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# Nanofiber-based sorbents: Current status and applications in extraction methods

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## ABSTRACT

Advanced sorbents gradually become a research hotspot on account of the increasing attention paid to environmental problems. Due to the prominent physicochemical features of nanofibers (NFs), such as high porosity, large surface area, favorable interconnectivity, high adsorption capacity, wettability, and the possibility of surface modification using functional groups, these nanostructures are regarded as excellent candidates for extraction applications. Therefore, the research in the field of NFs and their nanocomposites has been increasing in recent years. In the present review, we summarize the most recent studies on NFs-based sorbents focusing on strategies for preparation, characterization, and their unique capabilities as porous sorbents in various sorbentbased extraction methods. Moreover, we further described the performance and selectivity of sorbents to achieve improved extraction efficiency. Finally, some perspectives on the challenges and outlook are provided to aid future investigations related to this topic.

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## 1. Introduction

Although there are currently many analytical tools and modern techniques used to determine the presence of very low concentrations directly, the analysis is still difficult in many cases [1]. This is not only due to the insufficient sensitivity of the methods, but the main reason lies in matrix interferences [2]. It should be noted that to overcome these problems, sample preparation is still necessary before the analysis [3–7]. Up to now, there are some reports about sample preparation in our groups [8–10].

Among the available procedures, sorbent-based extraction methods are considered. In general, it can be stated that the main needs of sorbent materials include chemical stability, rapid adsorption and elution, and high adsorption capacity. Various nanomaterials, such as carbon nanotubes (CNTs) [11], molecularly imprinted polymers (MIPs) [12], MXene [13], magnetic nanoparticles [14], silica [15], metal-organic frameworks (MOFs) [16], covalent-organic frameworks (COFs) [17], and zeolites [18] have been used in sample preparation. Moreover, it can be mentioned that NFs materials with high porosity, selective wettability, high aspect ratio, large specific surface area, and multi-porous structures, as well as unique chemical, mechanical and physical functions, and ease of manufacturing [19], may be suitable sorbents in extraction techniques such as solid-phase extraction (SPE), dispersive solid-phase extraction (d-SPE), magnetic solid-phase extraction (MSPE), and solid-phase microextraction (SPME). By modification of NFs with different functional groups like amino  $(-NH_2)$ , carboxyl (-COOH) and hydroxyl (-OH) groups or by hybrid sorbents, such as silica, carbon nanomaterials (CNMs), metal oxides, MIPs, zeolites, MOFs, and COF in/on NFs, the extraction capacity and selectivity can be significantly improved.

According to a large number of articles and studies that describe innovations in the field of NFs, including functionalization, preparation, and their use in sorbent-based extraction methods [20], the present review identifies only the main contributions that have emerged over the past decade and also summarizes and critically reviews the present trends resulting with novel extraction characteristics.

# 2. Synthetic strategies for NFs

Different strategies have been developed for the synthesis of NFs, ranging from current methods (*e.g.*, electrospinning [21], self-assembly [22], sonochemical [23], polymerization [24] and template-based synthesis [25]) to emerging strategies (*e.g.*, CO<sub>2</sub> laser supersonic drawing [26], solution blow spinning [27], centrifugal jet spinning [28], and electrohydrodynamic writing [29]). Due to the electrospinning method

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being one of the most established and widely adopted techniques, we thoroughly investigated it in detail.

## 2.1. Electrospinning

The electrospinning technique is used to prepare NFs from a polymer solution or melts under an electric field, which results in the production of NFs with controllable morphology. As can be seen in Fig. 1, in general, conventional electrospinning devices have several parts: a syringe pump, polymer solution, spinneret system (uni-, co-, tri-axial), a liquid jet, a high-voltage power supply, and collectors. First, the pump forces the polymer solution inside the syringe towards the high-voltage electric field and the polymer solution to be charged, leading to rapid movement and transfer to the collectors and overcoming surface tension and viscoelasticity. Then, the collector will receive the NFs after the solvent evaporates by a liquid jet. The morphology of the formed NFs in these conditions will be different depending on the type of technique used [30], multi-needles electrospinning (smooth) [31], bubble electrospinning (porous) [32], co-axial electrospinning (core-shell and hollow) [33], tri-axial electrospinning (core-shell and hollow) [34], and emulsion electrospinning (smooth) [35].

In polymer solution, there are several effective factors, such as solvent type [36], the molecular weight of polymer [37], and polymer concentration [38], which lead to the preparation of uniform and stable NFs with various diameters. Also, the design of the collector and spinneret directly affects the morphology and structure of NFs [39,40].

# 2.2. Functionalization of NFs

Functionalization is regarded as the most convenient technique used to modify physicochemical characteristics, extraction efficiency, and selectivity of the NFs via surface modification. These processes can be performed in two ways: the first method is a one-step operation that can occur during electrospinning. The second method is related to subsequent treatments that can occur after electrospinning (Fig. 2) [41].

#### 2.2.1. One-step modification

The properties of polymer NFs can be improved by mixing one polymer with another and in certain proportions, which can be applied in one step [42]. These properties are added to the ratio, surface energy, and also to the ratio of the molecular weight of the polymer, which depends on the solvent. Thus, the composition of a polymer containing functional groups with hydrophobic polymers, such as poly(vinylidene fluoride) (PVDF) [43], polystyrene (PS) [44], and poly(ethylene terephthalate) (PET) [45], plays a key role in tuning its hydrophilicity and increasing the number of active adsorption sites and also decreasing the cost.

#### 2.2.2. Post-treatment methods

The post-treatment of surface functionalization is applicable through four procedures: wet modification, surface coatings, grafting, and plasma-induced grafting.

2.2.2.1. Wet modification. Polar functional groups are created through hydrolysis processes as well as aminolysis processes [46]. The studies are predominantly concentrated on the introduction of sulfhydryl (–SH), –OH, –COOH, –NH<sub>2</sub>, amidoxime (=NOH) groups, *etc.* In the –NH<sub>2</sub> group, the nitrogen atom is a strong electron donor, which is attributable to its lone pair electrons to modify the surfaces of PET NFs chemically [47,48]. In addition,–COOH groups have strong chelation ability as sorbents, so it is important to note that –COOH functionalization at the NFs level can enhance their adsorption efficiency effectively [49]. Furthermore, in general, multiple co-existing functional groups on the surface of NFs are capable of achieving synergistic adsorption.

2.2.2.2. Surface coating. Surface coatings occur through the delivery of materials applied to the surfaces of NFs, the layer thicknesses of which range from a few nanometers to a few micrometers. In addition, the type of bond formed between them is in the form of physical bonds, including electrostatic, hydrogen bonds, and  $\pi$ - $\pi$  stacking. Surface properties, such as adsorption capacity, polarity, hydrophilicity, as well as homogeneity properties of coating materials, and layer thickness are important items for processing this procedure. In addition, it should be noted that the coating method can be accomplished through a variety of processes, such as NFs immersion processes that are in solution, self-assembly, layer-by-layer, and polymerization on the NF surface. For instance, the surface of poly( $\varepsilon$ -caprolactone) (PCL)/ polyethylene oxide (PEO) NFs was coated via an *in-situ* oxidation process through the self-polymerization of polydopamine (PDA) [50].



Fig. 1. An electrospinning setup with conventional spinneret systems utilized in electrospinning, the morphology of electrospun fibers, and the collector types. Reproduced from [123] with permission.



Fig. 2. . Preparation and surface modification of different NFs.

2.2.2.3. Surface grafting. Grafting is an effective method used to enhance the surface characteristics of NFs, and their capability to absorb ionic contaminants through the introduction of a variety of functional groups [51]. Such a process is conducted by two techniques of grafting-from and grafting-onto. The grafting-from requires initiators to be created onto the surface of the NFs, which are producible by wet chemistry, plasma, treatment with ultraviolet radiations, or through the incorporation of initiators onto the surface of NFs in the course of electrospinning [52]. In contrast, the grafting-onto method necessitates pre-polymer preparation followed by its subsequent reaction with the surface of NFs [53].

2.2.2.4. Plasma-induced grafting. Plasma is regarded as a posttreatment technique utilized to increase the frequency of adsorption sites on the surface of NFs [54]. The plasma treatment is dependent on employing the ionized gases to generate polar functional groups (for example, -COOH, -OH,  $-NH_2$ ) onto the surface of NFs [55].

#### 3. Selectivity of different NFs-based sorbents

The selectivity of different NFs-based sorbent materials plays a significant role in extraction applications. Over the years, various sorbent modification strategies have been employed to induce selectivity based on acidity, basicity, polarity, size, and molecular recognition of analytes.

(1) Selectivity based on ion exchange: A wide range of modification processes can be used to highlight the great potential of electrospinning as a fabrication technique for selective sorbents. For example, copolymerization PS produced different copolymer nanofibers and the extraction results for different chemistries of analytes indicated that PS, poly(styrene-co-*p*-sodium styrene sulfonate), and poly(styrene-co-methacrylic acid) nanofibers have selectivity based on hydrophobicity for non-polar analytes, strong cation exchange properties for basic and neutral analytes, nespectively. Due to the ease of spinnability of PS copolymers and the demonstrated performance of the resultant fibers as sorbents, a wide range of functionalities can be introduced on the PS backbone by an experimental approach that involves copolymerization and electrospinning [56].

- (2) Selectivity based on polarity: Another possible way to selective separations is the incorporation or immobilization of some molecules such as Cibacron blue F3GA (CB) [57] into/onto the surface of the nanofibers by a covalent bond. For example, the novel polysulfone (PSU) nanofiber mat showed higher water permeability than commercially available microporous membranes as well as good capturing for bovine serum albumin (BSA). In addition, CB is a dye ligand for the purification of many enzymes and blood proteins like BSA due to its widespread. Therefore, CB was attached to the PSU fiber surface by covalent bond formation with the amino groups to show better performance. This functionalization opens up possibilities for fabricating sorbent material in which hydroxyl (normal phase property for polar analytes), carboxyl (weak cation exchange property for strong bases), and amino (weak anion exchange property for strong acids) functionalities.
- (3) Selectivity based on the incorporation of molecularly imprinted polymers: Through electrospinning, it is possible to incorporate the selectivity of MIPs either by encapsulating MIP nanoparticles into electrospun nanofibers or by imprinting the electrospun fibers. For example, the encapsulation of molecularly imprinted nanoparticles into some nanofibers like PET through electrospinning is used as a sorbent material for batch solid phase extraction of propranolol. As confirmed by radio ligand binding analysis, the specific binding sites in the composite nanofibers remained easily accessible and were chiral-selective. The results demonstrated that without the electrospun nanofiber-based solid phase extraction step, the existence of propranolol residues in water could not be confirmed even with the sensitivity of HPLC-MS/MS analysis [58].

#### 4. NFs as sorbents in analytical applications

The determination and identification of the trace levels of analytes in different samples require sample preparation and/or extraction methods. Because of the relative trace level of some analytes, the complicated matrices nature and to achieve precise and accurate results, pretreatment and preconcentration procedures are necessary before instrumental analysis. A new class of superior materials has now been made possible by the synthesis and introduction of NFs, which represents a significant advancement in sorbent-based extraction techniques. The design of NFs can be categorized into three groups: carbon NFs (CNFs), polymeric NFs, and composite NFs. These materials can be suitable as sorbents for the extraction of analytes in various shapes and sizes. The discussion that follows is about sorbent-based extraction techniques using NF-based sorbents in various extraction methods.

#### 4.1. Carbon NFs

CNFs are another class of CNMs with a diameter of 3-100 nm, and their typical structural forms are categorized as porous [59], helical [60], herringbone/stacked-cup [61], as well as tubular [62]. Amongst the whole techniques used for the synthesis of CNFs, electrospinning is the most facile and effective one, which is capable of producing CNFs of the diameters of 10 nm to 10 µm with a continuous and long structure. For example, the functionalized CNFs with β-CD (β-CD@CNFs) loaded into the polyethylene cartridge were utilized to extract the selected six nitroaromatic compounds (NACs) pollutants (3-nitrotoluene (3-NT), 1,3-dinitrobenzene (1,3-DNB), 2,6-dinitrotoluene (2,6-DNT), 4nitrotoluene (4-NT), nitrobenzene (NB), and 2-nitrotoluene (2-NT)) from aqueous solutions by off-line SPE procedure followed by highperformance liquid chromatography (HPLC) with UV detector. The present investigation selected  $\beta$ -CD as a coating agent over other polymers and saccharides due to its encapsulation capabilities [63], and given the hydrophobic natures of CNFs, it can transform NACs into a hydrophilic form so that they can be extracted. At least three different types of potential interactions exist that may occur between the NACs and  $\beta$ -CD@CNF sorbent, including (i) hydrogen bonding interactions between the hydrogen atom on the -OH group of the  $\beta$ -CD@CNF and the nitrogen atom of the NACs due to the hydrophilic nature of NACs and the hydrophilic exterior of  $\beta$ -CD, (ii) electrostatic interactions between the negative charge on the surface of  $\beta$ -CD and the cationic species of NACs, and (iii)  $\pi$ - $\pi$  interactions formed between the aromatic rings of β-CD functionalized on the CNF and the benzene rings of NACs [64].

#### 4.2. Polymeric NFs

Compared to many currently known materials, the notable characteristics of polymeric NFs are small pore size, high aspect ratio (length to diameter), high porosity, large surface area, optical transparency, suitable mechanical specifications (elastic modulus, tensile strength, toughness, stiffness), and high hydrophobicity surface, which make them more favorable compared to their macro-scale alternatives [65]. These NFs can be made from natural polymers (for example, cellulose, wool keratose/silk fibroin, chitosan), their derivatives (cellulose acetate), and synthetic polymers (e.g., PS, PA6, PAN) as homopolymeric NFs. For example, a comparison has been conducted between PA6, PVDF NFs, polyethylene microfibers (PE MFs), PCL, and PCL/PVDF polymers for the extraction of ochratoxin A (OTA) from beer. The results indicated that all polymer fibers were not mechanically and chemically stable enough when used alone, and their stability was significantly increased when used in combination with other polymers [66]. Due to the poor mechanical specifications, hydrophobic nature, and low adsorption capacity of homopolymers, which are spinnable and insoluble in water, their widespread applications for adsorption can be limited. In addition, the characteristics of the natural polymers, such as high inter- and intra-chain hydrogen bonding, high viscosity at low concentrations, low solubility in organic solvents, and swelling in aqueous mediums result in some challenges in their electrospinning process. To overcome these dilemmas and enhance the mechanical specifications of generated NFs, researchers have made great efforts to generate combined NFs as the substituent and efficient sorbents using the three techniques of functionalization, copolymerization, and blending. In the functionalization of polymer, synthetic polymers (i.e., PAN) can be modified by various functional groups and produce effective materials

for extraction. For example, hydrazine-modified PAN (HM-PAN) NFs were synthesized for extraction of three endocrine disrupting chemicals, including bisphenol A (BPA), nonylphenol (NP), and octylphenol (OP), from environmental samples by a homemade disk SPE device before HPLC coupled to tandem mass spectrometry (HPLC-MS/MS). Hydrazinolysis generates ion-exchanging amine groups in NFs and makes their extraction features more selective for estrogenic substances. The results of extraction showed their advantages as lower consumption of sorbent and organic solvent, higher precision, and improved repeatability. The suitable extraction efficiency of the HM-PAN NFs for NP, OP, and BPA is attributable to its -NH2 functional groups and large specific surface area [67]. The reusability of the sorbent is one of the important factors influencing the repeatability of the extraction and can be evaluated by carrying out several successive adsorption-desorption tests. For this sorbent, the reusability is an advantage compared with other SPE sorbents, which could be used seven times at least before being discarded with no significant statistical differences (P > 0.05) in the recoveries of the three analytes. Satisfactory recoveries of above 90% for all three compounds can be achieved at the seventh use. In another type, the combination of different types of polymers or copolymerization can bring about the desired functionalities. For instance, magnetic PVA/chitosan electrospun NFs have been introduced as new nanosorbents for the determination and extraction of acidic red dyes (Amaranth, Ponceau 4R, Allura red, Carmoisine, and Erythrosine) in juice samples using filled in-tube solid-phase microextraction (FIT-SPME) followed by HPLC-UV. In such a way, using the electrospinning technique, the wires made of stainless steel were coated with PVA as a safe co-polymer and chitosan as a natural polymer to obtain NFs featuring high surface area and porosity. Subsequently, the whole fibers were suited within the lumen of a stainless steel tube to prepare the extraction medium, and the results showed good dynamic linearity. In this device, there was no back-pressure during the extraction and desorption procedure so high flow rates were applied which led to an extensive reduction of the extraction time. Also using the electrospun fibers increased the contact surface area. The fibers also were physically stabilized by thermal treatment. The merit for the determination of the analytes such as LOD, LOQ, and the recovery rate was listed in Table 1. The intraday and inter-day RSDs (relative standard deviation) for the precision of the proposed method in three replicates indicated that FIT-SPME-HPLC-UV is acceptable and reliable [68].

In the third case, blends are physical mixtures of a variety of polymers, which hold them through noncovalent bondings, such as dipoledipole interactions and hydrogen bonds.

In 2017, ten types NFs blended with poly(dibenzo-18-crown-6) (PDB18C6) in different weight fractions were prepared as a sorbent for selective extraction of catecholamines in human plasma by SPE. The functionalized NFs packed in SPE columns at pH > 7, which containing 20% PS – 5% PDB18C6 = 5:2, v/v coupled with HPLC-electrochemical detection are capable of enhancing the extraction efficiency of the catecholamines with high reproducibility [69].

## 4.3. NF Composites

The incorporation of materials with significantly different physiochemical properties into the polymer NFs through the dispersion of them into the polymer solution followed by electrospinning is a suitable technique for improvement of the mechanical and surface specifications of polymer NFs and also their adsorption capacity. The most widely used materials for such incorporation include metal/metal oxide NPs, silica, CNMs, MIPs, MOFs, COFs, and zeolites that are utilized to modify the surface of polymer NFs and are applied to extraction methods.

## Table 1

Summary of NFs-based sorbents.

Sorbent	Extraction method	Analyte	Sample	Analytical technique	LOD	LOQ	Recoveries (%)	Mechanism adsorption	Refs.
PS	SPE	Diazinon, Fenitrothion	Water	HPLC-DAD	0.09 and 0.07 ng.mL <sup>-1</sup>	0.3 and 0.23 ng.mL <sup>-1</sup>	92.1 and 95.3	Hydrogen bonding interactions and hydrophobic effects	[135]
HM-PAN	SPE	BPA, NP, OP	Water	HPLC-MS/ MS	0.01–0.03 ng mL <sup>-1</sup>		84.6–101.9	Dipole-dipole electrostatic and Hydrogen bonding interactions	[79]
β-CD@CNFs	SPE	NACs	Water	HPLC-UV	3.8–23.1 µg.L <sup>-1</sup>	12.8–76.9 μg.L <sup>-1</sup>	32.6–102.2	Hydrogen bonding and $\pi$ - $\pi$ stacking interactions	[76]
PVA/Chitosan	FIT-SPME	Acidic red dyes	Juice	HPLC-UV	0.3–7.6 μg L <sup>-1</sup>	$125~\mu g~L^{-1}$		Dipole-dipole electrostatic and hydrogen bonding interactions	[80]
CuO/ZnO- chitosan NPs	SPE	Pesticides	Water	HPLC	0.002-0.046 µg.mL <sup>-1</sup>	0.006-0.154 μg.mL <sup>.1</sup>	31.2–93.88	Hydrophobic, hydrophilic effects and inclusion interactions	[84]
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> / PVA-TEOS	MSPE	SMZ and TMP	Drug	-	0.0317 and 0.0748 mg.L <sup>-1</sup>	0.104 and 0.247 mg.L <sup>-1</sup>	95.1 and 98.2	Electrostatic interactions	[87]
PS/graphene	TFME	Aliphatic aldehydes	Human exhaled breath condensates	TFME-HPLC	4.2–19.4 nmol.L <sup>-1</sup>	13.8–64.6 nmol.L <sup>.1</sup>	79.8-105.6	π-π stacking interaction and hydrophobic effects	[92]
PA/GO/PPY	SC-µSPE	Parabens	Milk	HPLC-UV	3-7 ng.mL <sup>-1</sup>	10-20 ng.mL <sup>-1</sup>	81.7–97.8	Hydrogen bonding, π-π stacking interactions and hydrophobic effects	[101]
PVA-PAA@CNT- CNC	PT-µSPE	OAs	Biological fluids	HPLC-UV	0.15–0.50 ng mL <sup>-1</sup>	-	87.3–97.8	Hydrogen bonding, π-π stacking interactions and hydrophobic effects	[91]
MI-ENFs-SPME	SPME	Chlorpyrifos	Fruits and water	SESI-IMS	0.1 μg.L <sup>-1</sup>	-	82–112	Hydrogen bonding interactions	[110]
PAN/Ni-MOF	HS-SPME	OPPs	Water and fruit juices	CD-IMS	0.3 and 0.2 ng.L <sup>-1</sup>	-	89–98	Hydrogen bonding, π-π stacking interactions and hydrophobic effects	[120]
PANI/SiO <sub>2</sub>	dSPE	FQs	Honey	LC-FLD	0.1-1.3 ng.g <sup>-1</sup>	0.4–4.3 ng.g <sup>-1</sup>	81.4–118.1	π-π stacking interactions and hydrophobic effects	[90]
MIR/PDA	SPE	SAs	Water	HPLC-MS/ MS	0.26-0.76 ng.L <sup>-1</sup>	1–2.60 ng.L <sup>–1</sup>	82.8–115.6	Hydrogen bonding interactions	[112]
PAN/UiO-66	PT-SPE	Phytohormone	Vegetable	HPLC-FLD	0.01-0.02 ng.mL <sup>-1</sup>	-	84.4–111.2	Electrostatic interactions	[119]
PAN/NH <sub>2</sub> -Zr- MOF	TFME	Chlorpyrifos	Agricultural wastewater and river water samples	CD-IMS	$0.6~\mu g.L^{-1}$	-	86–109%	Hydrogen bonding and $\pi$ - $\pi$ stacking interactions	[70]
PAN@SNW-3	PT-SPE	PGRs	Food	HPLC-DAD	0.24–3.19 ng.mL <sup>-1</sup>	1.65–5.72 ng.mL <sup>–1</sup>	82.8-113	Hydrogen bonding and $\pi$ - $\pi$ stacking interactions	[125]
PAN@COFs	SPME	OCPs	Water	GC	0.05–20 ng.L <sup>-1</sup>	0.1–100 ng.L <sup>–1</sup>	70.93- 116.38	π-π stacking interaction and hydrophobic effects	[127]
CCF@UiO-66- NH <sub>2</sub> @TpBD	PT-SPE	BPs	Water	UPLC	0.16–0.75 ng.mL <sup>-1</sup>	0.54-2.50 ng.mL <sup>-1</sup>	89.6–106.2	$\pi$ - $\pi$ stacking, Hydrogen bonding interactions, and hydrophobic effects	[129]
PAN/CP	SPME	PAHs	Agricultural water, rain and spring water samples	GC-FID	0.10-0.32 ng.mL <sup>-1</sup>	0.45–1.12 ng.mL <sup>-1</sup>	86 <	$\pi$ - $\pi$ stacking interactions	[133]

# 4.3.1. Metal oxide NPs/NF composites

Because of the limitations of chemical corrosion and dissolution at lower pH, the use of metal oxide NPs to extract analytes in acidic mediums is still challenging in experimental conditions. So, the metal oxides incorporated into polymeric NFs are capable of solving the low chemical stability and the corrosion issue of metal oxides. Also, the specific surface area of NFs and their adsorption efficiency can be significantly improved and the nanoparticles will possess great prospects in chromatographic analysis, especially SPE and SPME techniques [70]. For example, two new types of CuO- and ZnO-chitosan composites were prepared as sorbents used for the extraction of seven pesticides, i.e., diazinon, abamectin, imidacloprid, fenamiphos, methomyl, thiophanatemethyl, and lambda-cyhalothrin followed by HPLC. By compressing a frit located on the bottom, followed by the addition of sorbent and stopcock frit on the upper, the SPE cartridge was filled up with no gaps [71]. Then, different concentrations of each pesticide were passed through the SPE cartridge, and acetonitrile/methanol (1:1, v/v) was used to elute the adsorbed amount of each pesticide According to the results, the extraction performance of ZnO-chitosan exceeded that of CuO- chitosan. These authors also proposed a reversed-phase retention mechanism based on hydrophobicity, inclusion interactions, and also

weak hydrophilicity for the polar pesticides, including methomyl based on surface adsorption process and partitioning [72].

The combination of different amounts of Fe<sub>3</sub>O<sub>4</sub> and α-Fe<sub>2</sub>O<sub>3</sub> NPs with polymeric NFs can be used to generate new subtitle composites, namely magnetic NF composites. The embedding of Fe<sub>3</sub>O<sub>4</sub>/graphene NPs in PVA NFs significantly reduced diameters and increased thermal stability as compared to pure PVA NFs [73]. In addition,  $Fe_3O_4$  or  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NPs can be functionalized to avoid NPs agglomerations using polyethylenimine (PEI), (3 aminopropyl)triethoxysilane, polyethylene glycol, and TEOS before electrospinning [74]. Another work fabricated Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/PVA-TEOS nanofiber and successfully applied it for MSPE of some antibiotics including sulfamethoxazole (SMZ) and trimethoprim (TMP), which lead to producing the electrostatic and strong bond between -NH<sub>2</sub> group in antibiotics and aldehyde functionalized nanoparticles in the sorbent, and so gelatinous and swelling of nanofiber in water [75]. To verify the reliability and applicability of this sorbent, it was used for the extraction of drugs from some real samples including tap water and wastewater samples. The extraction results are given in Table 1. Due to the relative recoveries for SMX and TMP and RSDs less than 3.0% (n = 5), it was indicated a repeatability and sensitive method for the extraction and determination of SMX and TMP with high accuracy and an approximate probability of 0.95 (95%).

#### 4.3.2. Silica/NF composites

Given the low cost, good biocompatibility, and excellent chemical stability of the component  $SiO_2$ , in the course of the adsorption process, it shows no evident negative impact on the ecosystem. As a result, the  $SiO_2/NF$  composites have a widespread application prospect in analytical chemistry. In addition, it is a suitable nanofiller used to enhance the characteristics of NFs, including mechanical specifications, adsorption characteristics, and surface area. However,  $SiO_2/NF$  composites cannot be produced by electrospinning directly, but one can prepare a gel sample with suitable rheological characteristics for the electrospinning process [76].

PANI-coated SiO<sub>2</sub> NFs (PANI/SiO<sub>2</sub>) have been prepared in two steps. First, SiO<sub>2</sub> NFs were fabricated by electrospinning [77], and then it was utilized as templates for in situ polymerization of aniline monomers to acquire PANI/SiO2 NFs. PANI NPs could be dispersed uniformly on the surface of  $SiO_2$  NFs with no aggregation. Then, the as-prepared PANI/SiO<sub>2</sub> NFs were used as the sorbent for in-syringe dSPE to extract five fluoroquinolones (FQs), including cipro-floxacin hydrochloride, ofloxacin, enrofloxacin, difloxacin hydrochloride, and lomefloxacin from honey samples (FQs contain a piperazine substituent that is available as anionic, cationic, or intermediate forms in aqueous solutions resulting from the charged -NH2 and -COOH groups. As a result, one may attribute the high extraction performance to the considerable hydrophobic and  $\pi-\pi$  interactions between PANI/SiO<sub>2</sub> composite and FQs. The repeatability can be evaluated by the measurement of intra- and inter-day precisions, in which the results showed that the intra- and interday RSDs were less than 14.4% and 14.9%, respectively, and demonstrated good repeatability of dSPE coupled LC-FLD [78].

#### 4.3.3. CNM/NF composites

Over the years, there have been several developments in CNM-based NF composites for extraction methods, with the latest being CNMs, like CNTs [79], graphene [80], graphene-oxide (GO) [81], and activated carbon [82].

As a type of tubular CNMs, CNTs show excellent advantages, such as rich aromatic structure, large specific surface area, facile surface modification, and suitable chemical stability. Nonetheless, nanosized dimensions and high surface tensions of CNTs contribute to their aggregation, which limits their application when extracting a variety of analytes [83]. One can use cellulose nanocrystals (CNCs) with -OH groups to hinder the aggregation of CNTs and improve the adsorption capacity and structural stability of the nano-sorbent [183]. For example, PVA-PAA@CNT-CNC electrospun NFs were utilized as the efficient sorbent in pipette-tip micro-solid phase extraction (PT-µSPE) for the simultaneous extraction of seven opioid analgesics (OAs) from biological fluids before the HPLC-UV analysis. This NFs composite can be used more than 20 times without a considerable loss of extraction efficiency and performance for the extraction of trace-level of OAs in plasma samples. So, the PT-µSPE technique for this electrospun NFs shows high potential in sample pretreatment as a result of the low consumption of NFs, organic solvents, fast method and sensitivity, wide linear range, great reusability, high extraction recovery, long lifetime and good reproducibility. Also, due to applying chromatographic separation (HPLC-UV), the peaks of the intended analytes can easily be recognized for the quantitative measurements and the presence of CNT-CNC causes more analytes to be captured based on hydrogen bonding,  $\pi$ - $\pi$ , and hydrophobic interactions between NFs composite and OAs [79].

The unique properties of graphene, such as superb electrical, mechanical, optical, and thermal characteristics, and extremely high specific surface area, make it very attractive for SPE [84] and SPME [85]. Nonetheless, blocking and leakage may take place when nano-sized graphene is directly used as a sorbent in SPE [86]. Additionally, graphene is readily aggregated, which results in decreased frequency of accessible active surfaces. So, a novel composite nanofiber film with PS and graphene (PS/graphene) has been proposed for thin film microextraction (TFME) coupled with HPLC of six aliphatic aldehydes (pentanal, butanal, heptanal, hexanal, nonanal, and octanal) in exhaled human breath condensates. In the comparison of TFME-HPLC with SPME–GC/MS, TFME-HPLC provided a better sensitivity (4.2–19.4 nmol. L<sup>-1</sup> vs 23.4–130 nmol. L<sup>-1</sup>) and shorter analysis time (4 vs 30 min) [87]. In a comparison of TFME-HPLC with SPE–LC/UV, fast extraction is the advantage of TFME-HPLC (4 vs 15 min) [88], and the solvent consumption is reduced greatly (only 200 mL). Due to the large surface area and thin thickness of the membranous extraction phase in TFME, the extraction equilibrium can be achieved in a short time. Also, simple setup, convenient operation, low cost, and comparable sensitivity are the advantages of the TFME-HPLC [80].

GO, which owns many oxygen-containing functional groups, can interact with the analytes via hydrogen bonding, electrostatic interactions,  $\pi$ - $\pi$  stacking, etc. However, due to suitable intergranular interactions, GO is inclined to be agglomerated. To overcome this problem, GO was combined with other materials, such as NFs. For example, polyamide (PA)/GO/polypyrrole (PPY) electrospun composite was synthesized and exploited as the packing material in spin-column micro solid phase extraction (SC-µSPE) to determine parabens in milk samples The results indicated that the addition of GO into PPY and PA led to significant improvement of the extraction performance of the sorbent as a result of the provision of the possibility of different interactions with the target analytes, including hydrophobic and  $\pi$ - $\pi$  stacking, and hydrogen bonding [89]. Also, the RSD% values for inter-/intra-day evaluations of less than 5.8 and 8.6% and the inter-/intra-day errors% of less than 16.5 and 13.4% reveal that SC-µSPE offers acceptable precision and show accuracy and reliability for the quantification of the target analytes. Therefore, the SC-µSPE method turned out as an acceptable procedure for parabens quantification.

TFME-GC-MS method was successfully utilized for the measurement of trace levels of PAEs in milk solutions and water samples by PmAP/ N6/GO as sorbent [90]. In comparison with SPME-GC–MS (sorbent: MWCNTs@PPy), the extraction time is shorter (20 vs 60 min) [91]. Compared with SPE-GC–MS (sorbent: activated carbon), TFME-GC-MS provides a lower detection limit (0.1–0.15 ng.mL<sup>-1</sup> vs 1.3–1.9 ng.mL<sup>-1</sup>), and also the consumption of organic solvent is reduced noticeably [92]. In comparison with DMSPE-GC–MS (sorbent: MIL-101@Fe<sub>3</sub>O<sub>4</sub>) [93] and LLME-GC-IT-MS (without sorbent) [94], the reusability of PmAP/N6/GO sorbent is high and its consumption is reduced greatly. In addition, the usage of the sorbent with thin thickness and high surface area leads to fast analysis in the TFME method, and then, the coupled TFME-GC-MS method is applicable to various sample matrices due to its high tolerance limit.

#### 4.3.4. MIP/NF composites

MIPs are 3D covalent polymers surrounding the template molecules and are typically synthesized through the co-polymerization of crosslinking agents and functional monomers. After the template removal and polymerization, vacant recognition sites remain, which are capable of rebinding target molecules similar/identical to the template. Although MIPs have been successfully applied in investigations associated with extraction, some disadvantages, such as the low rate of the adsorption/desorption kinetic procedure, remain. Given the fact that the bulk polymer network surrounds the molecules of the template, and the mass transfer rate can be decreased [95], one can use the addition of nano-materials, such as NFs, into MIPs to solve these disadvantages. This results in more accessibility of the binding sites situated at/near the surface, making the binding kinetics and the mass transfer faster and making the adsorption more efficient. In addition to the above advantages, one can readily remove these materials through different types of solutions [96]. Many studies have focused on particle-based MIP-SPME devices and reported selectivity only for the MIP particles without comparing it with selectivity after their inclusion into the host [97]. For example, MIP/NF composites have been synthesized as sorbent in SPME extraction (MI-ENFs-SPME) *via* the electrospinning method, in which PVA, chlorpyrifos, and glutaraldehyde are utilized as the functional polymer, template molecule, and cross-linker, respectively. According to the results, the MI-ENFs-SPME is capable of extracting chlorpyrifos from samples (separation time <1 min) selectively, and the extraction efficiency of MI-ENFs composite was more than twice that of the fibers coated with electrospun MIP particles. The reason is attributable to the creation of numerous selective recognition sites on the surface of the NFs in MI-ENFs, whereas, in the case of the fibers prepared via electrospinning MIP particles, selective binding sites are lower and also encapsulated into the nanofiber matrix [98].

The comparison of different types of fibrous sorbents, such as PE and polypropylene (PP) MFs, PCL MF/NF composites, and PCL/PVDF NF composites with selective MIPs and conventional C18 core-shell particle sorbent demonstrated that, amongst all the tested sorbents, PE MFs showed the desired selectivity for resolution of ochratoxins (OTs) from the wine sample with the validation parameters comparable to those of the commercial C18 sorbent. According to the results, only six min overall analysis time was obtained after extraction via the C18 particles. Except for PE MFs, the NFs and their composites did not enable reliable and selective extraction of OTs from wine [99]. In another work, molecularly imprinted resin (MIR)/PDA NFs have been used to extract sulfonamides (SAs) in water. Moreover, possible adsorption mechanisms based on hydrogen bond interactions were also discussed. In comparison with MIR particles, the MIR/PDA NFs showed much higher adsorption efficiency. In particular, the notable mass transfer efficiency of MIR/PDA NFs was much higher compared to that of the orderreported sorbents for SAs. In addition, there was no degradation in the sorbent performance even after twenty cycles and MIR/PDA NFs was particularly stable with excellent reusability property. Furthermore, the adsorption performance of MIR/PDA NFs showed no decline over time,

and the extraction percentage for SAs remained between 88.3 and 93.5% over 28 days, confirming the good storage and operational stability of the adsorbent. In terms of reliability, SPE–HPLC–MS/MS method was reliable and reproducible for the detection of five SAs in water samples due to the relative recoveries from 82.8 to 115.6% with the RSDs in the range of 1.0 - 7.2% (Table 1) [100].

#### 4.3.5. MOF/NF composites

MOFs have received considerable attention in extraction methods as ideal sorbents for SPE [101], SPME [102], TFME [103], SC- $\mu$ SPE [104], PT-SPE [105], and PT- $\mu$ SPE [106] due to their specific structural characteristics, including highly porous morphologies, vast surface area, and significant thermal and chemical durability. However, the crystalline MOFs are fragile and easily disintegrated into fine powder, which results in several problems in the process of adsorption, such as low MOF recovery and separation efficiency. Hence, the incorporation of MOFs into NF structures can enhance their surface area and surface roughness.

MOF particles packed pipette tip can lead to high back pressure caused by the micron or submicron size of MOF particles; as a result, it severely limits the use of MOFs in PT-SPE. To resolve the above problem, one of the effective strategies is to combine MOF particles with nanomaterials, such as NFs. For example, PAN/UiO-66 composite has been produced as sorbent in PT-SPE to extract four phytohormones in mung bean and watermelon sprouts samples followed by HPLC-FLD (Fig. 3). So, the electrostatic interactions between the anionic forms of phytohormones and positively charged UiO-66 had a key role when extracting the phytohormones [107]. In addition, the recoveries of the phytohormones changed not significantly after ten cycles of the PT-SPE procedure, which demonstrated the good reusability of PAN/UiO-66 composite. Also, the RSD for three replicate extractions of the four phytohormones was in the range of 1.5–5.6%, showing the high precision for the determination of this analyte.



Fig. 3. Schematic process of the PT-SPE process. Reprinted with permission [107].

In another work, a superb thermal-resistant headspace solid-phase microextraction (HS-SPME) fiber coating has been proposed based on PAN/Ni-MOF nanocomposites. The results show that adding Ni-MOF nanoparticles into the PAN NFs improves the extraction performance for two organophosphorus pesticides (OPPs) of diazinon and chlorpyrifos by enhancing sorbent porosity and provision of different interactions between the mentioned analytes and the nanocomposite, such as hydrogen bonding, hydrophobic, and  $\pi$ - $\pi$  stacking. In addition, PAN/Ni-MOF showed suitable mechanical and thermal stability resulting in the application of the sorbent more than 160 times without causing extraction performance loss and the relative standard deviations are  $\leq 6.5\%$ , which indicates an acceptable performance and accuracy of the method for determining trace OPPs compounds [108]. Also, PS/MOF-199 can be used in the TFME method, in which the MOF-199 was prepared as an NF film featuring high surface area, porous structure, high hydrophobicity, and favorable mechanical stability. This technique, in combination with HPLC, was utilized for the selective separation of aldehydes in healthy people's urine samples [109]. In 2019, PAN/NH<sub>2</sub>-Zr-MOF NF film was fabricated through the electrospinning technique and evaluated as a new sorbent for TFME coupled by CD-IMS, followed by corona discharge ion mobility spectrometry to analyze an OPP known as chlorpyrifos in samples taken from river water and agricultural wastewater. The repeatability and reproducibility of this sorbent was less than 11% three times in one day and shows satisfactory results for analyzing chlorpyrifos in environmental water samples [110]. PAN/ZIF-8 composite is utilized as a sorbent to extract BPA monomers from environmental water samples by the TFME method. Using electrospinning in this work, the synthesized ZIF-8 was incorporated in PAN to prepare a PAN/ZIF-8 NF film. It is worth mentioning that, under the optimized conditions, including the volume and type of desorption solvent, extraction time, desorption time, as well as shaking rate, the analytical features of the technique were estimated. The authors found that adding ZIF-8 NPs to PAN polymer increased the extraction performance significantly due to the high surface area of  $\pi$ - $\pi$  stacking and ZIF-8 between the BPA and ZIF-8 [111]. In another study, a sorbent was developed by fabrication of the electrospun cobalt oxide fibers and then phase transformation to the ZIF-67 fibrous film. The developed film was employed to extract ethion analyte (as an OPPs) with a detection time of fewer

than 2 minutes in aqueous samples by secondary electrospray ionization-ion mobility spectrometry (SESI-IMS). Moreover, ethion was successfully decided in a variety of real samples, such as agricultural wastewaters and underground water, through the same technique [112].

## 4.3.6. COF/NF composites

COFs, such as imine-based Schiff base network 1 (SNW-1) [113], Schiff base network 3 (SNW-3) [114], and amide-based COF-SCU1 [115], were employed as main sorbents in extraction methods. These investigations reported that COFs showed appropriate adsorption efficiency concerning large adsorption capacity, good reusability, and fast desorption/adsorption kinetics. However, the use of COFs as PT-SPE sorbent has never been reported so far due to leakage and also high backpressure of the (sub)micron size of COFs particles along with direct packing COFs particles into the pipette tip. An effective strategy used to resolve these dilemmas is to combine COFs particles with substrate materials, such as NFs because they are useful for enhancement of the dispersion of COFs particles, which not only can avoid the aggregation of COFs particles and the issue of high backpressure but also increases the contact surface area between analytes and COFs. In addition, NFs exhibited superb extraction performance with lower consumption of solvent and demanding shorter time in comparison with other sorbents, which is in line with the benefits of the PT-SPE technique.

For example, PAN@SNW-3 was prepared by integration of PAN and SNW-3 via the electrospinning method as the PT-SPE sorbent for the extraction of plant growth regulators (PGRs) from watermelon (Fig. 4). By the combination of PT-SPE with HPLC-DAD, a satisfactory method was successfully developed for simultaneous determination of ten PGRs. Given the presence of –COOH groups, PGRs can easily create electrovalent bands with SNW-3 using ammonium ions by modifying the pH value. From another perspective, PAN is commonly regarded as a promising scaffold material due to its noticeable features of remarkable chemical resistance, good thermal stability, significant biocompatibility, and also high durability. As a result, not only does PAN@SNW-3 exhibit high attractive force to PGRs through the negative and positive affinities but also shows the potential of lowing seepage pressure and improvement of desorption/adsorption kinetics in the sample prepara-



Fig. 4. The schematic diagram for the extraction of PGRs with the help of the PT-SPE method. Reprinted with permission [114].

tion process. Also, the adsorption mechanism between PGRs and PAN@SNW-3 can be explained by specific structural properties of organic ligands, hydrogen bonding, as well as  $\pi$ - $\pi$  stacking interactions. The recoveries of the ten PGRs show negligible change after five successive cycles of the PT-SPE procedure under the optimum conditions, which confirms that PAN@SNW-3 electrospun nanofiber in PT-SPE method has excellent reusability, which benefits from the high stability of the COF and the PAN [114].

On the other hand, the introduction of COFs materials into the spinning solution for the construction of COFs modified electrospun membranes featuring high enrichment capacity is another feasible and effective method to enhance the detection and adsorption of trace organic pollutants, such as organochlorine pesticides (OCPs). However, given the poor dispersibility of COFs in the solution and coating inside the NFs, these disadvantages resulted in inadequate adsorption sites for analytical applications. For this reason, the researchers have tried to construct and grow COFs on the electrospun NF membranes using an in situ technique. For example, PAN@COFs were synthesized via in situ growing of COFs on the electrospun NF membrane subject to moderate conditions and used in SPME to enrich trace OCPs (a-Endosulfan, g-Chlordane, Dieldrin, a-Chlordane, b-Endosulfan, and Endrin) in water. The results of some characterizations like SEM (Fig. 5) approved the presence of COFs spheres on the surface of PAN NF membranes. Also, the results indicated that this composite could lead to the enrichment of a variety of OCPs under very low concentrations in the SPME experiment. Besides, PAN@COFs could be reused 100 times, while in pure COFs, the enrichment performance on OCPs exhibited an evident decline after 75 runs, indicating that the PAN@COFs fiber had better reusability and stability than pure COFs. The mechanism during the adsorption of trace OCPs was the hydrophobic effects and  $\pi$ - $\pi$  stacking interaction because of the steric hindrance, so the OCPs could be efficiently adsorbed on PAN@COFs, even under the extremely low driving force (Fig. 6) [116].

The introduction of -NH<sub>2</sub> group in UiO-66-NH<sub>2</sub> can improve water and hydrothermal stabilities by hydrogen bonding and provides the possibility of grafting COFs on UiO-66-NH<sub>2</sub> to enhance the adsorption capacity of the hybrid material. The hybridization of UiO-66-NH<sub>2</sub> and COF will result in favorable porosity, high stability, more binding sites for adsorption, and a large specific surface area [117]. To maximize the use of the raw materials at hand, the demand for developing NF composites based on the incorporation of MOF and COF can eliminate the adsorption demands for various compounds. So, MOF@COF-coated carboxyl NF (CCF@UiO-66-NH2@TpBD) composite has been prepared to extract three Bisphenols (BPs), i.e., BPB, BPF, and BPA by the PT-SPE method (Fig. 7). The fabricated composite showed favorable performance as a result of hydrogen bonding,  $\pi$ - $\pi$  conjugation, and hydrophobic interactions between the sorbent and the BPs. Several parameters, such as the sampling flow rate, dosage of sorbent, ionic strength, methanol concentration in the eluent, and sample solution pH, were modified to enhance the extraction performance of the SPE process. (1) The amount of adsorption increased when the amount of sorbent increased but in more than a specific value, potentially caused by the reverse extraction because when the sorbent volume in the pipette tip becomes higher, it causes a decline in eluted BPs. (2) Modification of the sampling flow rate indicates two sides of the effects on the degree of adsorption. From another perspective, excessively fast flow rates do not allow the analytes to link to the sorbent properly. However, excessively slow flow rates will increase the analytical time. (3) When pH < 7.0, the side effect of sorbent positively charged (UiO-66-NH<sub>2</sub>), as the pH value decreased, the electrostatic repulsion increased. In pH > 7.0, BPs were available in neutral form, and the side effect of sorbent gradually charged negative (TpBD). The declined electrostatic attraction led to re-



Fig. 5. SEM images prepared in the course of the preparation of PAN NF membranes with COF have grown: COFs powder (a-d), PAN electrospun NF membrane (e-h), PAN@COFs NF membrane (i-l). Reprinted with permission [116].



Fig. 6. Proposed synergetic adsorption mechanisms of OCPs by PAN@COFs. Reprinted with permission [116].

duced extraction performance. (4) The adsorption declined as the salt concentration (NaCl) increased. This is because NaCl can occupy the adsorption sites of sorbent and result in reduced extraction efficiency and high viscosity of BPs. (5) The eluent solutions featuring various eluent flow rates and percentages of methanol indicated that the adsorption increased as the methanol content increased. This is because different elution capacities. (6) The reusability of adsorbents was also evaluated by successive adsorption and desorption cycles and could be used up to 30 times with no significant changes, indicating that the adsorbent is highly reusable and has a long-life for adsorbing BPs. As result, the optimum experimental parameters for the PT-SPE process were determined as follows: pH of 7.0, sorbent amount of 15 mg, a sample flow rate of 1 mL/min, a methanol content of 80%, and no NaCl in the sample solution [118].

## 4.3.7. Zeolite/NF composites

Zeolites are crystalline and hydrated aluminosilicate frameworks featuring uniform acidic/basic sites, a well-defined microporous structure, and favorable hydrothermal/thermal stability. These 3D frameworks, due to having a negative charge on their structures, have a high ability for the adsorption of various analytes, such as heavy metal cations [119]. In recent years, the modification of polymer NFs with zeolites as fillers can improve the physicochemical stability, reusability, and adsorption capacity of sorbents. For example, zeolite/poly(ethylene-co-vinyl alcohol) (EVOH) composite is used for the adsorption of indoxyl sulfate (IS), which is a toxin associated with chronic kidney disease. This composite showed an adsorption capacity of 107  $\mu$ g/g, whereas the adsorption capacity by zeolite improved from 208  $\mu$ g/g in powder form to 386  $\mu$ g/g when dispersed within the polymeric matrix and resulted in increased cell viability from 86% to 96%. The authors also found that, due to different Si/Al molar ratios, the type of zeolite has a great influence on the improvement of the adsorption capacity of samples [120].

In another study, the zeolite-loaded PVA/PAA super hydrophobic NF (zeolite/PVA/PAA) was fabricated by electrospinning. Compared to PVA/PAA (54.94 mg/g), zeolite/PVA/PAA exhibited a higher adsorption capacity (205.75 mg/g) at acidic pH. Adding zeolite also enhanced the adsorption capability of pure PVA/PAA NFs by 275% approximately. The mechanical specifications of the PVA/PAA have been enhanced by loading with zeolite, which enabled the reuse of NFs. In addition, the sorbent indicated favorable regeneration capability and recycling for U(VI) ion removal [121].

Moreover, the electrospun PAN/clinoptilolite (CP) NFs to extract PAHs from water samples by SPME were reported in 2022. The studied analytes were detected by gas chromatography (GC-FID). The method was assessed for extracting PAHs from actual samples. The obtained relative recoveries exceeded 85% [122]. In summary, the fabrication of zeolite/NF composites provides advanced and effective sorbents with superior extraction capability for real samples.



Fig. 7. Scheme of preparation of CCF@UiO-66-NH<sub>2</sub>@TpBD and PT-SPE Reproduced with permission [118].

# 5. Conclusion and prospects

This review aims to highlight some of the recent developments that harness the great potential of NFs and their nanocomposites as sorbents for extraction processes. By highlighting some of the recent applications of NF-based sorbents, it is hoped that this review has provided enough evidence to support the hypothesis that mentioned nanomaterials will be an advanced class of sorbents with high repeatability and selectivity for SPE processes.

Due to NF-based sorbents' physico-chemical characteristics, it exhibits numerous advantages, which made them suitable for application in SPE techniques. Moreover, it is very important that type of SPE method and operating conditions such as the amount of packed sorbent and temperature in extraction efficiency.

Currently, the SPE systems can offer numerous important advantages in terms of cost, flexible performance, environmental impact, and scalability moving into the future, and increased focus on the realworld application of these technologies would facilitate further innovation. On the other hand, academic researchers have made strides toward the development of practical, industrial-scale SPE systems for materials recovery and purification. Overall, various preparation strategies have been used to produce NF-based sorbents. Among them, electrospinning is the most efficient method that can produce NFs from a variety of polymers. This approach can be a potential way to design new and selective nanocomposites for extraction. Currently, most NFs preparation methods are done on a small scale though may have the potential for scale-up.

While NF-based sorbents have been widely implemented in SPE research and have shown tremendous potential, there is still a paucity of understanding of the mechanism behind this phenomenon. One critical direction for researchers is to approach the adsorption mechanism based on characterization techniques, including spectroscopy and computational simulations to figure out how to affect the adsorption properties of NFs. However, it is possible that shortly, studies on the mechanism and optimization of synthesis will benefit from one another and bring about inspiring progress. This approach can provide feedback on the structure-property relationship.

Studies on the use of MOF or COF as a reinforcing component for composite NFs fabrication are still limited. Hence, there are opportunities for incorporating MOF or COF into NFs structures can improve their surface roughness and surface area. in addition, the presence of various non-covalent interactions between the composite NFs and analytes plays an important role in the extraction efficiency. Thus, composite NFs research and development promises to bring good results in the future. Notwithstanding, for the prospect to be realized, there is a need for more focused experimental work to address the many issues regarding the use of NF-based sorbents.

### CRediT authorship contribution statement

**Elham Torabi :** Writing – original draft. **Milad Moghadasi :** Writing – original draft. **Masoud Mirzaei :** Writing – review & editing. **Amirhassan Amiri :** Writing – review & editing.

# **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**

No data was used for the research described in the article.

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