic Pm3n
Anionic S ⁻	Electrostatic interaction	S ⁻ I ⁺	Lamellar iron oxide
		S ⁻ M ⁺ I	Lamellar aluminum oxide, zinc oxide
Neutral S ⁰ /N ⁰	H-bonding interaction	S ⁰ I ⁰	Hexagonal silica HMS
		N ⁰ I ⁰	MSU-X

S is the surfactant, I is the precursor, X and M are the intermediate species (anion and cation), S⁰ is a neutral amine, I⁰ is a hydrated inorganic oligomer and N⁰ is the non-ionic template.

Table 2.
 Types of interactions between the surfactants and the inorganic precursor.

Mesoporous materials present unique advantages for the adsorption of both small and large molecules because they can interact with them not only at the external surface, but also throughout the whole internal pore system [67]. These materials have special characteristics such as: (1) mesoporous structures with controlled pore sizes (2–50 nm) and highly ordered pores, which allow size-selective extraction of molecules, retaining small molecules and excluding larger ones, (2) extremely large surface areas, (3) a high degree of stability and (4) they can be easily functionalized with organic groups or imprinted molecular polymers. Therefore, the number of published articles applying silica-based mesoporous materials as SPE sorbents for the pre-concentration of organic contaminants in environmental samples has increased considerably in recent years [71].

In the last decades, the main applications of silica-based mesoporous materials in the sample treatment of inorganic and organic pollutants in different matrices have been summarized in different reviews [71, 75–77].

This chapter focuses on the optimization and validation of analytical methods for the pre-concentration of organic pollutants in water by SPE using different silica-based mesoporous materials as SPE sorbents.

4.1 Application of pure silica-based mesoporous materials as SPE sorbents in water

Due to the high capacity of adsorption of mesoporous materials, MCM-41 and SB-15 were firstly used to remove organic pollutants from environmental water [78–80] and air [81], while the first application as SPE sorbents (SBA-15) occurred in 2015 for the enrichment of flavanones from citrus fruits [82]. The results obtained demonstrated the potential of these mesoporous materials to be used as sorbents in SPE.

Table 3 shows some of the applications of pure silica-based mesoporous materials as sorbent for the SPE of organic pollutants in water.

In 2016, Dahane et al. [58] published the first application of MCM-41 as a SPE sorbent to pre-concentrate pharmaceuticals of very different polarity (atenolol, nadolol, pindolol, timolol, bisoprolol, metoprolol, betaxolol, ketoprofen, naproxen, ibuprofen, diclofenac, tolfenamic acid, flufenamic acid and meclofenamic acid) in surface water, obtaining recoveries close to 100% for all analytes. The MCM-41 was synthesized in the laboratory and 100 mg of this sorbent were hand-packed in 3 mL syringe bodies of polypropylene, obtaining the SPE cartridge. The optimization of

SPE sorbent	Analytes	Analytical method	Amount (mg)	Samples	Ref.
MCM-41	Drugs	UPLC-MS/MS	100	Surface water	[58]
	Pesticides	UPLC-MS/MS	100	Surface water	[59]
MSU-1	Pesticides	UPLC-MS/MS	50	Surface and Groundwater	[39]
	Pesticides	UPLC-MS/MS	100	Groundwater	[45]
TiUVM-7	OPPs	GC-MS	75	Irrigation and WWTP water	[83]
	FRs	GC-MS	200	Irrigation and WWTP water	[84]
Au/TiUVM-7	OPPs	GC-ECD	300	Environmental water	[85]
MTMOS-TEOS	OPPs	GC-MS	100	Tap, drinking and river water	[86]

Table 3.
Application of mesoporous silica-based as SPE sorbents in water.

the experimental conditions of both retention and elution of the target analytes into the MCM-41 cartridge was performed. The proposed method was validated and applied to determination of drugs in surface waters, atenolol, timolol, betaxolol, nadolol and diclofenac being found in some of them, at levels higher than their LOQs (4.5–10 ng/L). Subsequently, the same authors [59] investigated the use of MCM-41 sorbent for the pre-concentration of eight different polar pesticides (organophosphates, carbamates and triazoles) in water samples. The precision study showed that most pesticides pre-concentrate satisfactorily in MCM-41, with recoveries between 65 and 126%, except methomyl (the most polar) with recoveries <30%, demonstrating the usefulness of MCM-41 as a SPE sorbent for low and intermediate polarity pesticides, but it is not suitable for the pre-concentration of high polarity pesticides.

To overcome the low adsorption capacity of MCM-41 for highly polar compounds, Karbouche et al. [39] synthesized a silica-based MSU-1 mesoporous solid for the pre-concentration of 13 pesticides in water, including methomyl. The optimized SPE methodology was validated in river water and satisfactory recoveries were obtained for all pesticides at LOQ levels (70.1–113.5%). Recently, increasing the amount of sorbent MSU-1 (100 mg) enabled the pre-concentration of 218 multiclass pesticides in water [45]. The effect of the matrix compounds in the analyte signals and the low adsorption of some pesticides in the MSU-1 were corrected using standard addition methodology by adding pesticide standards before SPE-pre-concentration. A monitoring study of groundwater samples was performed applying the proposed methodology and 38 different pesticides were found but most of them in concentrations below 0.1 µg/L, with imidacloprid, hexaflumuron and oxadixyl being the most frequently detected. However, in five groundwater samples, high level of methiocarb (three samples), pyrethrin I and pyrethrin II (one sample) and hezaflumuron (one sample) were found.

Researchers at the University of Valencia [87] developed a nanoparticulate bimodal silica material (UVM-7) to extract phospholipids from human milk. This mesoporous material exhibited selective extraction of target analytes and restricted access for biomacromolecules. Next, UVM-7 was doped with titanium (Ti) to pre-concentrate Organophosphorus Pesticides (OPPs) [83] and Organophosphorus Flame Retardants (FRs) [84] in water samples. The matrix compounds of the WWTPs samples affected negatively the recoveries obtained for OPPs and FRs, in the range 48–87% and 65–78%, respectively. Both analytical methods were applied to the

determination of the target analytes in irrigation water and in effluent and influent WWTP water, with only three FRs found in concentrations in the range of 0.2–1.5 ng/mL in three water samples of the WWTPs. Recently, TiUVM-7 mesoporous silica material doped with gold (Au) nanoparticles was tested to improve OPP recoveries in real water samples [85]. The TiUVM-7 modified with Au was proved to increase the retention of the OPPs pesticides, with analytical parameters comparable to or even better than other alternative sorbents (C18). In addition, the authors argue that this new sorbent (Au/TiUVM-7) is cheap and environmentally friendly.

In the same way, Ibrahim et al. [86] synthesized a new mesoporous organic-inorganic material based on Methyltrimethoxysilane-Tetraethoxysilane (MTMOS-TEOS) and 100 mg of this sorbent were used for the pre-concentration of 5 OPPs using only 10 mL of sample (water and fruit samples). The incorporation of MTMOS helped to increase the hydrophobic character of the material and promoted the interaction between the pesticides and the sorbent. LOQs ranged from 1 to 3 pg/L, which were 500–600 times lower than those obtained using commercial C18. The reuse of the mesoporous sorbent was reported for the pre-concentration of at least 25 samples by washing the cartridge with 5 mL MeOH followed by 10 mL ultrapure water after each extraction.

4.2 Application of functionalized silica-based mesoporous materials as SPE sorbents in water

The functionalization of mesoporous materials with organic functional groups (-OH, -CH₂-, -COOH, -NH₂, -CN, -SH, -SO₃H) by inserting them into the channel walls is another approach to increase extraction, mainly for the most polar analytes. Thus, SBA-15 functionalized with different organic groups has been one of the most widely used for the pre-concentration of inorganic and organic species in various matrices such as water.

Table 4 summarizes some application for the pre-concentration of organic pollutants in water using functionalized mesoporous silica-based SPE sorbents.

Gañán et al. [88] synthesized two ordered mesoporous silicas with different morphology and structure and they were modified with octadecyl (C18) groups to obtain SBA-15-C18 and SM-C18 materials. The functionalized and non-functionalized silicas (200 mg) were studied as sorbents for pre-concentration of 17 β -estradiol in drinking water, and SBA-15-C18 was found to have the highest adsorption capacity against the extremely hydrophobic target analyte, which was attributed to its very high degree of functionalization. Moreover, these authors applied SBA-15-C18 sorbent for the pre-concentration of 12 EDCs [89] and four β -blockers [90, 91] in several environmental water matrices. Recoveries were obtained between 70 and 112% and between 58 and 105% for EDCs and β -blockers in real samples, respectively. To improve the recoveries obtained for EDCs, a bi-functionalized SBA-15 with octadecyl and amino groups (SBA-15-C18-NH₂) sorbent was prepared [92] and the recoveries were compared with those obtained using C18-functionalized amorphous silica sorbent (ExtraBondR). Recoveries close to 100% were obtained for all analytes with this new bi-functionalized SBA-15, except for estriol and prednisolone (66 and 82%, respectively), being in all cases better than those obtained with ExtraBond C18. The bi-functionalized SBA-15 provided mixed retention mechanisms for the analytes: reversed-phase sorption by hydrophobic interactions to the C18 and hydrogen bonding through the NH₂, being suitable for the extraction of a wide variety of moderately polar to non-polar EDCs.

SPE sorbent	Analytes	Analytical method	Amount (mg)	Samples	Ref.
SBA-15-C18	β -estradiol	HPLC-UV	200	Drinking water	[88]
	EDCs	HPLC-UV	100	Environmental water	[89]
	β -blockers	CE	100	Environmental water	[90]
	β -blockers	CE	200	River and wastewater	[91]
SBA-15-C18-NH ₂	EDCs	HPLC-UV	100	Ultrapure water	[92]
SBA-15-multifunctionalized	NSAIDs	HPLC-UV	500	River water and wastewater	[93]
MCM-41-SO ₃ H	PCPs	UPLC-MS/MS	100	Swimming pool water and wastewater	[94]
MCM-41-CN	PCPs	UPLC-MS/MS	100	Swimming pool and river water	[95]
SBA-15-MIP	Bisphenol A	HPLC	50	Ultrapure water	[96]

Table 4.

Application of functionalized mesoporous silica-based as SPE sorbents in water.

Li et al. [93] prepared a functionalized SBA-15 with 3-[2-[2-[2-(2-(2-(2-aminoethylamino)ethylamino)ethylamino)propyl-trimethoxysilane material and after reacting with an excess of finyl glycidyl ether obtained a reversed-phase/anion exchange mixed-mode sorbent. 500 mg of the material were used for the pre-concentration of 4 Non-Steroidal Anti-Inflammatory drugs (NSAIDs) in river water and wastewater. The enrichment factors in the range 806–1109 were achieved, as well as LODs between 0.006 and 0.070 $\mu\text{g/L}$ for tap water and between 0.014 and 0.16 $\mu\text{g/L}$ for river water and wastewater and good recoveries ranging from 80.6 to 110.9% were obtained in all cases.

On the other hand, two organic-inorganic hybrid silica-based mesoporous MCM-41 functionalized with sulfonic [94] and cyanopropyl [95] groups were synthesized in the laboratory and they were tested as SPE sorbents for the pre-concentration of personal care products (PCPs) of very different polarity in environmental water. Similar recoveries were obtained for PCPs with both functionalized MCM-41 sorbents, but MCM-41-SO₃H showed better adsorption capacity for the more polar PCPs (75–100%). Four parabens and two UV filters were detected in the wastewater sample at ng/L and, in addition, the same four parabens were detected in the swimming pool water, but at lower concentrations than those found in wastewater [94]. In the case of the MCM-41-CN sorbent [95], all PCPs were found in the swimming pool water sample, whereas only methylparaben was detected in the river water.

Finally, W Cheng et al. [96] prepared silica-based Mesoporous Molecular Imprinted Polymers (M-MIP), using MCM-41 and SBA-15 mesostructures to extract bisphenol A from aqueous samples. MIP-SAB-15 maintained the mesoporous structure of SBA-15 and also exhibited excellent selectivity toward the bisphenol A, with recoveries of over 87% in fortified water samples.

4.3 Other applications of mesoporous silica-based materials

In addition to the SPE extraction of organic pollutants from water using silica-based mesoporous sorbents, these materials have been applied as sorbents in

Solid-Phase Microextraction (SPME) [97, 98], Micro-Solid-Phase Extraction (μ -SPE) [99], Dispersive Solid-Phase Extraction (DSPE) [100] and Stir-Bar Micro-Solid-Phase Extraction (SB- μ -SPE) [101].

Jiang et al. [97] have prepared a SPME fiber coated with Ordered Silica-based Mesoporous (OMS) film for the pre-concentration of chlorophenols in aqueous samples. The extraction capacity of the OMS fiber was 1.5–1.8 times higher than those of a commercial polyacrylate (PA) fiber. In addition, the selectivity of the OMS fiber for further application was evaluated using three types of organic compounds with different physico-chemical properties (non-polar compounds with benzene rings, non-polar compounds without benzene rings and polar compounds), and it was observed that the extraction efficiency of the OMS coating increased as the polarity of the compounds increased. Likewise, a fiber coated with uncalcined MCM-41 (MCM-41/CTAB) was used for SPME pre-concentration of four Polycyclic Aromatic Hydrocarbons (PAHs) in well water and surface water [98]. The durability of the MCM-41/CTAB fiber was investigated and found to maintain more than 95% of the initial efficacy over five SPME extractions. The proposed method was applied to the analysis of surface and well water and phenanthrene and anthracene were found in concentrations between 8.8 and 99 ng/L in surface water.

The μ -SPE technique using calcined and uncalcined MCM-41 sorbents was applied to the pre-concentration of Perfluorocarboxylic Acids (PFCA) in water samples [99]. The μ -SPE device consisted of a porous polypropylene membrane bag containing 5 mg of mesoporous sorbents, which did not allow the passage of some matrix components. The extraction efficiency of both mesoporous sorbents was compared with that of other conventional sorbents, obtaining the best results with the uncalcined MCM-41. The proposed method offered good sensitivity and reproducibility (recoveries between 64 and 127%) and was successfully applied to PFCA extraction in river and rainwater samples.

MCM-48 sorbents functionalized with different organic groups, including amine-functionalized MCM-48, phenyl-functionalized MCM-48, octadecyl-functionalized MCM-48 and quaternary ammonium-functionalized MCM-48 [100] were applied to extract EDCs in water by DSPE technique. The best results for the determination of EDCs in water were obtained using MCM-48 functionalized with quaternary ammonium as sorbent, with recoveries close to 95%. However, with the other synthesized materials, recoveries of around 25–30% were obtained.

Finally, 4-phenyl-1,2,3-triazole-functionalized SBA-15 sorbent was synthesized from the reaction of azide-functionalized SBA-15 with phenylacetylene [101]. The mesoporous sorbent was inserted inside a polypropylene membrane along with a tiny stir-bar and sealed with a heater. The stir-bar extraction increased the interaction between the polypropylene membrane and the water sample due to continuous stirring and rotation, thus increasing the effective surface area of the sorbent. The method was applied to the determination of phenols in wastewater. The recovery studies were performed with wastewater samples spiked at three concentration levels (1, 100 and 400 ng/mL), showing recoveries in the range of 88.5–99.2% for all selected phenols.

5. Conclusions

The synthesis of new silica-based mesoporous materials offers a new field of research in the sample treatment by their application as sorbents for inorganic and

organic pollutants in water. Silica-based mesoporous materials have demonstrated to show several advantages over conventional sorbents such as:

1. High adsorption capacity for both organic and inorganic compounds because they possess high surface areas and large pore volumes.
2. Good chemical stability, allowing its use with water samples with a wide range of pH values.
3. Selectivity to pre-concentrate a specific type of compounds, as they offer the possibility to modify their properties by functionalization with different organic groups (hydrophilic, hydrophobic, polar or charged functional moieties) or by doping with some metals depending on the nature of the analytes. But, they can also be functionalized with two different organic groups (bi-functionalized sorbents), increasing their potential use for the extraction of analytes with different nature and properties. Thus, silica-based mesoporous materials exhibit different types of interactions with target analytes, including chelation, hydrophobic, hydrophilic, hydrogen bonding and electrostatic interactions or mixed-mode mechanisms.
4. Flexibility linked to the synthesis of mesoporous materials in the laboratory allows a tailor-made design to solve specific problems in the treatment of samples.
5. Versatile to be applied in a wide variety of pre-concentration techniques such as MSPE, SPE, SPME and SBSE because the mesoporous material can be added directly to the water sample or used inside different devices such as cartridges, metallic fibers and stir-bars.
6. Easy to prepare in the laboratory and inexpensive as most synthesis procedures for mesoporous materials require both inexpensive instrumentation and reagents. Regarding the cost, the price of one Oasis HLB cartridge was 7.5 euros, whereas an MSU-1 cartridge (100 mg) cost 1.5 euros, including the polypropylene syringe and frits.
7. Reuse of the sorbent for several samples (recycling), which is in line with the Circular Economy, and also means a reduction of the waste generated and the cost of analysis, in agreement with the Green Analytical Chemistry.

Therefore, it can be concluded that the possibility of synthesizing tailor-made mesoporous materials in the laboratory improves and expands the possibilities in the sample processing stage.

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