



Nanofibers prepared from synthetic polymers and biopolymers as advanced extraction materials for sample preparation prior to liquid chromatography

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ABSTRACT

Since the beginning of this millennium, there has been an increasing interest in nanofiber-based sorbents for extraction due to their accessibility, scalability, ease of handling, high surface area, variety of chemistries available, and applications in miniaturized methods. Organic and inorganic materials have been converted into nanofibers using various techniques to obtain sorbents for use in analytical chemistry, such as sensors, filter membranes, sorptive phases, and extraction media. Polymer nanofibers are mainly prepared by electrospinning of polystyrene, polyamides, and polyacrylonitrile. In contrast, this review aims to survey other polymers, including biopolymers and biodegradable polymers. In addition, the possibilities of innovative alternative fabrication techniques leading to fiber materials with unique mechanical properties are described. We also focus on unexplored extraction formats using polymer nanofibers. Examples of recent applications benefiting from desorption with minimal solvent volume and on-line hyphenation to chromatographic methods are reported. Finally, the future prospects of these nanosorbents are discussed.

1. Introduction

Sample preparation is an important step prior to sample analysis. This is even more true, the more complex the samples to be analyzed are. Complex matrices derived from living organisms, the environment, food, and many other sources cannot be used directly for analysis because they contain too many components, i.e., analytes and interferences, many of which are not relevant to the purpose of the analysis. It is therefore desirable to remove these components from the sample. Similarly, many instrumental methods cannot handle such a large number of components, and sample simplification is a *conditio sine qua non* for their successful analysis. Another issue related to the current developments in sample preparation techniques is their ever decreasing size. Examples include biological samples obtained by biopsy for diagnostic purposes and to monitor patient treatment. Typically, the small sample needs to be divided into several parts needed for analysis using a variety of methods. Finally, the number of these complex samples is growing rapidly, as their analysis by advanced methods is now common practice and fast parallel approaches must be used to ensure that the speed of their preparation and analysis matches the speed of their generation.

The current literature contains many methods used for sample preparation prior to their HPLC analysis [1,2]. One of the most commonly used methods is solid phase extraction (SPE). This method is a solid-liquid extraction technique in which compounds that are dissolved in a liquid mixture are separated, isolated, or purified from other compounds in the mixture, according to their physical and chemical properties. The “classical” format of SPE has also been modified, e.g. fiber-packed in-tube extraction, packed pipette tips, disks, coated devices such as stir bar sorptive extraction [3–7].

Nanomaterials have gained much attention among extraction sorbents in the last decade. Their large surface area, which allows fast kinetics of adsorption and desorption, and their small size make them suitable for application in miniaturized formats of solid phase extraction (SPE), such as dispersive solid phase extraction (dSPE), magnetic dSPE, and microextraction in packed sorbents. All of these formats aim at handling of small samples and at minimizing the volume of the organic solvents used to achieve desorption of extracted compounds in as small a volume of elution solvent as possible. They are used for a standard solid phase extraction procedure with its typical steps of conditioning, sample passage, washing, and elution from the sorbent. Alternatively, sorption techniques are selected when rapid equilibration and easy desorption

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are critical.

Comprehensive reviews of nanomaterials in general, including magnetic nanoparticles, graphene-based nanosorbents, carbon nanotubes, metal-organic frameworks (MOF), covalent organic frameworks (COF), and molecularly imprinted polymers have been presented by Plotka-Wasyłka et al. [8,9]. Specific analytical control including environmental contamination has been addressed by Nouri et al. [10] and Santoyo Treviño et al. [11], food analysis by Casado et al. [12], and cosmetics by Grau et al. [13]. Biocompatibility, reusability, and application of nanomaterials in microextraction techniques addressing green analytical chemistry in terms of miniaturization, automation, and maximization of sample throughput were summarized by Saura-Cayuela et al. [14].

The interest in nanofiber-based sorbents for extraction has been growing since the beginning of this millennium [15]. Since then, various organic and inorganic materials have been converted into fibers using different techniques and attempts to obtain narrow-sized nanoscale fibers for use in analytical chemistry as sensors, filter membranes, sorptive phases, and extraction media [16,17]. Nanofiber sorbents are a special class of nonparticulate materials that offer the advantage of convenient handling because they can be prepared in large nonwoven sheets or mats that can be shaped into a variety of formats. Particle-related problems, such as the release of free particles that can clog capillary systems or their aggregation, are largely avoided. In addition, reusability through recycling steps is easy because nanofibers are used in compact layers. Compared to nonporous nanoparticles of the same diameter, their surface area is smaller, typically in the range of units of m^2/g due to the stretched shape of the fibers. On the other hand, the surface area can be increased by modifications, improved surface roughness, and preparation of composite materials.

Most of the recent reviews on nanofiber sorbents have focused on nanofibers made of synthetic polymers, typically including polystyrene, polyamides, and polyacrylonitrile since these can be easily prepared by electrospinning [17–20]. In contrast, we review the use of other polymers, including more environmentally friendly biodegradable ones, and the possibilities of alternative fabrication techniques leading to unique mechanical properties and unexplored SPE formats using these nanofibers. We also present innovations in modification techniques along with the benefits of their unique properties that make them advanced materials and potential sorbents. Recent advances to improve the greenness of analytical methods using nanofibers such as the use of biodegradable polymers, solvent-free fiber preparation, and microextraction applications, are also considered.

2. Production of polymer nanofibers

Spinning methods are the most widespread techniques for fiber formation, including electrostatic spinning (electrospinning), centrifugal jet spinning, wet spinning, bubble spinning, and fiber drawing [21]. Other methods involve melt blowing, phase separation [16], and more specific methods such as self-assembly of peptides [22], wet chemical fabrication techniques such as hydrothermal synthesis and sol-gel method for metal oxide nanofibers [21], chemical vapor deposition and template method for carbon nanofibers [23,24]. In general, the electrospinning of any new material requires the optimization of numerous empirical parameters because no available model exists to predict optimal conditions [25].

2.1. Electrospinning using direct current

Electrospinning is a well-known and the most widely used technique for the preparation of polymer nanofibers, which uses electrostatic force to expand fibers from liquid polymer [17–19,26,27]. Gilbert was the first to describe the deformation of a drop caused by the presence of electrically charged material in the early 17th century [28,29]. Since then, there has been a long journey of partial discoveries and patents

carried out to reach the current technology. In particular, the understanding of the electric field and high-voltage generators was not developed until the 19th century. In 1888, Boys constructed the first apparatus for electrospinning connected to a high-voltage electrical supply and prepared fibers from beeswax and collodion [28,29]. Cooley and Morton in the early 1900s and later Formhals in the 1930s filed the first patents on electrospinning fiber formation [25,28]. In the 1960s, Taylor presented the mathematical model of the deformation of fluid droplets caused by an electric field [28]. However, the industrial production of nanofibers was unrealistic throughout most of the 20th century. Their boom can be dated to the 1990th with the research of Reneker's team, which tested the electrostatic spinning of various polymers and investigated the optimization of spinning process parameters [30,31]. More recently, in 2004, the development of a needleless multijet spinning enabled larger production of nonwoven fabrics [32,33].

Electrospinning is a universal process and consists of a simple polymer dispenser, a high-voltage direct current (DC) generator, and a fiber collector. By adjusting many variable parameters, as reviewed by Ibrahim et al. [34], and selecting from a wide range of polymers and their blends, or incorporating dispersed hybrid agents, electrospinning is versatile in providing diverse ultrathin fibers. Originally, the polymer, melted or most often dissolved in a volatile solvent, is driven under high voltage to the tip of a syringe, capillary, or spinneret needle and ejected as a jet from the Taylor cone. The fiber is formed when the critical level of the electric field is reached. Depending on the viscosity of the solution, a continuous jet is propelled toward the oppositely charged collector and the fiber is pulled as the solvent evaporates or the polymer cools and hardens prior to deposition on the collector. However, this basic system has very low productivity. Needle- and syringe-based systems are intended for laboratory purposes, challenging materials, and small-scale experiments. Coaxial electrospinning offers an approach to core-shell fibers, taking advantage of the combination of different polymers and sheathing [19,35], which also allows drug encapsulation in biopolymer nanofibers [36].

Current trends in sample preparation aimed at improving sustainability and greenness are also generating new methods in sorbent preparation. The use of toxic solvents is one of the critical aspects of nanofiber electrospinning [14]. Avossa et al. reviewed processes using solvents with low environmental impact [37]. However, the list of nanofibers electrospun under these conditions was short. Therefore, solvent-free solutions would be preferred, but they are limited to the use of thermostable meltable polymers. On the other hand, polymers electrospun from their water solution have less prospect as extraction sorbents due to their solubility, as water is often used as a solvent in sample preparation. This problem can be solved by stabilizing such nanofibers by cross-linking. Alternatively, so-called green electrospinning can be achieved by spinning non-water soluble polymers from aqueous dispersions or emulsions. Emulsion electrospinning also allows the encapsulation of water-soluble compounds in water-insoluble fibers [37,38].

Next-generation needleless, free-surface electrospinning systems with significantly improved productivity have finally enabled industrial production of nanofibers for protective masks and filters in recent years [19,39]. Notably, hybrid fibers formed from dispersions and colloids have a tendency to clog the needle, which is overcome in needleless electrospinning. Thus, new functionalized and hybrid nanofibers containing fillers have become available [39]. Needleless technology can be arranged in a rotating spinneret (ball, cylinder, disk, coil) that dispenses polymer solution on its surface, and Taylor cones and jets are forced from the liquid layer [40]. From an environmental perspective, needleless electrospinning exposes a large surface area of liquid to air, resulting in the evaporation of toxic solvents while their recycling remains unresolved. Another needleless approach is represented by bubble electrospinning. The jets are generated when the electrostatic force overcomes the surface tension of bubbles, which are formed on the surface of the polymer solution using auxiliary air flow [41,42]. Since

spinning is always strongly affected by ambient conditions such as temperature and humidity, absolute batch-to-batch reproducibility can be difficult to achieve.

2.2. Electrospinning using alternating current

Since drawing fibers from one electrode to another typical of DC spinning appears simple, stable, and well managed, the application of an alternating current (AC) power remained rather neglected. The instrumentation was not available and optimization of processing conditions was also more difficult. In contrast to DC electrospinning, AC electrospinning offers a higher productivity of more robust fibers in voluminous mats with more homogeneous porosity. Fig. 1 shows the process of the AC spinning. Multiple jets are ejected from a droplet surface as the polarity changes [43], and the resulting fibers self-organize into plums. Opposite charged jets are attracted and neutralized [44]. Therefore, there is no need for a grounded charged collector. Fibers are transported from the spinneret by electric corona or ionic wind and can be deposited

on any type of substrate [45].

Kessick et al. found that poly(ethylene oxide) nanofibers produced by alternating current (AC) electrospinning allowed to overcome fiber instability and oscillation inherent in DC electrospinning. AC electrospinning improved nanofiber alignment and stability due to reduced electrostatic repulsion with alternating positively and negatively charged regions [46]. On the other hand, AC electrospinning resulted in slightly thicker nanofibers and higher residual solvent content due to reduced evaporation [44,46]. This can also be related to a shorter shelf life, making AC spun fiber mats less stable and crumbly, which does not happen with DC spun counterparts even after years of storage.

Identical polymer solution concentrations can be spun in both AC and DC [47,48]. The polymer solution is dispensed through a needle [44, 47] or needleless spinnerets, nozzles, and electrode tips [43,45,49], or a rotating corona spinneret [50]. For AC electrospinning, a higher voltage can be applied, resulting in a more intense electric wind that drives a more stable stream of produced fibers, in contrast to no benefit of higher voltage in DC electrospinning [47]. Sivan et al. used a signal generator

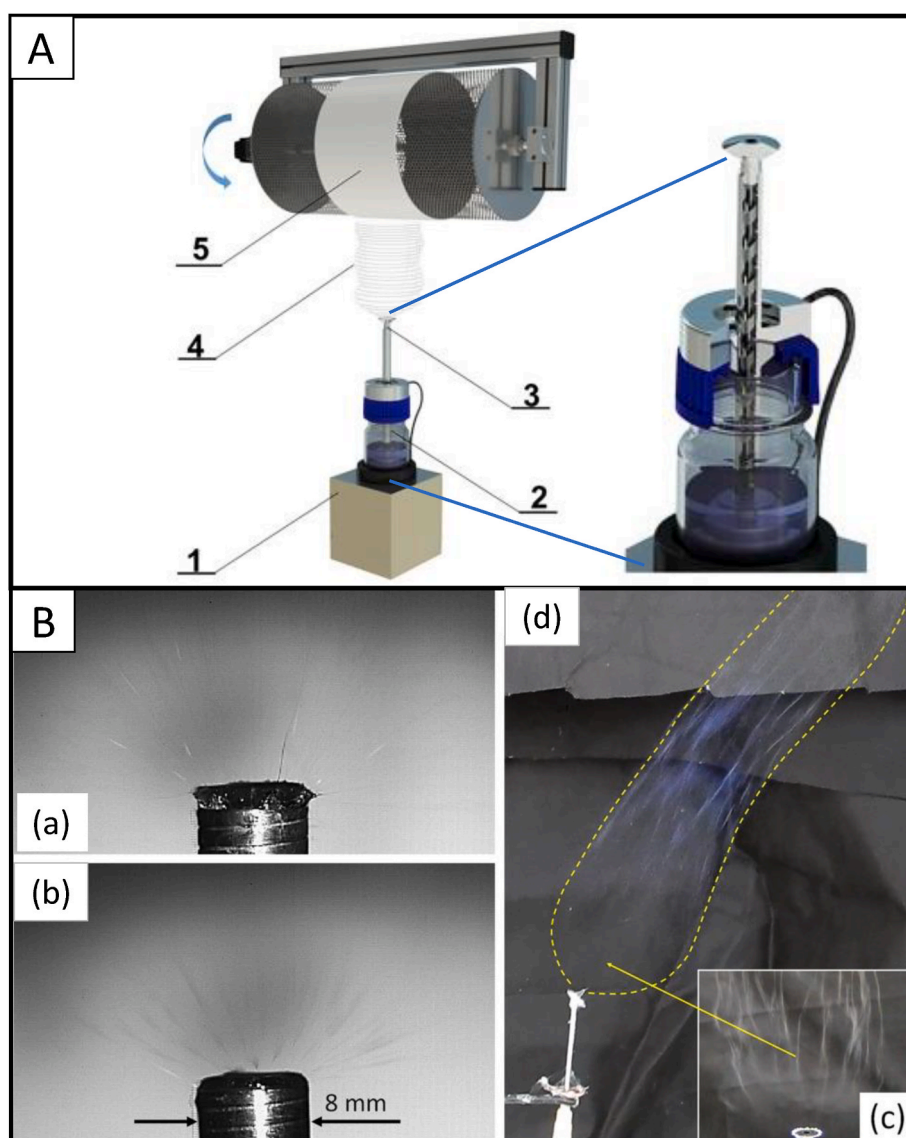


Fig. 1. Electrospinning of nanofibers using alternating current. (A) Schematic of the instrumentation: 1) the motor and magnetic clutch of the screw pump with detailed image, 2) the polymer solution reservoir with the magnetic screw feeder, 3) the steel overflow electrode, 4) the nanofiber plume transported to the collector, 5) the electrically inactive drum collector. (B) Polymer jets emitted from the electrode surface during AC electrospinning of polymer solutions: a) 20 % PCL, b) 10 % PCL, c) the formation of a stream of partially bundled fibers, d) slowly propagating stream of polymer fibers. Reproduced with permission (A) from Ref. [48] and (B) from Ref. [49].

connected to a high-voltage amplifier to generate the required high AC potentials in tunable waveforms and frequencies. The AC frequency was an additional parameter that can be tuned in AC electrospinning to influence the process because too low or too high waveform frequency of changing the polarity affects the spinnability of a polymer [45].

Erben et al. described improved productivity using AC electrospinning on polyamide 6 model, resulting in higher surface density and fiber layer thickness. Elimination of a charged collector allows the continuous production of thicker nanofiber layers while the charged collector in the DC system quickly becomes insulated with nanofibers, and the electrospinning process stops. AC electrospun nanofibers were then tested as extraction sorbents that showed better wettability with aqueous samples and changes in the surface composition in favor of the oxygen-to-nitrogen ratio. The nanofiber mats were also significantly more robust and stable under high pressure when used in a packed column for an on-line SPE-HPLC system [48].

The preparation of original extraction sorbents as composite nanofibers incorporating nanoparticles is a promising trend. We used AC electrospinning to significantly increase the amount of carbon modifier incorporated into the polymer nanofibers [51]. A thicker layer of AC spun nanofibers, as shown in Fig. 2, allows for their easier handling and support-free treatment, which also opens new options in SPE formats and applications.

2.3. Melt blowing

Melt blowing is the method of choice for commercial production of nonwovens. The polymer melt is extruded by hot air to form fibers. This simplicity makes it a low-cost, non-toxic, solvent-free process. However, it only works with thermally stable plastics. Typical polymers used in meltblown technology are polypropylene, polyethylene, polystyrene, polyesters, polyurethanes, and polyamides. Other polymers such as polycaprolactone (PCL), poly(lactic acid) (PLA), and poly(vinylidene difluoride) (PVDF) can also be used, although their use is less common [52].

The melt-blowing extruder was, for the first time, demonstrated by Wentz in the 1950s [53,54]. He attenuated fibers of nylon, polystyrene, polyethylene, and some other polymers. The polymer melt was forced through a nozzle-shaped die consisting of a large number of orifices between two air streams at a controlled speed and temperature [55], which ensured fiber elongation. A comprehensive review of further technique development and industrialization of the technique has been published by McCulloch [54]. Meltblown fibers are mostly over a micrometer in size, but efforts have been made to obtain nanoscale fibers by increasing the air flow rate or a new die design [56,57].

Although meltblown fibers are typically 1–10 μm in diameter compared to thinner fibers produced by electrospinning, their advantage is the robustness and airy, cotton-like structure of the mats with excellent permeability. In addition, this technology can be combined

with electrospinning to form composite fibers. Meltblown fibers act as a scaffold to support the more fragile electrospun nanofibers, providing robustness. The combination of fibers with different polymer chemistries is also accessible [58]. Raabová et al. demonstrated the application of this low-cost composite type of PCL material using column-switching HPLC with a separation typically achieved only with the expensive restricted access media [59].

Some biodegradable polymers can also be melted and attenuated into filaments. For example, PLA has been used as a replacement for respirators and filters [60,61]. Zatrochová et al. applied meltblown fiber disks made from various polymers, including PLA and polyhydroxybutyrate (PHB), for sorptive extraction of environmental contaminants [62].

3. Nanofiber-based sorbents

3.1. Natural polymers

The detailed description of biopolymers-based sorbents has recently been reviewed elsewhere by Werner et al. [63]. Therefore, only briefly, chitosan, cellulose, alginates, silk fibroin, wool keratin, collagen, and zein are biopolymers used in the fabrication of nanofibers. These polysaccharides, proteins, and other biomacromolecules are derived from natural resources and are sustainable, non-toxic, and biodegradable. Although the focus of their use is in drug delivery systems, controlled drug release, wound dressing, and tissue engineering due to their poor mechanical strength and rapid degradation [64], they can be also utilized for filter and extraction media, as supports in composite sorbents in combinations with other materials, such as other polymers, magnetic particles, MOF, and graphene oxide [14,63].

Corresponding nanofibers are prepared mostly via electrospinning. Kandehe et al. reported electrospun chitosan composite nanofibers composed of poly(vinyl alcohol), citric acid, and aloe vera gel for thin-film micro-extraction of pesticides from water and food [65]. Amini et al. prepared electrospun combined polyacrylonitrile and agar nanofibers with silver nanoparticles [66]. Agar in the nanofibers improved the dispersion of nanoparticles and prevented their aggregation. Keratin/polyacrylonitrile composite nanofibers were electrospun by Goyal et al. [67]. Fibers from solution with concentrations of keratin higher than 6 wt% with respect to polyacrylonitrile as well as pure keratin were not spinnable. Yao et al. electrospun protein zein from ethanolic solution, concluding that at concentrations higher than 30 %, the fibers collapsed [68]. Cross-linking significantly enhanced the poor mechanical strength of the zein nanofiber mat.

Alternatively, a nanofiber chitosan membrane decorated with crown ethers was formed by low-temperature phase separation by Cheng et al. [69]. Shahi et al. obtained cellulose nanofibers directly from sugar cane by ultrasound-assisted extraction after hydrolysis to remove soluble hemicellulose and lignin from the agricultural raw material [70].

3.2. Synthetic degradable polymers

Synthetic polymers are characterized by high versatility, customizability, durability in terms of mechanical strength and chemical resistance, and cost effectiveness. Their electrospinning is more stable and more reproducible from batch to batch [19]. To deal with the large quantities of discarded polymers previously used in sample preparation so far, attention should be focused on degradable polymers, the reusability of extraction sorbent, and the minimization of extraction steps involving disposable materials.

PLA, PCL, and PHB are promising biodegradable polymers for nanofiber preparation. They can then be used in medical applications due to their excellent biocompatibility [71]. PLA is an emerging biodegradable polymer for filter and membrane production that has been proposed to replace polypropylene with comparable filtration efficiency [60,61]. PLA has also been studied as an extraction sorbent,

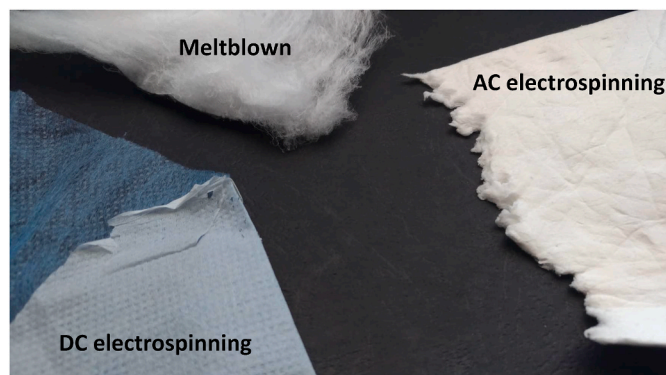


Fig. 2. Comparison of fiber mats produced by different techniques.

especially in combination with other materials, such as MOF, which increase the porosity and surface area of the nanofibers [72].

Nectoux et al. reported that PCL can be used for the extraction of lipophilic compounds because it is more hydrophobic than more common polyamide 6 due to the ester functional group and the longer carbon chain [73]. Raabová et al. and Kholová et al. came to similar conclusions in their comparison of different polymeric nanofibers, focusing on their selectivity with respect to the lipophilicity of the analytes and matrix ballast cleanup efficiency. PCL and PHB were more effective for lipophilic analytes with a log P greater than 2 [74,75]. On the other hand, PLA is a much more hydrophilic polymer, and its electrospun nanofibers are slightly less mechanically stable under high pressure [75].

Poly(vinyl alcohol) (PVA) is also biodegradable but water soluble. Therefore, stable preparation of nanofibers is challenging, and cross-linking via thermal treatment and esterification is necessary to avoid their rapid dissolution in aqueous samples [65,76].

3.3. Stability of synthetic polymer sorbents

When using polymer nanofibers as extraction materials, their selectivity based on chemistry is a keystone for their selection. Today's polymer chemistry offers an almost infinite variety of materials with different chemical compositions. Another issue to consider is their stability. For example, the chemical stability in a range of organic solvents and pH values, thermal stability, strength under pressure in flow system can significantly affect their applications options in SPE, formats, and desorption solvents. A careful study of the fibers and the mats stability is essential at the beginning of the development of an extraction procedure to avoid nanofiber dissolution, significant swelling, and/or collapse of the nanofiber mat structure.

Stability is typically determined by immersing a piece of a mat in various solvents for 24 h, drying it, and measuring the weight loss. This can be caused by simple dissolution of the polymer or by solvolysis of the polymer chains. It is also useful to control the effect of elevated temperature at the same time. Common solvents that are typically tested for SPE include methanol, acetonitrile, water, acidic, and basic solutions. All of the polymers shown in Fig. 3 do not change in the pH range of 2–11. Most of the polymers, such as polystyrene (PS), polyethylene (PE), polypropylene (PP), polypropylene (PP), polyacrylonitrile (PAN), and PVDF are also stable in all the mentioned solvents. PCL nanofibers dissolve in acetonitrile when the temperature is raised above 30 °C. Therefore, it is desirable to work at 20 °C [58] or to avoid acetonitrile altogether [62]. In our preliminary studies, nanofibers electrospun from long-chain heteropolymides, such

as semi-aromatic PA 6(3)T made of trimethyl hexamethylene diamine and terephthalic acid, dissolved in methanol, which was even visible to the naked eye (unpublished results, Fig. 4C). In contrast, the biodegradable polymers PCL, PLA, and PHB can be solvolyzed. We also observed significant size shrinkage of polyurethane (PUR) disks in methanol, preventing their use in centrifuge filters (Fig. 4B). This can be explained by the methanolysis of PUR to methylcarbamate as described by Asahi et al. [77].

Our experience is that long-term stability, as demonstrated with the shelf life of dry nanofiber mats, is generally not an issue, except for AC spun nanofibers due to the higher solvent residue in the fibers.

Synthetic polymers feature good mechanical stability, which is sufficient for conventional SPE. High pressure resistance is important for sorbents packed in cartridges used in flow systems or for on-line coupling to an HPLC analytical column, where the back pressure is typically well above 10 MPa. Extraction efficiency decreases rapidly as the nanofiber mat structure collapses (Fig. 4A). In particular, loss of the mat structure has been reported for PVDF [58], PLA [75], and PS [19] nanofibers. The fibers in the collapsed structure are compressed close to each other and this effect blocks effectively accessibility of the fiber surface. Effects that cause the collapse of the fiber and mat shapes observed at the microscopic level can include swelling, crystallinity, and glass transition temperature T_g of polymers introduced by the pressure translated into the frictional heat in the holder or cartridge, causing their structure relaxation and increase in solvent permeability [78]. In fact, the effect of T_g , which is an important property of the polymers used for the preparation of nanofibers, is largely neglected in the analytical literature. It simply indicates whether the fibers are hard and brittle at typical working temperatures, such as PS and PAN with T_g +90 and +95 °C, respectively, or soft and flexible such as PE and PP with T_g –100 and –25 °C, respectively. Obviously, mats made of the former would tend to shatter under high unilateral pressure, whereas the latter will be compressed and relax again after the pressure is released.

4. Modifying nanofibers

Recent nanofiber sorbents based on synthetic polymers are presented in Table 1. Following current trends, polymers are mostly enriched with different types of nanoparticles, serve as carriers and spinnable fillers in composite fibers, and their surfaces are coated and functionalized. All the modifications enhance various sorbent features such as selectivity, surface area, wettability, and robustness. In general, typical polymers provide only non-specific interactions with a range of pronounced hydrophobicity according to the length of the carbon chain, which can be

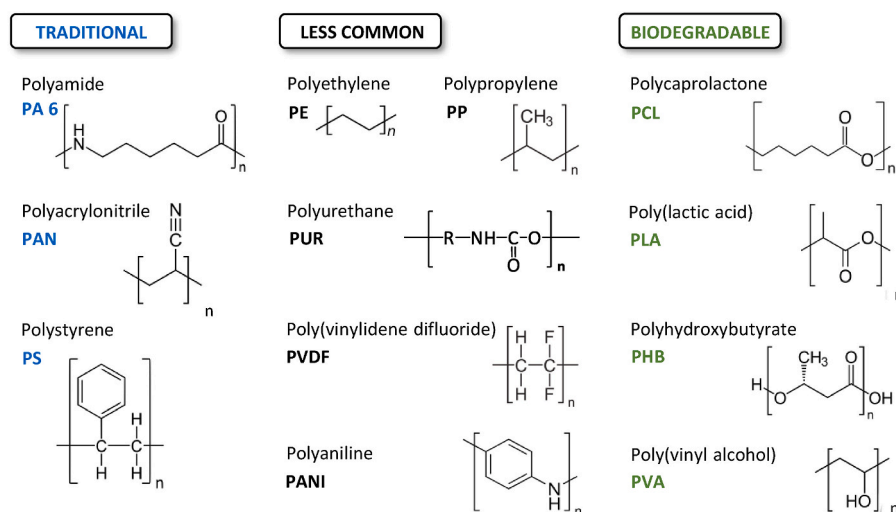


Fig. 3. Examples of synthetic polymers suitable for nanofiber preparation.

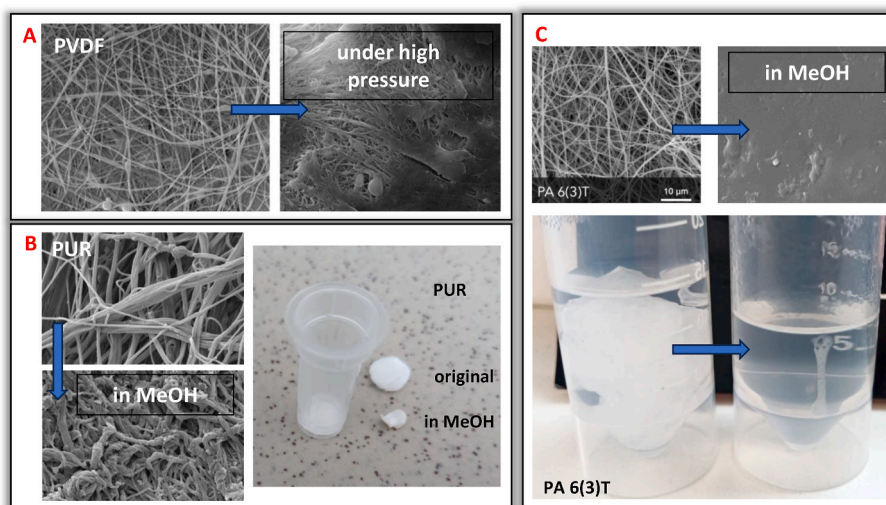


Fig. 4. Changes in shape of polymer nanofibers under pressure and in solvents. Collapse of the PVDF nanofiber structure under high pressure (A), PUR disk shrinkage in methanol (B), Dissolution of PA 6(3)T in methanol (C).

accentuated by lipophilic halogens, and/or aromatic rings providing π - π interactions. The presence of polar functional groups in the polymer allows for dipole-dipole and hydrogen bonding interactions. The most common polymers and their structures are shown in Fig. 3. Introducing carbon modifiers, molecular imprinting, phenolic coating, or simply combining polymers and fabrication techniques significantly changes their nature.

4.1. Blends and composite fibers

Polymer-polymer composites were studied to improve the properties of a single polymer. Chemical preparation of composites involves complex synthetic schemes, while a mechanical combination is less problematic and applicable for a broader range of polymers. There are the following possibilities: a physical blend of polymers, coaxial electrospinning of coated core-shell fibers, and mixed fibers via co-electrospinning or meltblown/electrospinning combination [19].

Tahmasebi et al. prepared nanofibers from a blend of conductive polyaniline (PANI) with high molecular weight PCL, enabling better spinnability of PANI [79]. Zatrochová et al. studied several blends of PHB and PP [62]. A compromise between more fixed fibers in the mat with a higher PP ratio but increased contact angle and reduced wettability needed to be solved, as well as a shift in selectivity towards model analytes. Similarly, composite fibers with adjusted selectivity were prepared with additives to the polymer before fabrication. Fang et al. used phytic acid as a chelating agent for the selective extraction of heavy metal ions [80]. Mehrani et al. tested aloin, rosin, and their combination into PAN to increase hydrophilicity, lipophilicity, or both in balance, respectively [81].

Combining different fabrication techniques provides interesting mixtures of fibers. Using meltblown-co-electrospinning, meltblown robust fibers serve as a scaffold for the more fragile electrospun fibers with smaller fiber diameters, thus increasing specific surface and extraction capacity at maximal robustness [58,74]. Xu et al. prepared a composite fiber filter in two sequential steps. PA nanofibers were afterward electrospun on a meltblown PE scaffold, providing better air and heat circulation [35]. Presley et al. produced core-shell nanofibers via coaxial electrospinning of two different polymer mixtures to ensure higher durability with the shell coating on fibers [82].

4.2. Hybrid fibers

A wide range of additives including fillers like carbon nanotubes or

various nanoparticles, specified further in the text, can be dispersed in the polymer solution and electrospun into nanofibers. These hybrid fibers have a larger surface area as the fiber surface becomes rougher, as can be seen in Fig. 5. Typically, inorganic nanoparticles can be the option, such as SiO₂ [83] or metals [44]. The modifiers also typically alter the selectivity of the fibers, as demonstrated with the incorporation of molecularly imprinted polymer particles [84]. Carbon-based additives typically increase the non-specific hydrophobic interaction as observed, for example, with the multi-walled carbon nanotubes [85], graphene [51], and graphene oxide [86]. Magnetic nanoparticles allow the sorbent to be fished out of the sample utilizing magnetic capture [87]. The polymeric nanofiber scaffolds can also be essential for holding particles such as MOF [72,88,89] and COF [90–92] to facilitate their handling in samples.

4.3. Coated fibers

Coating is a post-preparation modification of the nanofiber surface. For example, polydopamine polymerized in system containing the fibers was used for functionalization with hydroxy groups [83]. Deng et al. coated nanofibers by in situ polymerization of 3,4-ethylenedioxythiophene [93], while Jian et al. coated with sulfonated polyaniline [94]. Chen et al. functionalized the nanofiber surface with ionic liquid to endow them with abundant functional groups that participate in the retention mechanism [95]. Polyphenolic compounds such as heparin, hesperidin, and tannin have been proposed for simple dip-coating modification of the nanofiber surface to increase the retention for polar analytes and water wettability [74,75].

5. SPE formats

The major objective of this review is to summarize the current knowledge related to recent applications using synthetic polymer nanofibers as extraction sorbents followed by the solvent elution/desorption (SPE formats illustrated in Fig. 6). The extraction technique and format of nanofibers for the application is determined by (a) the type of sample/matrix, (b) the sample volume, whether preconcentration from a large volume or in miniaturized systems, (c) the number of samples to be handled, i.e. sample throughput in parallel runs and use of automated on-line approach, (d) cost, reusability, disposable material, (e) time and labor consumption, and (f) the 3D structure of nanofibers allowing easy handling and sufficient mechanical stability, which largely depends on the fabrication technique.

Table 1
List of polymer-based nanofiber sorbents reported within 2019–2024.

Polymer	Modification	Coating/hybrid/composite	Fiber formation	Format	Ref.
PAN	Postfabrication modification	Poly(3,4-ethylenedioxythiophene) coating by in situ polymerization	Electrospinning	Nanofiber mat, packed in SPE cartridge	[93]
PAN	Postfabrication modification	In situ chemical oxidation polymerization of 3-sulfoaniline and aniline (preparation of sulfonated PANI)	Electrospinning	Nanofiber mat packed in a cartridge	[94]
PAN	Postfabrication modification	Functionalization with ionic liquid 1-allyl-3-methylimidazolium chloride	Electrospinning	Nanofiber mat packed in a cartridge	[95]
PS	Nanoparticles in a spinning mixture, postfabrication modification	SiO ₂ nanoparticles in polymer, polydopamine coating by in situ polymerization	Electrospinning	Nanofiber mat packed in steel guard column	[83]
PAN	Nanoparticles in a spinning mixture	Covalent organic frameworks	Electrospinning	Nanofiber mat packed in a pipette tip	[90]
PAN	Nanoparticles in a spinning mixture	Covalent organic frameworks	Electrospinning	Nanofiber mat packed in a pipette tip	[91]
PAN	Nanoparticles in a spinning mixture	Covalent organic frameworks	Electrospinning (needleless)	Nanofiber mat	[92]
PAN	Nanoparticles in a spinning mixture	MXene - transition metal carbide Ti ₃ C ₂ T _x	Electrospinning	Nanofiber yarn packed in column	[96]
PAN	Nanoparticles in a spinning mixture	Agar + Ag nanoparticles	Electrospinning	Nanofiber thin film	[66]
PAN	Nanoparticles in a spinning mixture	Metal-organic framework with graphene oxide composite nanoparticles	Electrospinning	Nanofiber mat packed in steel guard column	[88]
PLA	Nanoparticles in a spinning mixture	Metal-organic framework with carbon	Electrospinning	Nanofiber sorbent	[89]
PBT	Nanoparticles in a spinning mixture	Magnetic nanoparticles Fe ₃ O ₄	Electrospinning	Nanofiber magnetic thin film	[87]
PS	Nanoparticles in a spinning mixture	Crown ether poly(dibenzo-18-crown-6)	Electrospinning	Nanofiber mat packed in steel guard column	[97]
PS	Nanotubes in a spinning mixture	Multi-walled carbon nanotubes	Electrospinning	Nanofiber mat, packed in SPE cartridge	[85]
PUR	Nanoparticles in a spinning mixture	Graphene oxide	Electrospinning	Nanofiber mat packed in a syringe filter holder	[86]
PAN	Nanoparticles in a spinning mixture	Molecularly imprinted polymers	Electrospinning	Nanofiber membrane wrapped on stir bar	[84]
PVDF	–	–	Electrospinning	Nanofiber membrane wrapped on Pt electrode	[98]
PAN	–	–	Electrospinning	Nanofiber membrane deposited on stirrer shaft	[99]
PCL, PA6	–	–	Electrospinning	Nanofiber membranes packed in SPE support	[73]
PANI + PCL	Composite blend nanofibers	Blend of conductive polymer PANI with high molecular weight polymer PCL	Electrospinning	Nanofiber membrane on chip	[79]
PLA + cellulose	Composite nanofibers	Metal-organic framework	Electrospinning	Nanofiber thin film	[72]
PUR	Composite nanofibers	Phytic acid (chelating agent)	Electrospinning	Nanofiber membrane	[80]
PAN	Composite nanofibers	Aloin and/or rosin	Electrospinning	Nanofiber mat packed in syringe	[81]
PA6	Composite nanofibers	Polymer deep eutectic solvent polyacrylic acid + arginine	Electrospinning	Nanofiber mat	[100]
PVA	Composite nanofibers, postfabrication modification	Citric acid + chitosan + aloe vera, thermal treatment and esterification for stabilization	Electrospinning	Nanofiber thin film	[65]
PVA	Composite nanofibers, postfabrication modification	Citric acid + β-cyclodextrin + Bi ₂ S ₃ @g-C ₃ N ₄ nanoparticles, thermal treatment and esterification of fibers for stabilization	Electrospinning	Nanofiber thin film	[76]
PCL	Core-shell nanofibers	PCL/gelatin/porphyrin chromophore as core with PCL shell	Coaxial electrospinning	Nanofiber sensor	[82]
PA6	–	–	DC and AC electrospinning	Nanofiber mat packed in steel guard column	[48]
PEO	–	–	DC and AC electrospinning	Nanofiber mat	[46]
PCL	Nanoparticles in a spinning mixture	Graphene	AC electrospinning	Composite disks	[51]
PEO, PS, PIB	Nanoparticles in a spinning mixture	PEO + carbon nanotubes, Au nanoparticles, AlFe nanoparticles	AC electrospinning	Nanofiber mat	[44]
PHB/PP	Composite nanofibers	Polymer blend	Meltblown	Microfiber disks	[62]
PLA, PUR	–	–	Meltblown	–	–
PCL	Composite nanofibers	–	Meltblown-co-electrospinning	Nanofiber mat packed in steel guard column	[74]
PCL	Composite nanofibers, postfabrication modification	Polyphenolic coating (dopamine, dopamine + heparin, tannin)	Meltblown-co-electrospinning	–	–
PE, PP, PHB, PLA	–	–	Meltblown	–	–
PE + PA	Two-step fabrication	PA nanofibers electrospun on PE metblown mat	Sequential meltblown and electrospinning	Composite filter	[35]

PA – polyamide, PAN – polyacrylonitrile, PANI – polyaniline, PBT – poly(butylene terephthalate), PCL – polycaprolactone, PE – polyethylene, PEO – poly(ethylene oxide), PHB – polyhydroxybutyrate, PIB – polyisobutylene, PLA – poly(lactic acid), PP – polypropylene, PS – polystyrene, PUR – polyurethane, PVA – polyvinyl alcohol, PVDF – polyvinylidene difluoride.

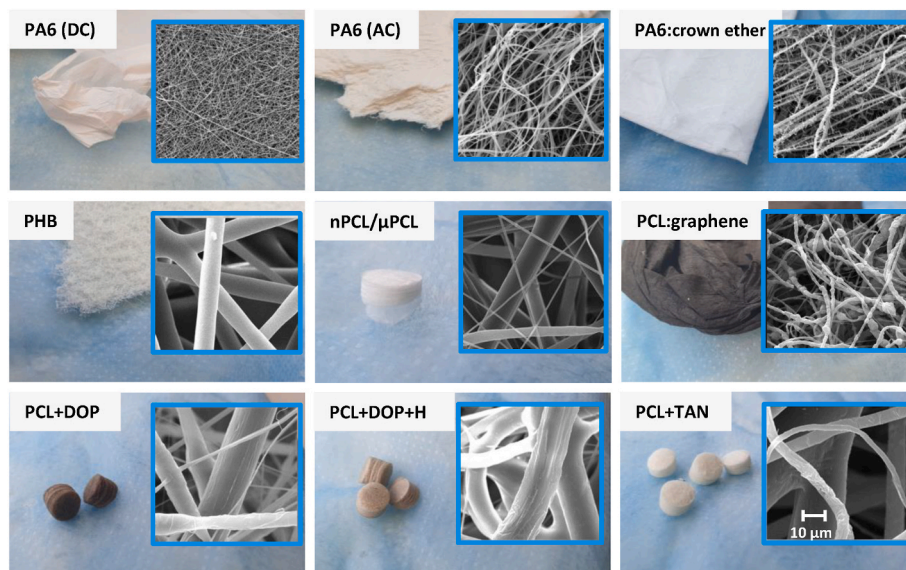


Fig. 5. Modifications of nanofibers illustrated by photographs and SEM images. Polyamide nanofibers prepared via DC vs. AC electrospinning (PA6 DC, PA6 AC); hybrid fibers with crown ether (PA6:crown ether); meltblown polyhydroxybutyrate (PHB); polycaprolactone composite nanofibers (μ PCL/nPCL); hybrid fibers with graphene (PCL:graphene); nanofibers coated with dopamine, dopamine + heparin, and tannin (PCL + DOP, PCL + DOP + H, PCL + TAN).



Fig. 6. Nanofibers in formats suitable for extraction.

5.1. Column format for SPE

Traditionally, nanofibers have been packed into columnar formats, including SPE cartridges, syringe barrels, centrifuge filter holders, and pipette tips. More recently, their use has been extended to sorptive techniques, to stirred devices using a holder or a stir bar, and to free-standing layers. It is worth noting that numerous terms to describe the devices including nanofibers have been introduced in the literature, derived from terms typical of standard SPE, such as packed-fiber SPE [85,97], packed in-tube solid phase microextraction [96], in-syringe SPE [86], and microextraction in packed syringe [81]. Recent publications on the use of polymer nanofibers for extraction are listed in Table 2.

Similar to other SPE sorbents, the electrospun nanofiber mats are filled into polypropylene columns, cartridges, and syringe barrels. Compared to particle-based sorbents, the nanofibers are mostly formed as compact layers and, therefore, less prone to leakage from the cartridge.

Recently, Wei et al. extracted aflatoxins from milk using hybrid PS nanofibers with carbon nanotubes packed in a syringe barrel, achieving good recoveries of 80–96 % with RSD less than 8 % [85]. Chen et al.

prepared ionic liquid functionalized PAN nanofibers for the extraction of veterinary drugs from milk. For the preconcentration, cut roundels were layered in a cartridge to achieve a higher sensitivity compared to previous methods [95]. The rapid extraction of short-chain fatty acids from wastewater was reported by Deng et al. using only 5 mg of coated PAN nanofibers placed in an SPE cartridge [93].

Nectoux et al. used a standard SPE membrane holder, filled it with nanofiber mat, and used it to determine estril in lake water [73]. Nouri et al. incorporated the graphene oxide-doped PUR nanofibers into a syringe filter holder to preconcentrate aflatoxins from soybean extract [86]. Nanofibers packed into pipette tips were used as a miniaturized device for SPE pretreatment of food samples [90,91].

5.2. SPE hyphenation on-line to chromatography

Automated on-line SPE-HPLC systems were optimized to achieve the extraction and transfer all the extracted compounds from the SPE sorbent directly to an analytical column. In general, all the methods demonstrated excellent repeatability of the automated procedure and proved reusability of the polymer nanofibers, since the devices containing nanofibers were used for tens or even hundreds of extraction cycles. Their good mechanical stability under high pressure was crucial.

Several authors reported on-line applications of original composite nanofibers packed in a short steel cartridge or empty guard column (usually less than 1 cm) for microextraction to minimize the solvent consumption. For example, Chen et al. prepared PS nanofibers with silica nanoparticles and polydopamine coating for the extraction of polyaromatic hydrocarbons from urine. The extraction cartridge containing 4 mg of nanofibers was incorporated into the HPLC instead of an injection loop [83]. Chen et al. embedded crown ethers into PS nanofibers for the extraction of catecholamines from urine via a column switching system, coupling the packed extraction cartridge and the analytical column in an HPLC system [97]. Similarly, Erben et al. used column switching to test the novel AC-spun PA sorbent. Compared to its conventional electrospun counterpart, the AC-spun sorbent exhibited higher mechanical stability and easier fiber packing into a cartridge [48].

Amini et al. prepared PAN composite fibers with highly porous MOF-graphene oxide to facilitate sample passage. Chlorobenzenes were pre-concentrated from 5 mL wastewater or extract from soil and vegetables

Table 2
Recent applications of synthetic polymer nanofibers for sample preparation.

Sample preparation	Analytes	Matrix	Analytical method	Polymer nanofibers	Ref
SPE	Fluoroquinolones	Water, urine, serum	UPLC-MS/MS	PANI sulfonated	[94]
SPE	Short-chain fatty acids	Waste water and faeces	GC-MS	PAN coated	[93]
Packed-fiber SPE	Desloratadine, catecholamines, and cortisol	Saliva, urine, plasma	HPLC-UV/FLD	PS, PAN, acrylic resin	[103]
Packed-fiber SPE	Paracetamol, florfenicol	Milk	HPLC-UV	PAN functionalized	[95]
Concentric layered SPE	Rhodamine B	Chili	HPLC-FLD	PS	[104]
SPE/DLLME	Aflatoxins	Soybean	HPLC-FLD	PUR + GO	[86]
MEPS	PAHs and polar phenoxyacetic acid herbicides	Industrial, farm, and sea water	GC-FID	PAN + aloin and/or rosin	[81]
Pipette-tip SPE	Plant growth regulators	Watermelon	HPLC-DAD	PAN + COF	[90]
Pipette-tip SPE	Inorganic arsenic	Rice	HG-AFS	PAN + COF	[91]
Packed-in-tube SPME	Betablockers	Urine, saliva	HPLC-UV	PAN/MXene	[96]
Radical electric focusing SPE	Organic acids	Water	UV/Vis	PVDF	[98]
Electromembrane extraction	Aspirin, nalidixic acid, pravastatin, and rosuvastatin	Water, plasma	HPLC-UV	PANI/PCL	[79]
Molecularly imprinted membrane	Sulfonamides	Animal feed	HPLC-MS/MS	PAN	[84]
μ -QuEChERS	Pesticides	Vegetables	GC-MS	PA6/polyacrylic acid + arginine	[100]
Online SPE	PAH monohydroxy metabolites	Urine	LC-MS	PS/SiO ₂	[83]
Online packed fiber SPE	Catecholamines	Urine	HPLC-FLD	PS + crown ether	[97]
Online μ SPE	Chlorobenzenes	Water, soil, and food	HPLC-DAD	PAN + MOF/GO	[88]
Online SPE	Pharmaceuticals	Solution of bovine serum albumin, human serum	HPLC-UV/VIS	PE, PP, PLA, PHB, PCL with polyphenol coating	[74]
Online SPE	Bisphenols, butylparaben, fenoxycarb	River water	UHPLC-DAD	PA6	[48]
Mechanical stir bar sorptive extraction	PAH	Water	GC-FID	PAN coating on a stirrer shaft	[99]
3D printed magnetic stirring cages, semidispersive SPE	Bisphenols	Water	HPLC-DAD	PCL, PA6, PID, PS, PVDF, PAN, PE, PCL/PVDF, PCL/PCL	[102]
Thin film microextraction	Triazine herbicides	Water	GC-FID	PBT + magnetic nanoparticles	[87]
Thin film microextraction	Pesticides	Water, food	HPLC-UV	PVA/chitosan + aloe vera + citric acid	[65]
Thin film microextraction	Heavy metal ions	Water, rice	ICP-OES	PAN/agar + Ag	[66]
Thin film microextraction	Pesticides	Fruit, milk, honey, juice	GC-FID	PLA/cellulose + MOF	[72]
dSPE	Quinolizidine antibiotics	Food	HPLC-UV	PAN + COF	[92]
Stirred disks	Bisphenols, fenoxycarb, kadethrin, deltamethrin	Water	UHPLC-DAD	PHB, PP, PHB/PP, PLA, PUR, PAN, PCL + graphene	[62]

COF – covalent organic framework, DAD – diode array detector, DLLME – dispersive liquid-liquid microextraction, dSPE – dispersive solid phase extraction, FID – flame ionization detector, FLD – fluorescence detector, GO – graphene oxide, HG-AFS – hydride-generation atomic fluorescence spectrometry, ICP-OES – inductively coupled plasma optical emission spectrometry, MEPS – microextraction by packed sorbent, MOF – metal-organic framework, PAH – polyaromatic hydrocarbons, QuEChERS – quick, easy, cheap, effective, rugged, and safe, SPME – solid phase microextraction. Other polymer names abbreviations are listed in Table 1.

using 5 mg nanofibers in a packed cartridge, followed by elution into an injection loop and loading onto the analytical column after the valve switch to HPLC [88]. Horstkotte Šrámková et al. incorporated a nanofiber membrane into an in-line filter to achieve a larger cross-sectional area of 350 mm². The in-line filter holder was coupled to the HPLC via a flow system, which allowed a higher sample volume loading than the usual injection loops in the autosampler. They used their system for the preconcentration of neonicotinoid pesticides from river water [101].

Raabová et al. and Kholová et al. benefited from the fully automated and unified column switching SPE-HPLC system for broad selectivity studies comparing a large number of different polymers used for the preparation of nanofibers and fiber modifications to discover their effect on the extraction of compounds from a complex matrix [74,75]. Raabová et al. also described the restricted access material functionality of composite PCL nanofibers, which allowed direct injection and analysis of protein-containing matrixes in an on-line SPE-HPLC system [59].

5.3. Sorptive techniques

5.3.1. Stirring devices

Sorptive techniques involve immersing of a sorbent in a sample for a period of time to ensure that the desired equilibrium of the analyte adsorption is achieved. Stirring the extraction device facilitates mass transfer driven by diffusion towards the sorbent and reduces the time for the preconcentration step. Cui et al. wrapped a membrane, which was formed from nanofibers doped with molecularly imprinted

nanoparticles, on a stir bar and achieved high selectivity for sulfonamides in animal feed [84]. Mollahosseini et al. deposited electrospun PAN nanofibers onto a metal stirrer shaft. The coating life exceeded 200 cycles without any significant change in performance. The coated shaft stirred a water sample to extract polyaromatic hydrocarbons [99]. The rotational speed had to be optimized to avoid creating a vortex that would disrupt the contact of the sample with the stirring device. Horstkotte Šrámková et al. 3D printed a custom-designed holder that accommodated nanofiber mat and a stir bar. The holder was designed as a cage to ensure free contact with the sample. Several bisphenols were preconcentrated 8–20 times from spiked river and lake waters [102].

5.3.2. Free nanofiber layers

Thin film microextraction is a method in which a nanofiber film, a compact, thin layer with a large surface area for adsorption, is directly immersed in a sample. For example, Bagheri et al. immersed the poly (butylene terephthalate) nanofibers containing Fe₃O₄ nanoparticles to extract triazines from water and recovered the fibers simply by a magnet [87]. Kandeh et al. prepared PVA composites with chitosan and aloe vera for thin film microextraction of pesticides from water and food [65]. Later, Hosseini et al. enriched PVA nanofibers with β -cyclodextrin and graphitic carbon nitride-Bi₂S₃ composite nanoparticles for the isolation of antidepressants from human plasma and urine [76]. Vosough et al. doped PLA and cellulose nanofibers with MOF to increase the surface area and porosity of the film sorbent for the extraction of pesticides from fruit, milk, and honey [72].

AC electrospinning results in nanofibers in thick compact layers. Zatrochová et al. and Lhotská et al. cut small disks from these materials and stirred them directly in water for preconcentration of environmental contaminants. In-vial elution was carried out by shaking the disk in solvent located in an HPLC vial that was placed directly into an auto-sampler with the extraction disk staying securely at the bottom, out of reach of the sample aspiration needle. This step reduced manual handling, reconstitution, and samples transfer [51,62]. Compared to the previous methods using a stirring device, this approach allowed use of only a small amount of nanofiber mat, thin film, or disk, followed by desorption into a very small volume of solvent.

6. Conclusions and outlook

The potential in polymer nanofibers as extraction sorbents can be seen in all three directions covered in this review: (i) use of new advanced polymers, (ii) modifications of the fibers, and (iii) their applications. First, the research should focus on biodegradable polymers in compliance with current concerns about environmental friendliness and sustainability. Similarly, innovations in nanofiber production are inevitable to avoid excessive use of harmful organic solvents. For example, there is growing interest in the electrospinning of organosilanes into fibers as promising tunable organic-inorganic hybrid materials. Molecular design allows the selection of prospective organosilane molecules according to the desired mechanical properties and selectivity of the final sorbent. Still, the preparation of spinnable sol-gels remains challenging and needs to be optimized to provide environmentally friendly fibers [105].

Polymers mainly provide nonspecific hydrophobic interactions, and some feature poor water-wettability. Thus, their modifications are often necessary to change the selectivity and surface characteristics. We can witness a burst of nanofiber modifications in the literature. New materials that can be incorporated into the fibers or to decorate them remain to be explored to modify the fiber properties. Incorporation of nanoparticles into polymer nanofibers seems to be a promising approach to change their surface chemistry and selectivity. Currently carbon-based materials and MOF dominate, but, for example, crown ethers with their donor oxygens and electrostatic interactions could open new avenues leading to fibers with unexpected properties and applications. Selectivity towards polar compounds remains a shortcoming of current polymer sorbents. The electrodeposition of metal crystals on conductive polymers, such as PANI or highly graphene-doped fibers, is also worth investigating. Modifying nanofibers still inspires researchers to discover original sorbents with higher adsorption capacity, increased selectivity, and excellent adsorption kinetics.

All these new materials enable original applications of nanofiber sorbents, including miniaturized SPE techniques, but also support-free handling of nanofiber mat in a sample followed by solvent desorption and chromatographic analysis. Polymer nanofibers can also serve as a solid support in supported liquid-solid phase extraction. Our preliminary tests with octanol-wetted discs showed significantly improved extraction of organic pollutants from water. Finally, although nanofiber materials are well established in the extraction followed by thermal desorption or elution with standard solvents, their use under supercritical fluid conditions remains unexplored. Supercritical CO₂ is an excellent green solvent that can solve the problem of instability of some polymers in organic solvents or water in the desorption step.

The above lines show that a lot has been done in the field of sample preparation since the introduction of nanofibers in the sample preparation arena about a quarter century ago. However, with the growing demand for the analysis of increasingly complex samples being available in ever smaller quantities with decreasing amounts of the compounds of interest, further exploration of new materials that will allow the preparation of designer nanofibers and their new applications is inevitable. This review aimed to highlight the avenues opened for further research in the field of sample preparation using nanofibers.

CRedit authorship contribution statement

Ivona Lhotská: Writing – review & editing, Writing – original draft, Visualization, Investigation, Data curation, Conceptualization. **Aneta Kholová:** Visualization, Investigation. **František Švec:** Writing – review & editing, Supervision, Conceptualization. **Dalibor Šatínský:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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