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New polymeric materials for solid phase extraction

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Abstract

Solid phase extraction (SPE) is a popular sample preparation technique which can be applied directly in gas-solid phase and liquid-solid phase, or indirectly to solid samples by using, e.g. thermodesorption with subsequent chromatographic analysis. Although SPE can be described as a physical extraction process involving a liquid phase and a solid phase, the increased use of packed sorbent formats seems to have led to a bias towards packed sorbent SPE devices. Without any doubt, the heart of the SPE technique is the sorbent material as it has a direct influence on the selectivity, sorptive capacity, and the format or the configuration of the resultant SPE device. There will always be a need for new sorbent materials, and therefore it is imperative to focus research efforts on versatile sorbent fabrication techniques that could address current and anticipated challenges. Various polymeric materials have been developed and implemented in everyday life. They are also extensively used in analytical chemistry. The review provides an updated summary of the most important features of polymeric sorptive materials used at the stage of preparing samples for analysis. The application of each new polymeric sorbent material is discussed in detail. Moreover, the comparison between these materials is done.

Keywords

Solid phase extraction, dendrimers, imprinted polymers, mix-mode polymeric sorbents, electrospun polymer nanofibers

1. Introduction

Striving for knowledge – as thoroughly as possible – about the composition of many types of material objects and the processes which occur in them forces scientists to conduct intensive

work on the development of analytical tools necessary to obtain reliable analytical information. The tools necessary for analytical chemists include the following (Namieśnik and Górecki, 2001; Tobiszewski et al., 2010):

a) control and measuring instruments used to analyse properly prepared environmental samples,

b) reference materials of different metrological values, necessary at the stage of control and quality assurance of obtained data,

c) analytical procedures used to study environmental samples in order to detect, identify and quantitatively determine the widest possible range of analytes. The development of such procedures is more difficult when the matrix of the studied samples is complex and the level of components which are interesting for an analyst is very low. Therefore, sample preparation stages are the key to appropriate procedures to ensure:

- simplification of matrix composition (by moving analytes from a sample to an appropriate solvent or a gas stream),
- removal of at least some of the interfering compounds from the sample tested,
- raising the concentration of an analyte in a studied sample to at least the limit of detection of the methodology or measuring instrument that was used.

Generally, all these tasks are called "the stage of analyte isolation and/or enrichment". These solutions should not only have appropriate metrological parameters, by should also fulfil requirements connected with the principles of green chemistry and green analytical chemistry (GAC), which are strictly linked to the concept of sustainable development (Gałuszka et al., 2013). Among these green sample preparation methods the following can be mentioned (Raynie, 2006; Ramos, 2012):

a) Microextraction
   - Single-drop microextraction (SDME)
   - Hollow fiber-based liquid-phase microextraction (HF-LPME)
   - Dispersive liquid-liquid microextraction (DLLME)

b) Extraction with accelerating factor:
   - Ultrasound-assisted extraction (UAE)
   - Microwave-assisted extraction (MAE)
   - Accelerated solvent extraction (ASE)

c) Extraction with environmentally-friendly medium:
   - Supercritical fluid extraction (SFE)
   - Superheated water extraction (SWE)

- Coacervates and reverse micelle extraction

d) Solventless extraction techniques:

- Extraction with stream of inert gas
- Solid-phase microextraction (SPME)
- Stir bar sorptive extraction (SBSE)
- Solid-phase nanoextraction (SPNE)
- Classical SPE formats (cartridges and discs).

Despite the possibility of applying different methodological approaches, it is worth noting that in laboratory practice the solid phase extraction (SPE) technique is one of the most frequently chosen by analysts. Since the early 1990s this technique has been used to isolate analytes from different types of environmental samples, and has gained more and more popularity and standardization (Poole, 2003; Huang et al., 2015). Currently, it can be classified as one of the classic sample preparation techniques. Since the moment the concept of the SPE of analytes was developed, there has been significant progress in this field, mostly based on automatization, miniaturization, and the limitation of stages of the primary approach (Żwir-Ferenc and Biziuk, 2006; Zygler et al., 2010; Płotka-Wasylka et al., 2016a). At present, SPE forms used in laboratory practice do not resemble at all the solution proposed in 1951 by Braus and his team (Braus et al., 1951), which was based on the use of iron cylinders which contained up to 1.2-1.5 kg of granular activated carbon (Płotka-Wasylka et al., 2016a). As mentioned before, apart from miniaturization and limitation of organic solvents used, the major tendency in the scope of the preparation of a sample for analysis consists of searching for new classes of sorbents. Intensive work conducted in many research centres all over the world in the field of polymer chemistry and material engineering has led to the development and characterization of new, advanced sorbent materials to improve selectivity or specificity towards target analytes, higher sorptive capacity, and enhanced physicochemical or mechanical stability. Figure 1 presents a classification of modern green sorption mediums used at the stage of isolation and enrichment of analytes from various types of environmental samples (Płotka-Wasylka et al., 2016a).

Figure 1.

Polymeric sorbent materials, which are most often cross-linked copolymers that have a considerably developed inner surface and a high selectivity and ability to regenerate, have

become one of the tools most frequently used by analytical chemists for the isolation and enrichment of a wide range of sample analytes with complex matrixes (Augusto et al., 2013). It is apparent that this interest is clearly reflected in the increasing, year by year, number of scientific articles devoted to the areas of application of commercially available polymeric sorbents, and of those describing procedures for obtaining new materials and possibilities of their potential application (Wardencki et al., 2007). The rate of this increase is presented in Figure 2.

Figure 2.

This review provides an updated summary of the most important features of polymeric sorption mediums used at the stage of preparation of environmental samples for analysis. The comparison and application of each new polymeric sorbent material is presented.

2. New polymeric materials

The fact that the most commonly used materials for SPE cannot effectively trap most polar compounds, has encouraged investigators to evaluate alternative sorbent materials, such as mixed-mode polymeric sorbents, molecularly imprinted polymers, ion imprinted polymers, electrospun polymer nanofibers and dendrimers. All these new sorbents types will be discussed here.

2.1. Mixed-mode polymeric sorbents

Mixed-mode polymeric sorbents (MMPs) also specified in the scientific literature as dual-phase sorbents, are described as materials created by merging polymeric skeleton and ionic groups. This solution has enabled the creation of sorption materials in which the retention of analyte may be based on two mechanisms of action, depending on the conditions present during the process: by utilising hydrophobic interactions (from the polymeric material) and by ion exchange (from the ionic groups) (Zhu et al., 2014). Depending on the type of ionic group, it is possible to create the following classification of sorbents: cationic strong (SCX) and weak cationic-exchange polymeric sorbents (WCX), and anionic also of varying strength of ion exchange (SAX/WAX) (Fontanals et al., 2010). Strong cationic exchange sorbents have a polymer matrix modified with SAX groups (most often it is a alkylsulfate group). The anionic group promotes ion exchange interactions with cationic compounds in the sample,

while most of the analytes and interferences (neutral and basic) can also be retained by a reversed phase mechanism (Fontanals et al., 2010). In the case of anion sorbents, the retention mechanism takes place by analogy. However, anion-exchange sorbents typically contain quaternary ammonium groups, or weakly basic functional groups such as primary or secondary amines (Augusto et al., 2013). In the case of applying this kind of sorptive material at the sample preparation stage, optimalisation of analytes isolation and preconcentration conditions is crucial to obtain high recoveries and selectivity factors. Conditioning of the deposit for each type of sorbent is carried out with organic solvent and the aqueous solution with characteristics similar to the sample (Fontanals et al., 2010). Whereas, further steps of conducting the process differ depending on the characteristics of the sorbent material. Figure 3 shows, in a schematic way, the recommended protocols for each type of mixed-mode ion-exchange polymeric sorbent (Fontanals et al., 2010).

Figure 3.

Currently, a very large quantity of different kinds of mixed-mode sorbents with differing ion-exchange properties is available, in the form of both cartridge and extraction disks (Poole, 2003).The review of literature data shows that for the isolation and enrichment of a wide variety of analytes, both in environmental and medical studies among commercially available sorbents, the most frequently used are:

- polyvinylpyrrolidone-divinylbenzene (PVP-DVB) modified with sulfonic groups,
- polystyrene-divinylbenzene (PS-DVB) chemically modified with pyrrolidone (Fontanals et al., 2010),
- divinylbenzene (DVB) resin modified sulfone acid (Zhang and Liu, 2016),
- polyvinylpyrrolidone-divinylbenzene (PVP-DVB) modified carboxylic acid groups (Fontanals et al., 2010)
- divinylbenzene-N-vinylpyrrolidone resin functionalized with quaternary amine groups (Augusto et al., 2013).

The benefits resulting from the combination of reversed-phase retention with ionic interactions into one single material have become a factor fuelling the search for new combinations which can provide even higher recovery-value, as well as selectivity and sensitivity. In recent years a considerable number of scientific articles describing ways to

manufacture, and on the characteristics of "in-house mixed mode sorbents" have appeared. Researchers received highly selective sorbent to isolate and enrich selective pharmaceuticals from water samples using para-vinylbenzyl chloride-divinylbenzene VBC-DVB precursor polymer and further modified through the remaining chlorine groups with lauryl sulfate groups (Bratkowska et al., 2010).

When it is impossible to isolate all analytes at a satisfactory level of concentration from samples with complex Scheldt matrix, it is possible to use two types of sorbents. Usage for the isolation and enrichment of tetracycline antibiotics from sewage samples, stanchion Oasis HLB and Oasis MAX, had an impact on obtaining higher recovery and purification rates than in the case of using only the stanchion Oasis HLB (De Zan et al., 2008). Whereas the use of cartridge with C18 sorbent and further with Oasis MCX to enrich hormones from plant extract samples enabled the simplification of the sample preparation process and contributed to obtaining a higher recovery rate (Izumi et al., 2009). The summary of applications of MMPs is presented in Table 1.

Table 1.

2.2. Molecularly Imprinted Polymers (MIPs)

Very well fit into this concept is a novel trend associated with the use of molecularly imprinted polymers (MIPs) as sorbent beds in various SPE system designs (packings of glass columns, plastic columns, or in-needle extraction devices) for the isolation and/or enrichment of analytes originating from various types of environmental samples (Martín-Esteban, 2001; Vasapollo et al., 2011; Cheong et al., 2013). According to the information listed the literature published over the last 15 years, polymer sorbents of this type may provide a viable alternative, both in economic and practical terms, to the commercially available sorbents used as sorbent beds in SPE columns. In addition, molecularly imprinted polymer sorbents are characterized by higher selectivity towards specific compounds or groups of compounds, leading to the efficacy and yield of the process of isolation and/or enrichment of analytes originating from various types of environmental samples, being higher than when using the commercial SPE tools (Cheong et al., 2013; Palenıkova and Hrouzkova, 2014; Chrzanowska et al., 2015a).

The concept of the synthesis, characterization and use of this type of polymer sorbents as a tool for the analysis of environmental samples were first described in 1994 (Sellergren, 1994).

This article was a stepping stone for a new area of research in environmental analysis, aimed at the design, synthesis, and application of ever-newer MIP sorbents in analytical procedures. The growing popularity and the dynamics of the expansion of the practical scope of the applicability of novel MIP sorbents are due to the fact that they facilitate the selective identification and attachment/sorption of specific chemical compounds or compound groups (Płotka-Wasylka et al., 2016a).

In line with the general principle described in the literature, molecularly imprinted polymer sorbents are obtained by sites characteristic for a specific molecule (reference substance/template molecule) or compounds of its similar structure (structural analogs) being imprinted into synthetic, highly cross-linked polymers. The procedure used for the synthesis of MIP sorbents is simple and does not require much financial expenditure. The following substrates are required for the synthesis of MIP sorbents: functional monomers, the reference substance/template molecule or its structural analog thereof, a cross-linking agent, an initiator, and a porogenous solvent. Polymerization may be initiated by appropriate temperature or by the effect of UV radiation. In order to obtain a novel type of molecularly imprinted polymer sorbent, a synthetic procedure should be carried out in appropriate thermal condition involving the sites complementary to the predefined reference sample or compounds/group of compounds with structure analogous to that of the reference sample being imprinted into the crosslinked polymer (Haupt and Mosbach, 2000; Cormack and Elorza, 2004; Shahar et al., 2016). The molecular imprinting process consists of three main stages (Płotka-Wasylka et al., 2016b; Figueiredo et al., 2016), namely:

a) formation of the template molecule (or its structural analog)-functional monomer complex;
b) polymerization; and
c) removal/flushing of the reference substance/template molecule or its structural analog.

Figure 4 provides a schematic outline of the process for the preparation of molecularly imprinted polymer sorbents (Garcıa-Calzon and Dıaz-Garcıa, 2007).

Figure 4.

Of much importance in the process of the preparation of the new type of MIP sorbents is the selection of an appropriate polymerization technique at the synthesis design stage (Lanza et al., 2002). The broadly known polymerization techniques used for the preparation of the new

type of sorbents are continuously modified so as to achieve the best desirable final effect, i.e. a polymer sorbent with satisfactory physicochemical properties and morphological characteristics. The most common polymerization techniques reported in the literature as being used for the preparation of MIP sorbents include (He et al., 2007):

a) bulk polymerization;
b) suspension polymerization;
c) two-step or multistep swelling polymerization;
d) precipitation polymerization;
e) surface-initiated polymerization;
f) in-situ polymerization.

Detailed characteristics of individual polymerization techniques as well as the benefits and limitations of their use in laboratory practice were described in earlier literature reports (Płotka-Wasylka et al., 2016b). The choice of the polymerization technique used for the synthesis of the novel type of MIP sorbents may be mainly determined by economic factors, i.e. the cost and time required for a single MIP sorbent preparation process, morphological characteristics and physicochemical properties of the particular sorbent obtained in the particular polymerization technique, the quantity of reagents used for a single synthetic process, or the amount of byproducts and contaminants generated from a particular polymerization technique.

The concept and the methodology of laboratory tests aimed at the development of an optimum analytical procedure involving the use of molecularly imprinted polymer sorbents as sorbent beds in SPE columns for the isolation and/or enrichment of analytes originating from various types of environmental samples is based on four basic steps:

1. Preparation of novel molecularly imprinted polymer sorbents:
   a) selection of appropriate substrates for the synthesis of polymer sorbents;
   b) defining optimum conditions for the synthesis of MIP sorbents;
   c) carrying out the procedure for the synthesis of novel MIP sorbents using an appropriately chosen polymerization technique;
   d) removal/flushing of the reference substance (or its structural analog) from the obtained MIP sorbent using an appropriate solvent;
2. Carrying out a series of analyses providing structural data as well as data on the morphological and physicochemical characteristics of the obtained MIPs;

3. Examination of the potential of the obtained molecularly imprinted polymer sorbents for application in selective enrichment and/or isolation of tested chemical compounds from predefined environmental samples;
4. Carrying out of the separation, identification and quantitation of studied compounds present within the predefined environmental samples by means of sophisticated analytical techniques, such as LC-MS or HPLC-MS. At the final stage of the analytical procedure it is necessary to carry out a process facilitating the identification/confirmation of analyte stricture, and verification of the complete washout of the reference substance/template molecule or its structural analog from the obtained polymer sorbents.

The development of novel MIP sorbents for use as SPE column packing allows for an increase in the efficacy and yield of analytical procedures used in environmental analysis, a reduction in the matrix effect-related bias of final results, and elimination of the impact of contaminants present within the environmental samples on the reliability of results. In addition, the use of MIP sorbents at the stage of the isolation/enrichment of analytes facilitates simplification of the analytical procedure and reduces the use of organic solvents. Due to their attractive properties, the molecularly imprinted polymer sorbents have gained the recognition of contemporary chemists, and have found their use as sorbent beds used as SPE column packing in many analytical procedures. Table 1 presents literature data on the use of MIP sorbents in the analyses of various types of environmental samples.

2.3. Ion imprinted polymers (IIPs)

Selective recognition of metal ions is a real challenge for a large range of applications in the analytical field. The perfect tool for isolating these types of analytes, which are often at trace levels in samples with a complex matrix, turned out to be a solution described by researchers in 1976. Researchers obtained a highly selective material by cross linking poly(4-vinylpyridine) with 1,4-dibromobutane in the presence of a metal ion (Prasada Rao et al., 2006). Despite the fact that the first mention of the use of such an approach appeared in the late 1980s, it is only in the last few years that a growth of interest in this material in separation fields has been observed (Shakerian et al., 2012). Additionally, one should pay attention to the fact that the force of the metal complex in IIPs is much larger than that of the hydrogen bound complex usually present in MIPs, and therefore it is better suited for the identification of

water-soluble ions and metal ions (Fu et al., 2015). However, there is a lack of an ideal solution in this field of research, and this material also exhibits disadvantages. Among the most serious the following must be listed: poor solubility of the analyte (template) in the imprinting mixture and poor homogeneity, time-consuming imprinting process and insufficient leaching of the imprint ion can occur, which results in bleeding of the materials (Płotka-Wasylka et al., 2016a).

The conventional methods of synthesized IIPs include the interaction between the ion with a suitable functional monomer, a cross linker agent, and an initiator. In Table 2 are presented commonly used functional monomers, cross-linkers and initiators in the preparation process (Branger et al., 2013; Fu et al., 2015; Płotka-Wasylka et al., 2016a).

Table 2

After formation of the three-dimensional structure, the ions are removed from the network by an appropriate chosen eluent, and the received sorbent is ready for the selective preconcentration of the target ion (Monier et al., 2016).

IIPs may be classified into four main groups based on the inclusion of the ligand in the polymer matrix (Płotka-Wasylka et al., 2016a):

a) linear chain polymers carrying metal-binding groups being cross-linked with a bifunctional reagent;
b) chemical immobilization by the preparation of binary complexes of metal ions with ligands having vinyl groups, isolation, and then polymerization with matrix-forming monomers;
c) surface imprinting conducted on an aqueous–organic interface;
d) trapping of a non-vinylated chelating ligand via the imprinting of binary/ternary mixed ligand complexes of metal ions with a non-vinylated chelating agent and a vinyl ligand.

In Figure 5 different approaches for IIPs elaboration are presented schematically (Branger et al., 2013; Płotka-Wasylka et al., 2016a).

Nowadays, the surface-imprinting technique attracts extensive research interest due to the fact that IIPs prepared by using this imprinting technique have many advantages, including fast adsorption kinetics, good accessibility to the target species, complete removal of templates,

low mass-transfer resistance, and easy preparation (Płotka-Wasylka et al., 2016a). The surface-imprinting technique in combination with a sol-gel process has been successfully used for the imprinted coating of silica gel and magnetic particles or even nanoparticles (Besharati-Seidani and Shamsipur, 2015; Płotka-Wasylka et al., 2016a). Information on the application of IIP sorbents is presented in Table 1.

Figure 5.

2.4. Electrospun polymer nanofibers

When a polymer fiber goes to the nanoscale, new characteristics appear, for example, improved mechanical properties, extremely large surface to volume ratio, and flexibility in surface functionalities (Reyes-Gallardo et al., 2016). Despite the fact that many techniques can be applied for the synthesis of nanofibres (NFs), such as drawing, template synthesis and phase separation, electrospinning has a leading edge over all of them, which is due to the ability to easily control the orientation of the NFs (Płotka-Wasylka et al., 2016a). Electrospinning is a fibre production method which uses electrical force to draw charged threads of polymer solutions or polymer melts up to fibre diameters in the order of some ten nanometers (Reyes-Gallardo et al., 2016; Płotka-Wasylka et al., 2016a). The electrospinning set-up comprises three basic components (Chigome et al., 2011) (Figure 6):

a) a high-voltage power supply;
b) a way to deliver a viscoelastic solution; and,
c) a means to collect the fibres

The extremely small diameter electrospun fibers possess a high aspect ratio that leads to a larger specific surface . The morphology, and physical and chemical properties of electrospun NFs and NF mats can be selected by optimizing the operational parameters in their production. Due to these features, electrospun NFs are extremely interesting materials for separation sciences, including as sorbents for SPEs (Płotka-Wasylka et al., 2016a).

The basic requirement for the formation of fibre through electrospinning is the viscoelasticity of the spinning solution (Chigome et al., 2011). The most popular electrospun materials are solutions based on high molecular weight polymers, due to the fact that they possess the requisite viscoelasticity due to their long chains. On the other hand, there is a huge number of pre- and post-electrospining modification processes that allow the broadening of the range of

materials that can be electrospun, what means, that it should be possible to fabricate almost all of conventional SPE sorbents to form NFs sorbents (Chigome et al., 2011).

The interaction mechanisms of electrospun nanofiber-based SPE sorbents are the same as those of classical sorbents. The main differences are that conventional polymeric sorbents are microparticles and, by virtue of being cross linked, exhibit high mechanical strength (Reyes-Chigome and Torto, 2012; Gallardo et al., 2016). The rigidity and the insolubility of polymeric microparticles as a result of cross-linking have made it a challenge to bridge the gap with electrospun polymer nanofibres. Consequently, electrospun nanofibre-based sorbents have mostly been limited to non-cross-linked, flexible and readily-soluble polymeric materials (Reyes-Gallardo et al., 2016; Płotka-Wasylka et al., 2016a). At the step of the development and optimization of electrospun NF-based SPE sorbents, it is necessary to take into consideration several parameters, with the most important being:

a) chemical composition of the polymeric material,
b) the procedure of electrospinning, and
c) mechanical strength.

Fabricated SPE devices that employ electrospun NFs as a sorbent bed are mainly based on polystyrene or nylon 6 polymers. Therefore, classification of electrospun NF-SPE devices can be proposed as follows (Chigome and Torto, 2012):

a) polystyrene type (characterized by relatively low mechanical strength), and
b) nylon type (characterized by relatively high mechanical strength).

The use of electrospun polymer nanofibres for packed sorbent SPE was first reported in 2007 (Kang et al., 2007). In that case, 1 mg of polystyrene NFs were packed into a 200 µl micro pipette tip to form a micro column (Figure 7A). The packing procedure took advantage of the ease of rolling polystyrene nanofibres into nanofibre clews. Several reports followed where either polystyrene or polystyrene copolymer nanofibres were employed as the sorbent bed packed in micro column format (Chigome and Torto, 2012).

Figure 7.

One of the main drawbacks of the micro column packing procedure is consistency, as it relies very much on the experience of the researcher. The main challenge is the rolling up of a uniform size of fibre clews.

In 2010, an alternative polystyrene fibre based on the SPE device fabrication procedure was reported (Chigome et al., 2010). The experimental approach consisted of copolymerization with subsequent electrospinning of the resultant polymer. Ten miligrams of electrospun polystyrene fibres were packed in a disk format. The study clearly demonstrated how the use of electrospun fibres can simplify SPE disk fabrication as the sorbent material was packed using simple homemade tools (Chigome and Torto, 2012).

In 2010, the fabrication of SPE devices that rely on relatively mechanically strong electrospun nanofibres as the sorbent bed was first reported (Xu et al., 2010). Nylon 6 nanofibre sorbent beds were "packed" by cutting out circular portions of the nanofibre sheet (Figure 7B). One year later, an alternative fabrication procedure for a nylon type SPE device was reported. In that case, a polypyrrole-nylon 6 blend was applied as a sorbent bed (Bagheri et al., 2011). However, the extraction procedure was not a flow through process as the sorbent bed was held by a wire and dipped into a sample solution.

A report on electrospun nanofibre based micro extraction in a packed syringe (MEPS) was published in 2012 (Bagheri et al., 2012). The packing procedure involved the manual compression of 8.1 mg of polypyrrole/nylon 6 nanofibre blend into a 1 mL injection syringe. The electrospun nanofibre sorbent bed was laid flat at the bottom of the syringe barrel between two SPE frits. Information on the application of electrospun polymer NFs is presented in Table 1.

2.5. Dendrimers

Dendrimers are a highly branched, unique class of macromolecules with nanometer-scale dimensions. They consist of three components (Figure 8): a central core, an interior dendritic structure, and an exterior surface with functional surface groups (Li et al., 2015; Hu et al., 2015). Due to the varied combination of these components it is possible to yield products of different shapes and sizes with shielded interior cores. The attached surface groups affect the solubility and chelation ability, while the varied cores impart unique properties to the cavity size, absorption capacity, and capture-release characteristics (Fréchet and Tomalia, 2001). Due to these specific properties they are ideal candidates for applications in many field of science.

Figure 8.

Dendrimers can be synthesized by two major approaches: a divergent method or a convergent one. In the divergent approach, the synthesis starts from the core of the dendrimer to which the arms are attached by adding building blocks in an exhaustive and step-wise manner. In the convergent method, synthesis starts from the exterior, beginning with the molecular structure that ultimately becomes the outermost arm of the final dendrimer (Abbasi et al., 2014).

It is reported that dendrimers have exhibited high capacities for encapsulating drugs and many pollutants, such as polycyclic aromatic hydrocarbons (PAHs), heavy metals and dyes (Li et al., 2015; Hu et al., 2015). High loading of ibuprofen has been achieved with SBA-15 supported poly(propyleneimine) dendrimers with high-density amine functionalities (Hu et al., 2015). Therefore, dendrimer functionalized mesoporous silica provides an effective route to producing highly efficient SPE sorbents by combing the advantages of dendrimers with the ease of separation of solid supports (Li et al., 2015). It is necessary to provide a mesoporous silica support with larger pores in order to perform such functionalization to eliminate the possibility of pore blocking resulting from the development of dendrimers.

Several applications of dendrimers as SPE sorbent have been reported (Table 1). A dendrimer modified silica multi-mode stationary phase that exhibited a reversed-phase/anion-exchange (RP/AEX) mixed mode retention mechanism for acid drugs has been developed (Li et al., 2014). This dendritic polymer-modified silica stationary phase (DPS) was prepared by a divergent synthesis scheme starting from propylamine on silica by consecutive amine-epoxy reactions with 1,4- butanedioldiglycidyl ether and aniline. Depending on solute structure and mobile phase composition, the DPS stationary phase provided multiple retention mechanisms, including reversed phase (RP), anion-exchange (AEX), and hydrophilic interactions. Basic, neutral and acidic molecules were well separated under RP/AEX mixed mode. Effective separation of small polar compounds (such as nucleobases and nucleosides) was also obtained under hydrophilic interaction liquid chromatography (HILIC) mode (Li et al., 2014).

In another work of the same author group (Li et al., 2015), the potential use of mesoporous silica (KIT-6) functionalized with dendrimers as a mixed-mode anion-exchange sorbent for the pre-concentration and cleanup of selected acid drugs in human urine samples is described. KIT-6 was chosen for this application due to its larger pore sizes and highly interconnected 3D cubic mesoporous structure as compared to other types of mesoporous silica. The application of the optimized methodology for the analysis of human urine provides good recoveries and reproducibility. It was also found that a compromise exists between the surface area, pore size and dendrimer generation, and therefore, the DF-KIT-6 with only two generations of dendrimers was applied for SPE (Li et al., 2015).

Functionalized metalloporphyrin [5,10,15,20-tetrakis-(4-carboxyphenyl)-porphyrin] was coupled with poly(amidoamine) (PAMAM) to form an adduct of iron porphyrin PAMAM dendrimer Mobil Composition Matter-41 (FeP/Dend-MCM-41) (Sanagi et al., 2015). MCM-41 was used as a mesoporous nanomaterial support for FeP/Dend to control pores for adsorption. The developed FeP/Dend-MCM-41-G3-SPMTE coupled with the HPLC method was successfully used for trace analyses of N-nitrosodiphenylamine (NDPhA) in selected water samples (drinking water, tap water, lake water and wastewater). Under optimized conditions the method showed good linearity, offered good limits of detection, limits of quantification and analyte recoveries.

3. Summary

In the last decade, SPE has become a very popular extraction technique replacing the very well-known liquid-liquid extraction approach. Sorbents in disks/frits overcome some of the drawbacks of cartridges, but the limited number of commercially available sorbents in this format means that there are fewer applications than with cartridges. The classical bonded silicas are being displaced by polymeric sorbents because the former cannot effectively trap most polar compounds. Polymeric SPE sorbents are used increasingly in the cleanup and analysis of many type of samples, such as pharamaceutical, environmental, and food. They have higher sample capacity, are more rugged, can tolerate accidentally drying out without affecting recovery and reproducibility, and use less solvent than traditional packed-bed, silica-based SPE products. Their spherical shape provides excellent flow characteristics, and the absence of silanol groups reduces nonspecific analyte interactions.

Although several types of polymeric sorbents exist and fulfill their role as a sorbent media perfectly, there is still a need for the development of new polymeric materials in order to monitor a wider range of micropollutants in samples of complex matrix composition by the selective SPE of specific groups of analytes.

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6. Figure captions

Figure 1. Classification of modern sorption mediums used in laboratory practice.

Figure 2. Data about the increasing number of manuscripts on application of polymeric materials in the analytical fields.

Figure 3. The schematic presentation of typical approach for different types of mixed-mode sorbent. SCX – strong cation exchange, SAX – strong anion exchange, WCX-weak cation exchange, WAX-weak anion exchange.

Figure 4. A general schematic outline of the process for the preparation of molecularly imprinted polymer sorbents (Garcıa-Calzon and Dıaz-Garcıa, 2007).

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Figure 8. The general scheme of the three main components of a dendrimer.

Table 1. Information on application of different SPE-polymer sorbents

Analyte type	Matrix type	Sorbent type		Final determination technique	Recovery [%]	LOD	Ref
Mixed-mode polymeric sorbents							
nereistoxin	blood	MCX (with hydrophobic sulfonate group)		GC-MS	97 ± 14	0,01 mg/mL	Park et al., 2015
bisphenols	beverages	MAX (with quater-nary amine groups)		HPLC-DAD	>93	0,1 µg/L	Regueiro and Wenzl, 2015
primary aromatic amines	water	WCX (with carboxyl and n-dodecyl groups)		HPLC-UV	85-111	0,08-0,28 µg/L	Zhu et al., 2014
corticosteroids	bovine milk	MCX, MAX		LC-MS/MS	90-105	0,02 – 0,07µg/kg	Tolgyesi et al., 2010
clenbuterol, ractopamine	porcine liver	WCX (with carboxyl and n-dodecyl groups)		HPLC-UV	92,5-105	6,1-8,4 µg/g	Zhu et al., 2014
Molecular Imprinted Polymers							
tetrabromobisphenol A	tap water, river water and lake water	template molecule	diphenolic acid; bisphenol a	RRLC-DAD	85 - 97	Up to 2 ng/mL	Yin et al., 2012
		functional monomer	3-aminopropyltriethoxysilane				
16 polycyclic aromatic hydrocarbons	natural seawater	template molecule	the 16 pahs mixture	GC-MS	83 - 113	5.2–12.6 ng/L	Song et al., 2015
		functional monomer	phenyltrimethoxysilane				
fenitrothion	tomatos	template molecule	fenitrothion	HPLC-DAD	89-97	0.050 µg/g	de Barros et al., 2010
		functional monomer	methacrylic acid				
chlorinated/brominated dioxins, polychlorinated biphenyls, polybrominated diphenyl ethers	animal tissues	Affini MIP phenolics 3ml molecularly imprinted polymeric SPEs supplied by Polyintell (Val de Reuil, France)		GC/IT-MS UPLC/TOF-MS	47-90	0.010 – 9.87 pg/g	Roszko et al., 2016
daidzein, genistein biochanin a	urine	template molecule	biochanin a	HPLC-DAD	65.7 - 102.6	0.040 – 0.060 µg/L	Chrzanowska et al., 2015b
		functional monomer	3-aminopropyltriethoxysilane				

18 amino acids	tobacoo	template molecule functional monomer	theanine methacrylate acid	HPLC-DAD	79 - 104	94 – 374 ng/L	Zhu et al., 2016
nitro musk compounds	river water, waste water, sea water	template molecule functional monomer	2,4-dinitrotoluene phenyltrimethoxysilane	GC-MS	69 - 92	1.5 – 2.7 ng/L	Lopez-Nogueroles et al., 2013
Ion imprinting polymers							
Pb (II)	beverages (milk, fruit juice, coffee)	Pb(II) imprinted polymer, grafted onto Fe_3O_4 nanoparticles		FAAS	95,8 – 99,3	1.7 mg / kg	Ebrahimzadeh et al., 2015
Hg (II)	surface waters	Hg (II)-imprinted nanoparticles		FAAS	92 - 96	-	Yordanova et al., 2014
Fe (III)	eggs	Fe (III)- imprinted polymer		FAAS	94,5 – 99,2	-	Roushani et al., 2016
Ni (II)	river water	Ni2+ - imprinted nanoparticles		UV-Vis spectrofotometer	106,7 – 108,46	0.001 µg/mL	Rajabi and Razmpour, 2016
Electrospun polymer nanofibers							
aromatic amines	wastewater	carbon NFs from soot		HPLC-UV	70-108	0.009–0.081 µg/L	Vadukumpully et al., 2011
trazodone	human plasma	PFSPE (with PS)		HPLC-UV	94.6–105.5	8 ng/mL	Kang et al., 2007
docetaxel	rabbit plasma	nylon6 nanofibers mat-based SPE		HPLC-UV	85	2 ng/mL	Xu et al., 2010
aldehydes	human exhaled breath condensates	PS/G NF		HPLC-VWD	79.8 - 105.6	4.2-19.4 nmol/L	Huang et al., 2015
Dendrimers							
acid drugs	urine	dendrimer-functionalized KIT-6		HPLC-UV-VIS	85.7–113.9	0.4–4.6 ng/mL	Li et al., 2015
nucleobases, nucleosides	standard solution	DPS		LC-DAD	-	-	Li et al., 2014
NDPhA	water	FeP/Dend-MCM-41		HPLC-UV	97-105	0.96 ng/mL	Sanagi et al., 2015

DAD, diode array detector; DPS, polymer-modified silica; FeP/Dend-MCM-41, iron porphyrin PAMAM dendrimer Mobil Composition Matter-41; HPLC, high performance liquid chromatography; LC, liquid chromatography; NDPhA, N-nitrosodiphenylamine

Table 2. Examples of the most common components used to IIPs synthesis.

Target analyte	Monomer	Cross-linker	Porogen	initiator	Leacher	Ref
Ag^{+}	4-vinyl pyridine (4-VP), 1-vinyl imidazole (1-VI)	ethylene glycol dimethacrylate (EGDMA)	chloroform/ acetonitrile (1:1)	azobisisobutyronitrile (AIBN)	thiourea	Monier et al., 2016
Ni^{+}	4-vinyl pyridine (4-VP),	divinylbenzene (DVB)	2-methoxy ethanol	azobisisobutyronitrile (AIBN)	acetic acid	Besharati-Seidani and Shamsipur, 2015
Pt^{2+}	methacrylic acid (MAA)	ethylene glycol dimethacrylate (EGDMA)	ethanol	azobisisobutyronitrile (AIBN)	acetic acid, thiourea in acetic acid, ammonia	Reyes-Gallardo et al., 2016
Ni^{2+}	2-(diethylamino) ethyl methacrylate (DEM)	divinylbenzene (DVB)	toluene	azobisisobutyronitrile (AIBN)	nitric acid	Chigome et al., 2011
Hg^{2+}	2-hydroxyethyl methacrylate (HEMA)	ethylene glycol dimethacrylate (EGDMA)	-	benzoylperoxide (BPO)	thiourea in acetic acid	Chigome and Torto, 2012
Hg^{2+}	methacrylic acid (MAA)	ethylene glycol dimethacrylate (EGDMA)	-	azobisisobutyronitrile (AIBN)	hydrochloric acid	Chigome et al., 2010
Sb^{3+}	styrene (STY)	ethylene glycol dimethacrylate (EGDMA)	chloroform, ethanol	azobisisobutyronitrile (AIBN)	hydrochloric acid	Xu et al., 2009
Nd 3+	N-methacryloylamido folic acid (MAFol),	ethylene glycol dimethacrylate (EGDMA)		azobisisobutyronitrile (AIBN)	nitric acid, sulfic acid	Bagheri et al., 2011
CN-	methacryli acid (MAA), 4-vinyl pyridine (4-VP),	ethylene glycol dimethacrylate (EGDMA)	acetonitrile/ ethanol (1:1)	azobisisobutyronitrile (AIBN)	water, ethanol, hydrochloric acid	Bagheri et al., 2012
CrO_4^{2-}	2-hydroxyethyl methacrylate (HEMA)	Ethylene glycol dimethacrylate (EGDMA)	isopropyl alcohol	azobisisobutyronitrile (AIBN)	acidified thiourea	Hu et al., 2015
UO^{2+}	styrene (STY)	divinylbenzene (DVB)	pyridyne	azobisisobutyronitrile (AIBN)	nitric acid	Fréchet and Tomalia, 2001

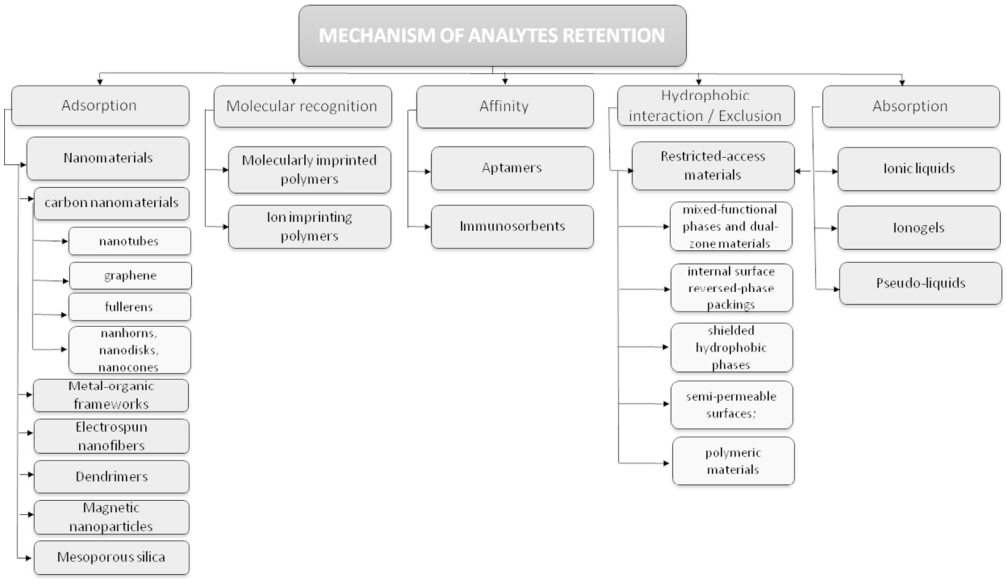

Figure 1. Classification of modern sorption mediums used in laboratory practice.

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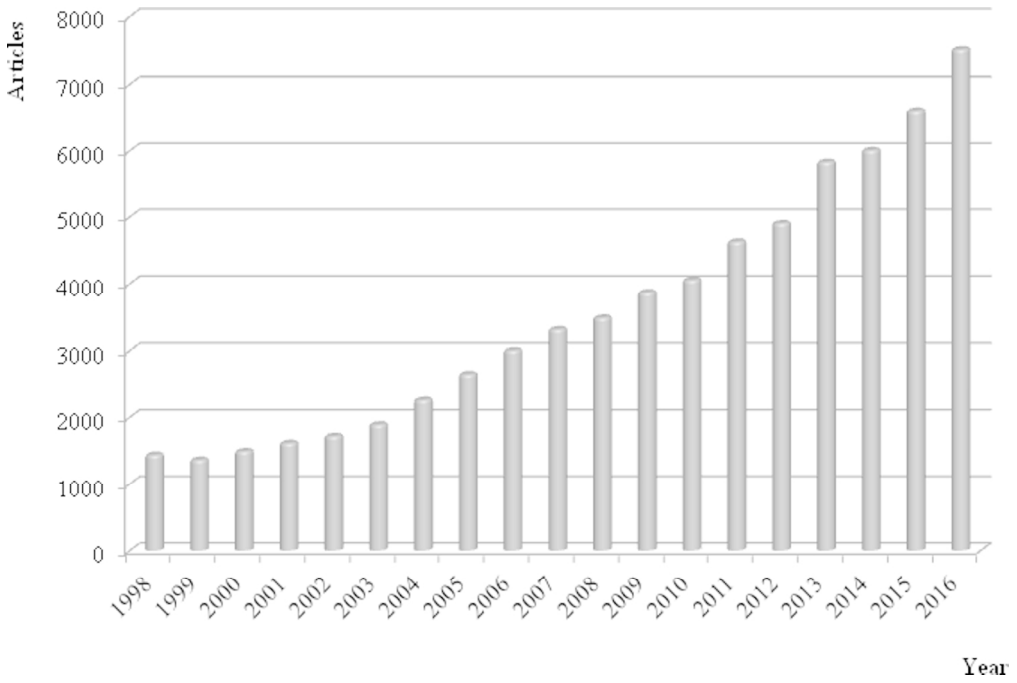

Figure 2. Data about the increasing number of manuscripts on application of polymeric materials in the analytical fields.

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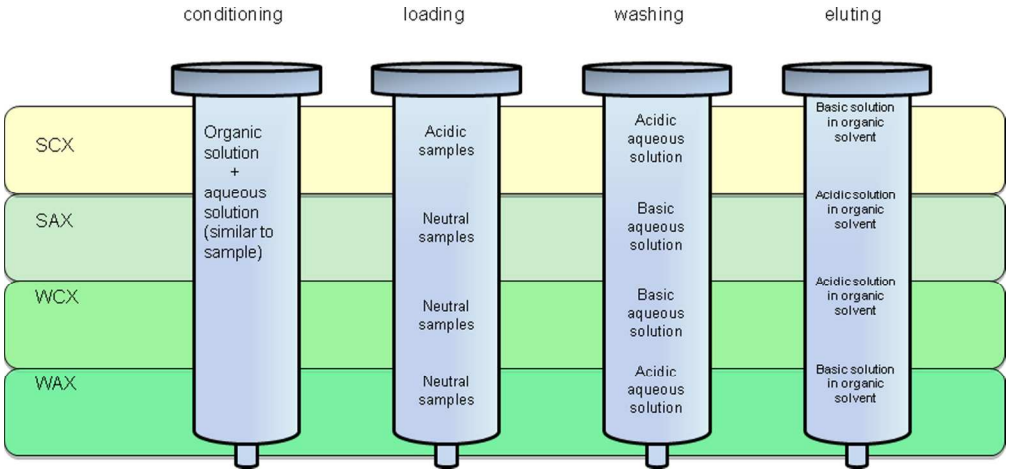

Figure 3. The schematic presentation of typical approach for different types of mixed-mode sorbent. SCX – strong cation exchange, SAX – strong anion exchange, WCX-weak cation exchange, WAX-weak anion exchange.

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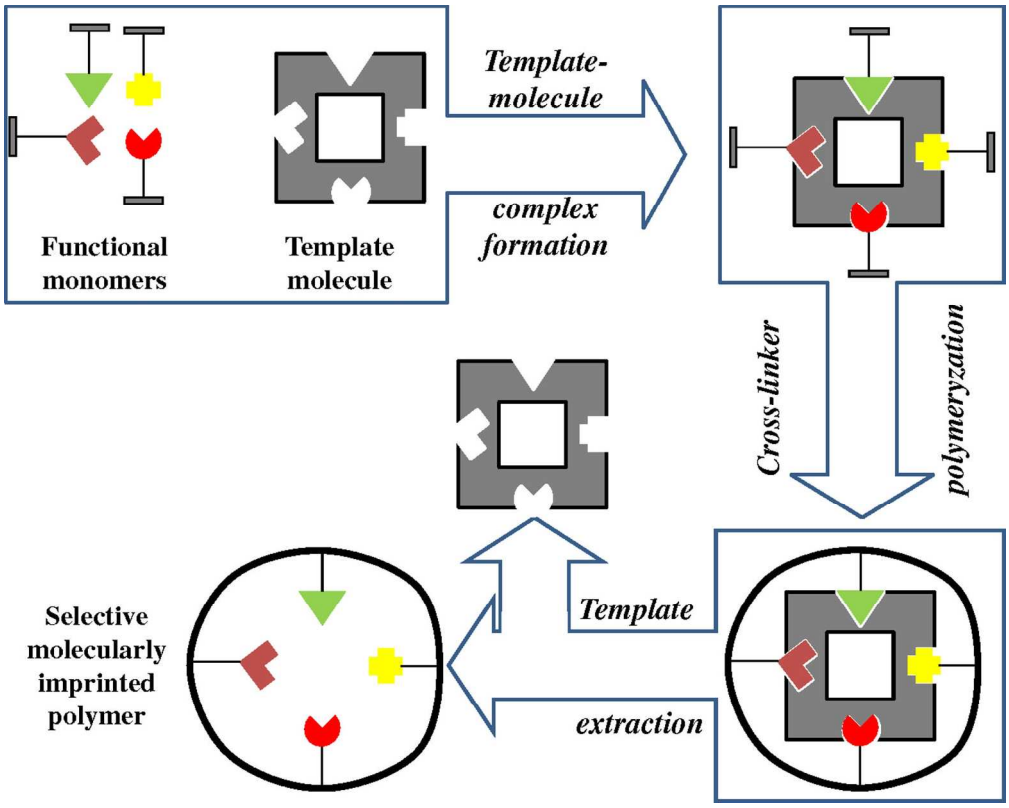

Figure 4. A general schematic outline of the process for the preparation of molecularly imprinted polymer sorbents (Garcıa-Calzon and Dıaz-Garcıa, 2007).

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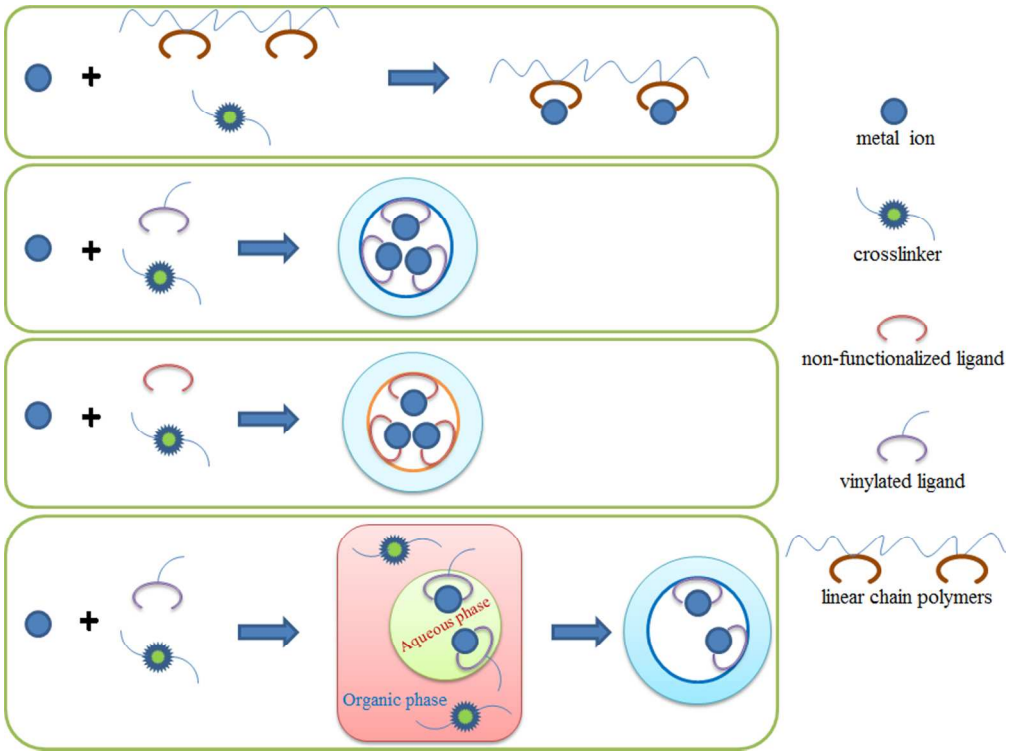

Figure 5. Schematic representation of different approach to IIPs preparation (Branger et al., 2013; Płotka-Wasylka et al., 2016a).

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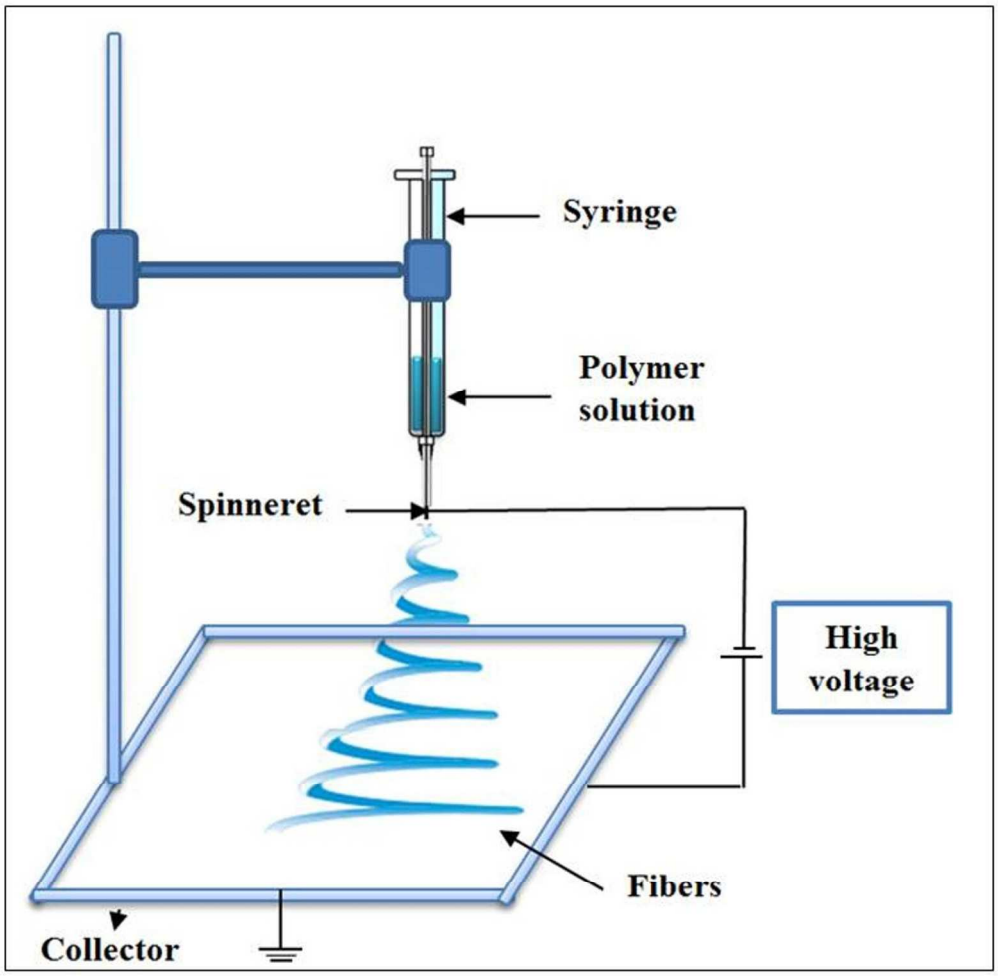

Figure 6. Schematic representation illustrating the set up of an electrospinning apparatus.

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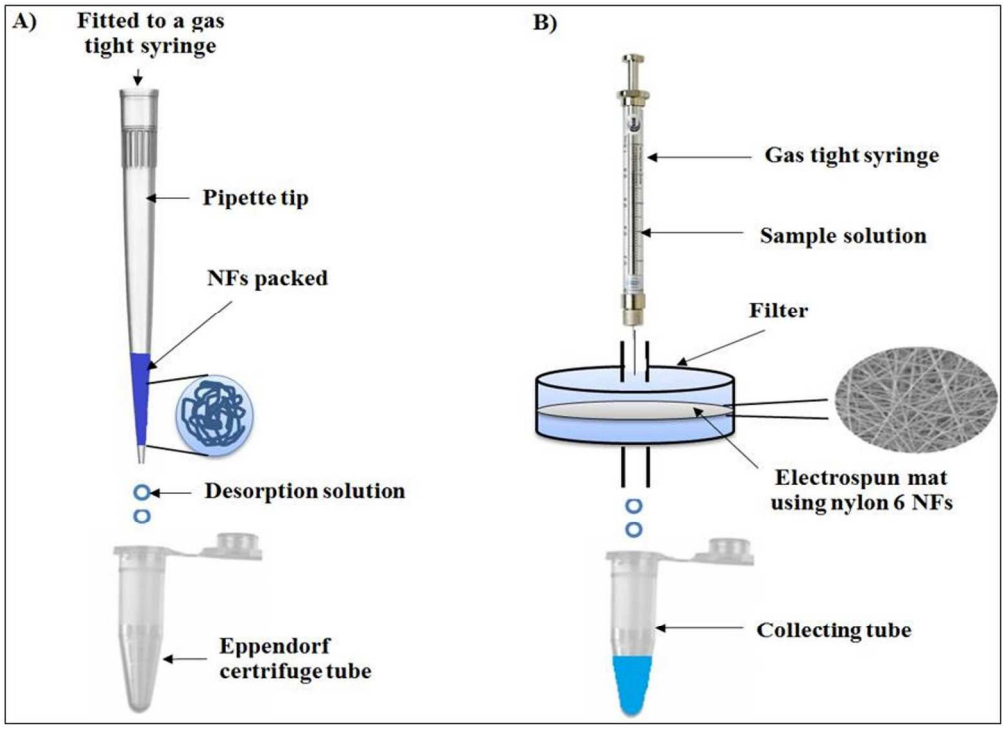

Figure 7. A) Micro column packed with polystyrene nanofibres and designed setup; B) The fiber-filter solid phase extraction (SPE) device.

230x167mm (300 x 300 DPI)

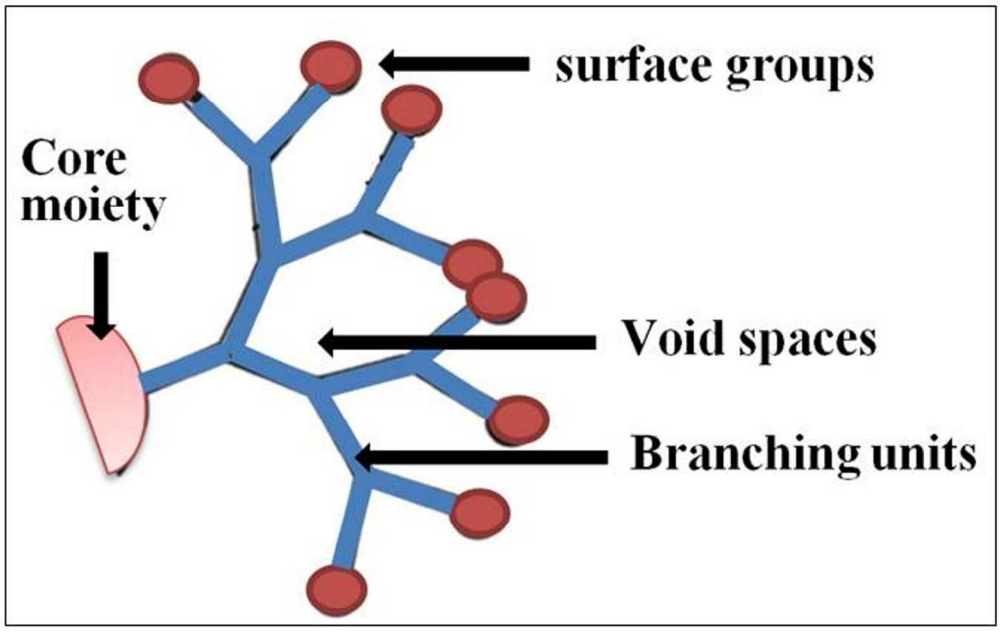

Figure 8. The general scheme of the three main components of a dendrimer.

171x108mm (300 x 300 DPI)