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Review

Advancements in Microextraction by Packed Sorbent: Insights into Sorbent Phases and Automation Strategies

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Abstract: Miniaturized solid-based approaches have added an eco-friendly dimension to analytical procedures, establishing themselves as promising strategies for a wide range of applications. Among these, microextraction by packed sorbent (MEPS) stands out due to its ability to facilitate efficient sample interaction with a densely packed sorb ent phase within the microextraction system. MEPS offers several advantages, including preconcentration capabilities and the use of minimal sample and solvent volumes, making it an appealing choice for modern analytical workflows. Since the extraction efficiency is largely dictated by the sorbent phase, recent advancements in sorbent design have garnered considerable attention in the field of sample preparation. Innovations in sorbent phases have not only enhanced the MEPS efficiency but also enabled the development of semi- and fully automated systems, paving the way for high-throughput methodologies. These advancements have elevated MEPS beyond traditional offline miniaturized sample preparation methods, offering new opportunities for streamlined and scalable analyses. Therefore, this study provides a comprehensive overview of novel sorbent phases used in MEPS, with a particular focus on both bio-based and synthetic materials. Furthermore, it explores the semi- and fully automated aspects of MEPS, highlighting current trends, technological advancements, and future directions in this rapidly evolving field.

Keywords: microextraction by packed sorbent; automated methods; sorbent phases; miniaturized methods

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1. Introduction

The evaluation of complex samples, such as food or biological matrices, presents significant challenges due to the presence of endogenous compounds that can interfere with the detection of target analytes. Furthermore, their inherent complexity necessitates careful preparation, as direct infusion into liquid chromatography (LC) or mass spectrometry (MS) systems could compromise the integrity and performance of these analytical instruments [1,2]. To address these challenges, incorporating a sample preparation step is strongly recommended to mitigate the previously mentioned issues associated with complex matrices' analysis [3]. Effective sample preparation provides numerous advantages, including the preconcentration of target analytes and the removal of interfering matrix components, thereby enabling more accurate and reliable quantitative or qualitative analysis of target compounds [4]. By overcoming the challenges posed by complex matrices, sample preparation enhances the capability of analytical methods to detect low concentrations of target compounds, making it invaluable for tracing harmful substances across diverse sample types [5–7].

Solid-based sample preparation methods have been extensively documented in the literature due to their ease of handling and low-cost materials [8]. However, traditional solid-based methods are also known for their substantial consumption of organic solvents, resulting in significant amounts of chemical waste [9]. Furthermore, to adhere to the fundamental principles of green analytical chemistry (GAC), various miniaturized solid-based methods have been developed following the introduction of the pioneering solid-phase microextraction technique in the early 1900s [10,11]. Among these miniaturized solid-based approaches, microextraction by packed sorbent (MEPS) was introduced in 2004 as a potential strategy to address the challenges associated with complex samples, particularly in bioanalytical analysis [12].

MEPS is a miniaturized version of solid-phase extraction (SPE), where the sorbent is integrated directly into the syringe [13]. MEPS offers several notable advantages, including a diverse range of sorbent phases beyond the conventional reversed phases such as C6, C8, and C18 [14,15]. Furthermore, the literature highlights the remarkable reusability of MEPS in biological samples like urine and plasma, addressing the low reusability of conventional SPE columns, which are typically used only once [16]. Moreover, MEPS demonstrates significant preconcentration potential and can handle a wide range of sample volumes (10–1000 µL) [16]. The versatility of MEPS is demonstrated by its potential for integration with online methods such as liquid chromatography–mass spectrometry (LC-MS) protocols [17]. Additionally, MEPS protocols are suitable for semi or fully automated procedures, encompassing sample processing, extraction, and injection steps, thereby increasing the analytical throughput of the analysis [17–19].

As with all solid-based miniaturized methods, the analytical performance of MEPS primarily depends on the sorbent phase, which facilitates effective interaction with the target analytes in the matrix [20]. Numerous studies have been conducted to synthesize novel sorbent materials, offering various alternatives to traditional, high-cost sorbent phases [20–22]. The quest for improved sorbent materials has led to the development of synthetic and biodegradable alternatives, enhancing MEPS and expanding its applicability across various matrices [20,22,23]. Moreover, significant advancements in semi- and fully automated MEPS protocols have been reported, revealing untapped potential for high-throughput analysis compared to traditional offline methods [17]. The ongoing advancement of MEPS protocols, including the introduction of novel sorbent phases and enhanced devices for diverse applications, has propelled the MEPS technique in new directions, significantly enhancing its analytical performance. Despite these advancements, the literature still lacks updated review studies that comprehensively address various aspects of this versatile miniaturized strategy. Therefore, this study aims to bridge this gap by providing an extensive overview of developments in packed sorbent phases, including synthetic and biosorbent phases, and the application of MEPS in semi- and fully automated methods. By highlighting current trends and persistent challenges, this review seeks to offer valuable insights and substantial contributions to the field.

2. Microextraction by Packed Sorbent (MEPS)

Understanding the theoretical aspects of the MEPS technique is crucial for comprehending the design and the analytical parameters that can influence the performance of this miniaturized strategy. In short, the MEPS design includes the syringe (100–500 µL) and the barrel insert and needle (BIN) in a single device. Figure 1A illustrates the typical design of MEPS, which is composed of the BIN apparatus. Moreover, MEPS protocols usually involve the performance of four main steps, including (I) conditioning, (II) sampling, (III) washing, and (IV) elution (see Figure 1B). For the extraction procedure, a small amount of sorbent (approximately 2–5 mg) is packed inside the syringe or placed in the BIN as

a cartridge [16]. The sample is then aspirated and dispersed in repetitive cycles until equilibrium. Following this, standard cycles of washing and desorption are performed to achieve the final solution, which is used for the analysis [14]. The primary advantage of this technique is its ability to combine sample extraction, pre-concentration, and clean-up in a single device, significantly reducing the sample preparation time compared to performing these steps separately [24–26]. Once the sorbent phase reaches its maximum reusability, it can be easily replaced by unscrewing the locking nut and removing the BIN. This process is quick and can be completed in less than two minutes, thus not interfering with the analytical throughput of this approach [25].

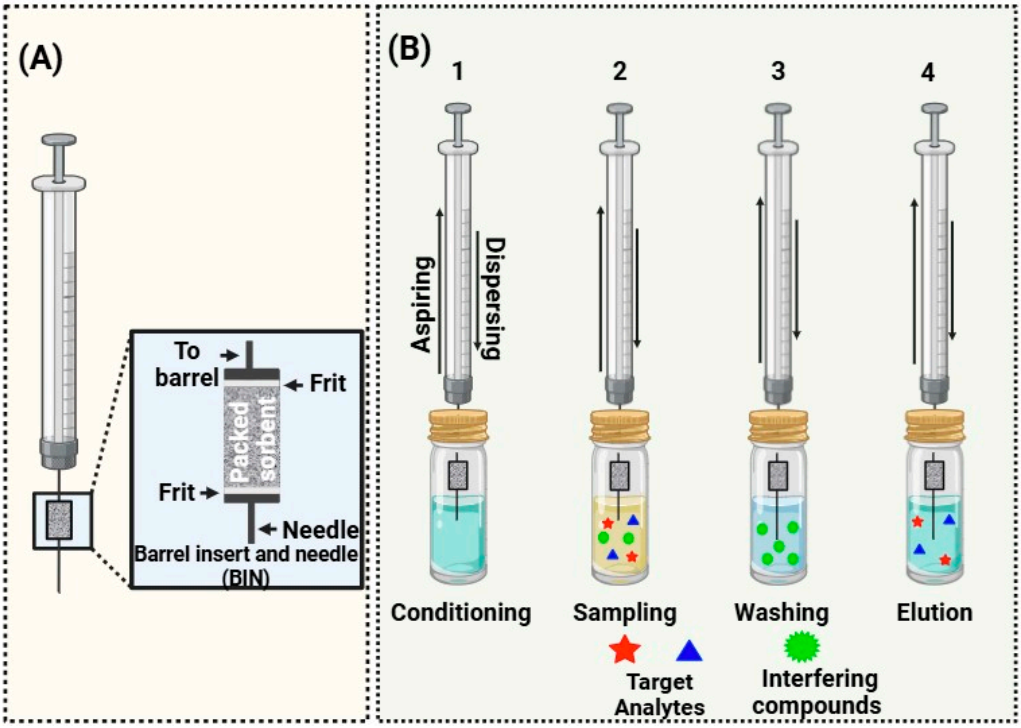

Figure 1. (**A**) Classical MEPS design utilizing the BIN apparatus, and (**B**) the extraction steps typically performed in MEPS protocols. Designed using BioRender https://www.biorender.com/ (accessed on 20 December 2024).

The optimization of the method typically involves studying the influence of several factors: (I) the choice of conditioning, loading, washing, and elution solvent; (II) the sample flow rate; (III) the volume of the conditioning, loading, washing, and elution solvent; and (IV) the sorbent phase [16]. Conditioning of the sorbent is generally performed using the same solvent as the sample. However, the type and volume of the solvent must be carefully evaluated during the washing and elution steps to prevent carryover effects between samples and ensure that the solvent is sufficiently strong to elute the analytes from the sorbent phase [27]. In the case of the flow rate, lower flow rates typically ensure better interaction between the analytes and the sorbent phase. However, offline MEPS methods do not evaluate this parameter since sampling is manually performed. The repetitive handling involved in manual sampling is user-dependent and thus highly susceptible to experimental errors.

Moreover, the sample volume and the number of sampling cycles are typically assessed to achieve optimal equilibrium between the sample and the sorbent phase, ensuring analytical performance and throughput [16,28]. The choice of sorbent phase must be carefully considered while evaluating the optimal parameters for MEPS extraction, which are closely related to the sample type and analytes. Since the sorbent phase is responsible for

the physicochemical interaction with the target analyte in the sample, the scientific community has continuously proposed new and improved phases for MEPS extraction [20]. These advancements have expanded the range of MEPS applications, offering unique physicochemical properties that have opened up new horizons for this miniaturized strategy.

3. Synthetic Strategies: Optimizing MEPS with Tailored Sorbents

Despite the use of traditional sorbents in MEPS protocols for various matrices, these materials exhibit significant limitations, including inadequate selectivity, limited reusability, and substantial acquisition costs [20,29]. Consequently, ongoing research has focused on developing advanced sorbent materials for MEPS applications [13]. These novel materials have garnered attention due to their versatile synthesis methods and enhanced physicochemical properties, which are widely utilized to improve the analytical performance of MEPS [13,16]. Moreover, many of these new sorbents strongly follow GAC principles by proposing green synthesis strategies and producing fewer chemical residues than traditional methods [21]. Therefore, this section aims to provide an overview of the current sorbent phases used in MEPS, mainly focusing on the synthesis of molecularly imprinted polymers (MIPs), magnetic nanoparticles (MNPs), metal–organic frameworks (MOFs), covalent–organic frameworks (COFs), and graphene-based materials (GBMs). Table 1 demonstrates the presence of studies in the literature reporting the use of synthetic sorbents in MEPS applications.

Table 1. Characteristics of methods presented in the literature that involve using synthetic materials as extraction phase in MEPS.

Analyte	Sample	Sorbent	Instrumentation	LOD	Ref
n-propyl gallate	Sesame oil	MIP	Digital image colorimetry (DIC)	0.03 μg mL^{-1}	[30]
Sulfonylureas herbicides	Corn	MIP	LC-ToF	2.5 μg kg^{-1}	[31]
Cocaine	Urine	MIP	LC-DAD	0.025 μg mL^{-1}	[32]
Fipronil and fluazuron	Drinking water and veterinary clinic wastewater	MMIP	LC-DAD	-	[33]
Pesticides	Apple juice	Core@mMIP	LC/UV	0.005 μg mL^{-1}	[34]
Caffeine	Soft and energy drinks	MIP	LC-UV	1 μg mL^{-1}	[35]
Cannabinoids	Human urine	MIP	LC-MS/MS	1–5 ng mL^{-1}	[19]
Estrogens	Human urine	MIP	LC-DAD	-	[36]
Levofloxacin	Plasma	DES-MIP	LC-DAD	0.012 μg mL^{-1}	[37]
Dinotefuran	Water and artificial saliva	MIP	LC-DAD	-	[38]
Mandelic acid	Urine	MIP	LC-UV	0.06 μg mL^{-1}	[39]
trans,*trans*-muconic acid	Urine	MIP	LC-UV	0.015 μg mL^{-1}	[40]
Dexamethasone, carbamazepine and naproxen	Urine	MI-IPN	LC-UV	1.3–1.5 μg L^{-1}	[41]

Table 1. *Cont.*

Analyte	Sample	Sorbent	Instrumentation	LOD	Ref
Clenbuterol	Pork	SMIPs	LC-UV	0.009 μg kg^{-1}	[42]
Fluoroquinolone	Wastewater	MIP	LC-MS/MS	0.5–3.8 ng L^{-1}	[43]
Estrogenic compounds	Water	MIP	GC-MS	1.3–22 ng L^{-1}	[44]
Sarcosine	Urine and plasma	DMIP	LC-MS/MS	1.0 ng mL^{-1}	[45]
Hippuric acid	Urine and plasma	MISM	LC-MS/MS	0.30 nmol L^{-1}	[46]
Triazines	Corn	MIP	LC-ESI-TOF	3.3 μg kg^{-1}	[47]
Local anesthetic drugs	Urine and plasma	MIP	LC-MS/MS	1.0 nmol L^{-1}	[48]
Parabens	Blood	3D Co_3O_4/C@HCNFs	LC-MS/MS	0.1–0.2 ng mL^{-1}	[49]
BTEX biomarkers	Urine	Fe_3O_4@TbBd nanobeads	LC-UV	0.02–0.5 μg mL^{-1}	[50]
PAHs	Soil	Amino ethyl-functionalized SBA-15	LC-UV/Vis	0.014–0.083 ng g^{-1}	[51]
NSAIDs	Urine	Layered double hydroxides (LDHs) of nickel and iron	LC-UV	1–10 ng mL^{-1}	[52]
Mandelic acid	Urine	MOF-5@ Fe_3O_4-NH_2 and MOF-5@ SBA-15	LC-UV/Vis	0.05 μg mL^{-1}	[53]
Phthalate ester	Water	Nano-hydroxyapatite	GC-FID	0.02–0.1 ng mL^{-1}	[54]
Antidepressants	Urine	PDA-Ag-Ppy nanocomposite	GC-MS	0.03–0.05 μg L^{-1}	[55]
Beta-blocker drugs	Saliva, plasma, and urine	Chitosan@MOF-199	LC-UV	1.5–4.5 μg L^{-1}	[56]
Nitroimidazoles	Water	MIL-101(Cr)/cellulose aerogel/melamine sponge composite	LC-MS/MS	8.25–16.33 ng L^{-1}	[57]
Parabens	Vegetable oils	HKUST-1(Cu)	LC-MS/MS	-	[58]
Methylhippuric acids	Urine	MIL-53-NH_2(Al)	LC-UV	0.005 μg mL^{-1}	[59]
Opiates	Urine	COF-PPy-CTAB	LC-UV	0.1–1 μg L^{-1}	[60]
BTEX biomarkers	Urine	Hollow polymer nanospheres and Fe_3O_4@TFPA-Bd-COF	LC-UV	0.02–0.5 μg mL^{-1}	[61]
Pesticides	Coffee	ILz/Si@GO	GC-MS/MS		[62]
Isoflavones	Soy-based juice	β-CD@GO@Si	LC-MS/MS	0.5–1.5 μg L^{-1}	[63]
Local anesthetic drugs and metabolites	Plasma	PAN/GO nanofibers	LC-MS/MS	0.25–2.5 nmol L^{-1}	[64]
Carbamate pesticides	Juice	RGO–ZnO nanocomposite	LC-UV	0.23–1.21 ng mL^{-1}	[65]

Table 1. *Cont.*

Analyte	Sample	Sorbent	Instrumentation	LOD	Ref
Organophosphorus pesticides	Water	GO/PA/cellulose paper	GC-FID	0.2–1 μg L^{-1}	[66]
Local anesthetics	Plasma and saliva	rGO	LC-MS/MS	2–4 nmol L^{-1}	[67]
Tetracyclines	Milk	G-Si	LC-MS/MS	0.03–0.21 μg L^{-1}	[68]
Parabens	Breast milk	prGO/Mg-Al LDH	LC-UV	3–5 μg L^{-1}	[69]
Phthalate esters	Water	CNT/CNF-G	GC-FID	1–10 ng mL^{-1}	[70]
Parabens	Water	Si-G	LC-MS/MS	0.06–0.09 μg L^{-1}	[71]
Benzenes and phenols	Water	g-C_3N_4-IL@HNT	LC-UV	0.5–1 μg L^{-1}	[72]
Metanephrines	Plasma	Porous graphitic carbon	HILIC-MS/MS	12.3 pg mL^{-1}	[73]
Antipsychotics	Plasma	Restricted access carbon nanotubes	LC-MS/MS	-	[74]
Organochlorine pesticides	Water	Carboxyl-purified multiwalled carbon nanotubes	GC-MS	0.02–0.19 ng mL^{-1}	[75]
Local anesthetics	Plasma	CarbonX® COA	LC-MS/MS	1 nmol L^{-1}	[76]
Leukotriene B4	Urine	Porous graphitic carbon	LC-PDA	0.37 ng mL^{-1}	[77]
Beta-blockers	Plasma	Carbon-XCOS	LC-MS/MS	-	[78]
Rosmarinic acid	*Rosmarinus officinalis* L.	CMK-3 nanoporous carbon	LC-UV/Vis	0.059 μg mL^{-1}	[79]
Bisphenols	Rat plasma	CMK-3 nanoporous carbon	LC-UV	0.25–4.7 μM	[80]

3D Co_3O_4/C@HCNFs: graphitic carbon intermingled porous; Co_3O_4: nanopolks (Co_3O_4/C) coated in hollow carbon nanofibers with a 3D pattern; PDA-Ag-PPy: polydopamine, silver nanoparticles, and polypyrrole nanocomposite; COF-PPy-CTAB: covalent organic framework-polypyrrole-cetyltrimethylammonium bromide; β-CD@GO@Si: β-cyclodextrin, coupled to graphene oxide supported on aminopropyl silica; PAN/GO nanofibers: polyacrylonitrile/graphene oxide nanofibers; prGO/Mg-Al LDH: magnesium-aluminum hydroxide functionalized partially reduced graphene oxide; CNT/CNF-G: 3D carbon nanotube/carbon nanofibers-graphene; Si-G: graphene supported on silica; rGO: reduced graphene oxide; ILz/Si@GO: ionic liquids supported on silica, functionalized with graphene oxide through covalent bonding; LC-MS/MS: liquid chromatography coupled mass spectrometry; LC-PDA: liquid chromatography coupled with photodiode array detector; LC-UV/Vis: liquid chromatography coupled with spectrophotometric ultraviolet/visible detection; GC-MS: gas chromatography coupled with mass spectrometry; HILIC-MS/MS: hydrophilic interaction liquid chromatography coupled with mass spectrometry; GC-FID: gas chromatography coupled with flame ionization detector; LC-ToF: liquid chromatography coupled with time of flight mass spectrometer; ESI: electrospray ionization.

3.1. Molecularly Imprinted Polymers (MIPs)

MIPs are highly selective polymeric materials vastly used in sample preparation protocols. Their selectivity originates from using template molecules during the polymerization stage, which can be either the analyte or a similar compound. These compounds are eliminated from the final material, creating cavities in the polymeric structure that allow for specific interactions with a class of compounds or analytes. This process is similar to the 'lock and key' mechanism observed in antigen–antibody interactions. Their synthesis process is performed in three main steps. First, the polymer structure is formed by the reaction of the monomers around the template molecule. The second step involves the

formation of the monomer–template matrix by adding the cross-linker. The final step relies on the template removal from the polymeric matrix and subsequent final material application [81,82].

The application of MIPs in different sample preparation techniques is widely reported in the literature. Indeed, the use of MIPs for some of the applications presented in Table 1 has already been reported for other sample preparation techniques. However, as Andrade et al. [47] stated, using MEPS coupled with MIPs presents advantages such as a significant reduction in the sample, extraction phase, and solvent consumption. In addition, in most studies using MEPS, the extraction phase can be reused without any loss of extraction efficiency or operational problems, such as syringe clogging, e.g., 180× [31] and 50× [46].

The synthesis of MIPs is a significant step in obtaining a material with adequate selectivity, without problems such as template leakage, and sufficient for the MEPS procedure. Thus, some authors have been reporting the use of software to estimate the best reaction conditions, generating less residue. Sarnaghi and Ayazi [30] used Gaussian 03 software to calculate the best monomers and porogenic solvents to achieve the most significant interaction with the analyte. Teixeira et al. [35] used Gaussian 09 software to perform theoretical calculations to better understand the MIP formation. In another study, the authors also performed this step. They concluded that the stability of the complex pre-polymerization formed between caffeine (the analyte) and the methacrylic acid monomer is due to the hydrogen bonds established. The produced MIP was used to determine n-propyl gallate in vegetable oils with a limit of detection (LOD) of 30 ng mL^{-1} and relative recoveries in vegetable edible oils of 83.0 to 112.0%.

To avoid problems with using the target analyte as the template, some authors have been using different compounds with similar structures to those of the analyte. Using different compounds as templates, named dummies, is a practical solution for analytes whose standards are difficult to obtain. However, it is important to evaluate this factor since some changes in the interaction sites can provide lower recovery in actual samples [32]. Some examples of dummy compounds for MIPs in MEPS procedures are the use of caffeine to determine cocaine [32], catechin hydrate for the determination of cannabinoids [19], and glycine for the determination of sarcosine [45].

Moreover, Table 1 highlights innovative solutions for synthesizing and using these materials, which will be discussed in further detail in the current section. Meng and Wang [37] used an MIP for the MEPS protocol synthesized using a deep eutectic solvent (DES) as a porogen agent. Organic volatile solvents are typically used for this function; however, other solvents, such as a DES, can also be evaluated to improve the material's porosity and green aspects of this process [37,81]. Indeed, the authors compared MIPs formed using a DES and methanol, and the characterization assays demonstrated that MIP-DES presented lots of small cavities with increased surface area [37].

Another potential application of MIP materials is their use as coating substrates for different applications. Du et al. [42] reported an MIP formed on the silica gel surface through a sol-gel process for determining clenbuterol from pork samples. The authors compared the use of this material in MEPS and SPE, mainly focusing on demonstrating how green MEPS protocols are compared to SPE by using a smaller quantity of samples and organic solvents. The main findings demonstrated a good analytical response, with an LOD of 0.009 μg kg^{-1}, with the relative recovery and relative standard deviation lower than 101.6% and 10.1%, respectively. In another study, Moein et al. [46] used an MIP synthesized through a sol-gel process on the surface of a polysulfone membrane in MEPS extraction. The produced material was used for the online detection of hippuric acid in plasma and urine samples with an LOD of 0.30 nmol L^{-1} and precision in plasma and urine samples lower than 6.7 and 4.8%, respectively. Dinali et al. [34] used silica

nanoparticles coated with MIP to determine pesticides in apple juice. The material was synthesized by the hydrolysis of tetraethylorthosilicate, followed by modification with 3-methacryloxypropyltrimethoxysilane to provide a connection with the MIP. Figure 2 presents a schematic illustration of the production process. The authors reported several benefits of this approach compared to conventional MIPs, including reduced mass transfer resistance and improved interaction with analytes. The analytical parameters of merit showed the great potential of the method, with LODs of 0.005 μg mL^{-1} and relative recoveries that varied from 76.18 to 96.12%. On the other hand, the authors stated that the material could not be reused without compromising the analytical performance of MEPS, thus necessitating further studies.

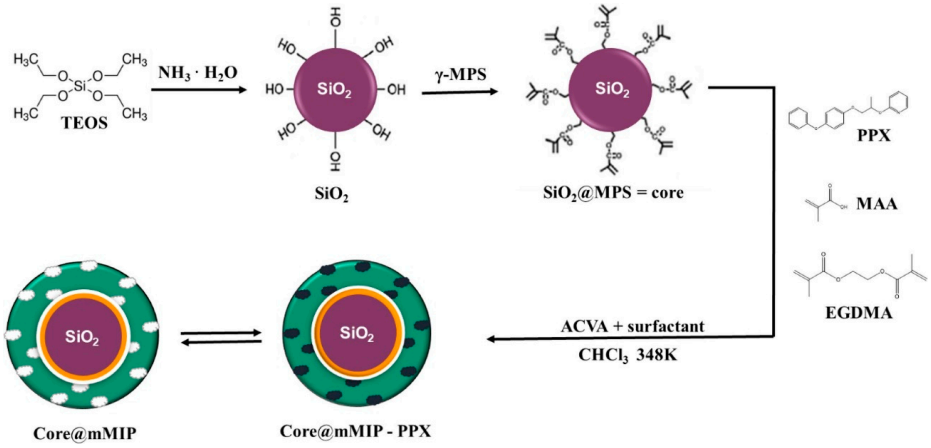

Figure 2. Schematic illustration of the synthesis methodology for the Core@mMIP-PPX polymer. Reproduced with permission from Elsevier, published initially in *Food Chemistry* [34]. Copyright 2022 ELSEVIER.

Sarnaghi and Ayazi [30] used cellulose paper as a substrate for producing a thin MIP film in MEPS to determine n-propyl gallate in sesame oil. First, the cellulose paper was activated using an H_2O_2 solution and then soaked in the polymerization solution to form a thin film. Before adding the extraction phase to the syringe barrel, the thin film was immersed in a Fe (II) solution, responsible for the chromogenic reaction with the analyte. An interesting innovation in this work is the use of smartphones to capture the color change of the thin film after the MEPS procedure, enabling the detection and quantification of the analyte.

These materials are attractive synthetic alternatives, as shown in Table 1, having been used to determine analytes in various samples, such as blood, urine, water, corn, and pork. This remarkable versatility is due to the high selectivity of these materials, which is particularly beneficial in microextraction methods, such as MEPS. For example, Moein et al. [45] compared the protein precipitation method with a molecularly imprinted polymer-microextraction by packed sorbent (MIP-MEPS). The authors concluded that using the MIP-MEPS approach demonstrated a considerable reduction of the matrix effect. Furthermore, these materials can provide better sample clean-up and preconcentration of trace-level concentrations. In this sense, Sartore et al. [19] compared extraction using MEPS with MIPs and C18. The main findings demonstrated a cleaner final extract using MIP than those obtained with C18, which retained a yellow color similar to the sample. This highlights the advantages of combining highly selective materials like MIPs with MEPS, resulting in a selective method with reduced sample and material consumption, waste generation, and matrix effects.

3.2. Nanomaterials

Nanomaterials have been a trending topic in various fields. They are characterized by having at least one dimension on the nanoscale [83]. Moreover, they present unique physical and chemical properties widely explored in several microextraction techniques, including MEPS. Nanomaterials are typically classified into different categories, and several of them have been reported in the literature for their use in MEPS methodologies. Some examples will be discussed in this section. It is also important to highlight that the materials described in this section were classified as nanomaterials in the original published studies.

Layered double hydroxides (LDHs) are two-dimensional inorganic nanomaterials that have gained attention due to their environmentally friendly synthesis, possible combination with other materials, excellent chemical and thermal stability, and remarkably high surface area [20]. Seidi and Sanàti [52] synthesized an LDH of Ni and Fe produced via the co-precipitation method. To make this material, $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in deionized water, with the later addition of urea and citric acid under constant stirring. The solution was transferred to an autoclave, heated at 120 °C for 12 h, and then washed with water and ethanol. The final material was used as a sorbent phase for MEPS to determine nonsteroidal anti-inflammatory drugs in urine, with LODs varying from 1.0 to 10.0 ng mL^{-1} and precision lower than 10.2%. Manouchehri et al. [69] reported using a magnesium–aluminum layered double hydroxide functionalized partially reduced graphene oxide nanosorbent. In this procedure, graphene oxide (GO) was dispersed in water under agitation, with the later addition of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$. Then, Na_2CO_3 and NaOH solutions were added to the pH adjustment. The resulting solution was treated in an autoclave at 180 °C for 12 h, washed with water, and dried at 80 °C. This sorbent was used in MEPS to extract parabens from breast milk samples, with LODs between 3.0 and 5.0 μg L^{-1} and the relative recovery performed with spiked breast milk samples varying from 87.2 to 104.4%. According to the authors, the main advantage of these materials compared with commercial sorbents such as C18 are the different interactions provided by the material, such as anion exchange, hydrogen binding, and electrostatic interactions [52].

Rahimi et al. and Khoshdel et al. [79,80] used a carbon nanoporous material as a sorbent phase in MEPS extraction, named CMK-3. Rahimi et al. compared this material with activated carbon (AC) and found that the synthesized material performed better in MEPS extraction due to its higher porosity. Their results indicated that extraction with CMK-3 in the MEPS protocol produced peak areas 17 times higher than those obtained with AC. This material presented promising analytical results. For example, Rahimi et al. [79] used this material in MEPS to extract rosmarinic acid and obtained an LOD of 0.059 μg mL^{-1}, recovery of 90%, and precision of 4.5%.

Bagheri et al. [55] proposed the combination of polydopamine, polypyrrole, and silver nanoparticles as a sorbent for MEPS extraction. The authors highlighted the unique contributions of each component: polypyrrole provides π–π, dipole–dipole, and hydrophobic interactions, while polydopamine incorporates various organic groups that enhance interactions with polar compounds, and silver nanoparticles increase the surface area-to-volume ratio, thereby improving the material's adsorption capability. The authors compared the individual components with the nanocomposite and found that the nanocomposite exhibited significantly greater extraction efficiency, demonstrating the great potential of this combination. Using this sorbent and MEPS approach, the authors proposed a method for the determination of three antidepressants in urine samples and obtained LODs, relative recovery studies performed in spiked urine samples, and relative standard deviations lower than 0.05 μg L^{-1}, 104%, and 9%, respectively

Ayazi et al. [66] proposed using a thin film composed of a nanocomposite of polyamide and GO coated on paper as the extraction phase for MEPS. A GO suspension was first prepared in formic acid to prepare the thin film, and then polyamide was added to the mixture. The prepared filter paper was immersed in this solution for a few seconds and rinsed with distilled water. After drying, the thin film was inserted into the syringe between two SPE frits using several layers of paper. Characterization assays showed that combining GO and polyamide improved the interaction with the cellulosic fibers. The authors used this material to extract and determine organophosphorus pesticides in water samples, obtaining good values for analytical parameters such as the precision and accuracy, with relative standard deviation lower than 11.9% and accuracy and relative recovery assay results varying from 77.8 to 113.3%. Additionally, this material could be reused over 50 times without losing extraction efficiency or experiencing clogging issues

Amiri et al. [70] proposed using a hybrid nanomaterial composed of graphene (G), carbon nanotubes (CNTs), and carbon nanofibers prepared by chemical vapor deposition for MEPS applications. The synthesis involved immersing a quartz boat in a copper nitrate trihydrate and nickel nitrate hexahydrate solution, followed by ultrasonic agitation. The reactor was then heated to remove any residual nitrates and form carbon nanotubes and nanofibers under an acetylene flow. According to the authors, combining G with carbon nanofibers and CNTs helps prevent G agglomeration. Surface area measurements revealed that the synthesized hybrid material had a greater surface area compared to pure G. This method combines MEPS with the hybrid nanomaterial as the extraction phase and dispersive liquid–liquid microextraction (DLLME), using the MEPS extract as a disperser solvent to determine phthalate esters in water samples. The analytical results were considered adequate, with the LODs varying from 1 to 10 ng mL^{-1}, relative recovery studies performed with spiked water samples ranging from 90.3 to 98.8%, and precision of the measurements with RSD lower than 10.3%. These examples underscore the advantages of employing nanomaterials as sorbents in MEPS. A key factor contributing to the effectiveness of these phases is their high surface area, which results from their nanoscale dimensions. This increased surface area enhances the material's adsorptive capacity, allowing for more efficient interaction with analytes and improving the overall analytical performance of MEPS.

3.3. Metal–Organic Frameworks (MOFs) and Covalent Organic Frameworks (COFs)

MOFs and COFs are advanced porous materials with distinct structural characteristics. MOFs feature one-, two-, and three-dimensional network structures of metal centers linked by organic ligands, creating open channels and small pores. In contrast, COFs consist solely of light elements—such as hydrogen, carbon, boron, nitrogen, and oxygen—forming porous two-dimensional and three-dimensional networks. Both frameworks exhibit high surface areas and, consequently, significant adsorptive capacities. They offer tunable properties due to their adjustable structures and, in many cases, exhibit thermal stability, thus presenting remarkable potential for MEPS applications [84–86].

Rahimpoor et al. [53] investigated two hybrid materials formed by MOF-5, which consist of zinc nitrate and 1,4-benzene dicarboxylate (1,4-BDC) and are coated with amino-functionalized Fe_3O_4 and mesoporous silica (SBA-15). These coatings enhanced the properties of the MOF-5, such as the hydro-stability, and both materials demonstrated effective performance as extraction phases in MEPS. For the synthesis of MOF-5 coated with amino-functionalized, Fe_3O_4 nanoparticles were first prepared. 1,4-BDC was then dissolved in DMF, followed by the addition of $Zn(NO_3)_2$ and Fe_3O_4 nanoparticles. The solution was subjected to ultrasonic agitation for 30 min before being transferred to an autoclave, where it was heated at 100 °C for 24 h. The resulting material was washed with DMF and dried

under a vacuum at 115 °C for 1 h. A similar process was employed in the case of the MOF-5 combined with SBA-15. Here, 1,4-BDC and $Zn(NO_3)_2$ were dissolved in DMF, after which SBA-15 was added at room temperature. The solution was then transferred to an autoclave and heated at 100 °C for 22 h. The resulting crystals were washed with DMF, purified with chloroform, and dried under a vacuum at 105 °C for 1 h. The obtained analytical responses were LODs lower than 0.13 μg mL^{-1} for both materials produced and recoveries for both materials of approximately 90%, with an RSD lower than 3.54%. When comparing the developed method for analyzing mandelic acid in urine samples, the authors noted several advantages, including the reusability of the materials for up to 85 cycles and reduced solvent consumption.

Samadiffar and Yamini [58] reported the use of a composite material combining chitosan (CS) and MOF-199, which is based on copper and benzene-1,3,5-tricarboxylate (BTC), as an eco-friendly extraction phase in MEPS for the determination of β-blocker drugs in saliva, plasma, and urine. MOF-199, known for its high surface area, enhanced its stability by incorporating CS, a biopolymer that contributes additional interaction mechanisms such as hydrogen bonding, electrostatic interactions, and π–π stacking. The synthesis involved preparing a CS aqueous solution with 1% acetic acid, which was stirred at room temperature for 12 h. Copper acetate dihydrate ($Cu_2(OAc)_4(H_2O)_2$) and BTC were then added to the solution, followed by sonication for 60 min. Glutaraldehyde was added dropwise to cross-link the CS chains, and the final product was obtained through centrifugation, washing with water and methanol, and freeze-drying for 24 h. In addition to the benefits of MEPS, such as low solvent and sorbent consumption, the produced material was biodegradable and featured meso- and microporous structures, contributing to reduced back pressure during MEPS. The proposed method was validated for determining three beta-blocker drugs in saliva, plasma, and urine samples, with LODs in the 1.5 to 4.5 μg L^{-1} range. Relative recovery assays were performed for each sample, and the results were in the range of 77–96% for plasma, 81–108% for saliva, and 80–112% for urine, demonstrating the great potential and applicability of the extraction technique and material.

Li et al. [57] developed an MOF/melamine sponge composite as the extraction phase for MEPS. The composite was prepared using MIL-101(Cr), cellulose, and a melamine sponge. A cellulose hydrogel and MIL-101(Cr) solution were prepared to impregnate the sponge. The resulting material was then freeze-dried for 12 h and packed into a syringe for use in MEPS. Using this composite instead of MOF powder reduces the sorbent loss during MEPS. The cellulose hydrogel acts as a bio-adhesive, enhancing the interaction between the MOF and the sponge. This composite was effectively applied for the extraction of nitroimidazoles from water samples, with the LODs varying from 8.250 to 16.33 ng L^{-1}, precision with RSD lower than 6.7%, and accuracy evaluated through recovery with values ranging from 70.4 to 96.7%. Zanganeh et al. [60] utilized a nanocomposite consisting of COF, polypyrrole, and cetyltrimethylammonium bromide for MEPS applications. The integration of COF with polypyrrole enhances the performance by mitigating the back pressure in the syringe, a challenge typically associated with MOFs, and by addressing the low surface area of polypyrrole. This composite facilitates various interactions with analytes, including π–π stacking and acid–base interactions. The material is structured in a nanowire form. COF nanocomposites are first synthesized to produce this composite, followed by incorporating polypyrrole and cetyltrimethylammonium bromide. The authors applied this material to determine opioids in urine samples, demonstrating its effectiveness in analytical applications. LODs varying from 0.1–1.0 μg L^{-1}, precision with results lower than 10.1%, and relative recovery studies in 94.4 to 103.1% were obtained.

MOFs and COFs are promising materials for use as extraction phases in MEPS due to their high surface areas resulting from their tunable structures. However, as many

examples demonstrate, other materials can significantly enhance the performance. These additional materials can improve the mechanical properties and augment the interactions with analytes by introducing new functional groups. Despite their considerable advantages as sorbents, the application of MOFs and COFs in MEPS remains relatively underexplored.

3.4. Graphene-Based Materials (GBMs)

GBM adsorbents are promising materials for various sample preparation techniques, including MEPS, as shown in Table 1. They possess critical physicochemical properties that turn them into effective sorbents, such as high porosity and extensive surface area, besides thermal and mechanical stability. Notable examples of this group include fullerenes, G, CNTs, and their numerous derivatives [87–89].

Ahmadi et al. [67] used reduced graphene oxide (rGO) in MEPS to determine the local anesthetics in plasma and saliva. rGO is an affordable and accessible material that interacts well with aromatic compounds. The authors also highlighted that the combination of rGO with MEPS allowed the development of a selective method due to the lack of interfering compounds in the chromatogram of the sample analysis. The authors reported limit of quantification (LOQ) values of 2 nmol L^{-1} and 4 nmol L^{-1} and relative standard deviation values lower than 19.14% for both samples studied.

Most studies involving graphene typically involve modifications to the material. For instance, Maciel et al. [68] employed G particles supported on silica to address issues such as the overpressure and syringe obstruction commonly encountered with graphene in MEPS. The authors proposed a straightforward approach to produce this composite: first, GO was bonded to silica, and then the material was reduced to achieve the final product. This material was used in MEPS to extract tetracyclines in milk samples, with the LOQs varying from 0.05 to 0.9 μg L^{-1} and the RSD lower than 19%. Fumes and Lanças [71] also used G supported on silica to determine parabens in water, with adequate results for analytical parameters, with LOQs of 0.2 and 0.3 μg L^{-1} and inter-day precision with RSD lower than 19.2%. Sun et al. [65] supported G on ZnO nanocomposites; this could prevent the aggregation of G sheets and improve the extraction of water-soluble compounds due to the hydrophilic surface of ZnO nanocomposite. The material was used in MEPS to determine carbamate pesticides in fruit juice samples, with LODs of 0.23–1.21 ng mL^{-1} and an RSD lower than 5.9%.

Another material combined with GO supported on silica is an ionic liquid (IL) reported by Jordan-Sierra and Lanças [62]. The resulting composite, ionic liquids supported on silica, functionalized with graphene oxide through covalent bonding (ILz/Si@GO), was employed as a sorbent in MEPS for pesticide determination in coffee samples. To produce this material, GO was first dissolved in DMF. Zwitterionic ionic liquid, anchored to silica, was added with N, N′-dicyclohexylcarbodiimide (DCC) as a coupling agent. The reaction was conducted under stirring at 50 °C for 30 h. The final product was obtained after washing with methanol and lyophilization.

Darvishnejad and Ebrahimzadeh [72] proposed a hybrid material combining graphitic carbon nitride (g-C_3N_4)-reinforced polymeric ionic liquid with halloysite nanotubes for the extraction of benzene and phenol pollutants from water samples using MEPS. The proposed method presented LODs varying from 0.5 to 1 μg L^{-1} and inter-day precision lower than 11%. While g-C_3N_4 and halloysite nanotubes are known for their durability and chemical stability, they may not exhibit optimal extraction capabilities for certain analyte classes. Incorporating polymeric ILs aims to enhance the overall extraction performance of the composite material.

CNTs have been utilized in MEPS due to their unique structure and electronic properties, which enable interactions with a wide range of analytes. They also offer a high surface

area and excellent chemical and thermal stability. For instance, commercial multi-walled carbon nanotubes were employed as the extraction phase in MEPS to determine organochlorine pesticides in water. The proposed method presented linearity in the range of 0.1 to 25 ng mL^{-1}, with LODs lower than 0.19 ng mL^{-1}; additionally, the method presented good precision, with the RSD varying from 3.3 to 8.5% [75]. In another study, the authors used restricted access carbon nanotubes (RACNTs) in MEPS to determine antipsychotics in plasma samples. The method presented an LOQ of 10 ng mL^{-1} and precision values lower than 13%. RACNTs are produced by the cross-linked bovine serum albumin (BSA) layer adhesion to commercially available CNTs. This provides a material with a high surface area and chemical stability; however, it has a restriction toward macromolecules, representing a great asset in the preparation of biological samples [74].

As reported in Section 3, developing novel sorbent materials for microextraction methods has introduced many synthetic materials extensively explored in these approaches, particularly in MEPS protocols. Our study investigated various sorbent materials, including MIPs, MNPs, MOFs, COFs, and GBMs, as potential analytical strategies for MEPS applications across different target analytes and samples. These materials have been studied for their application in MEPS due to their remarkable physicochemical properties, such as selectivity, high surface area, low cost, high adsorption capacity, and excellent reusability. These features enable MEPS protocols to effectively evaluate target analytes' trace-level concentrations in complex matrices.

Moreover, as reported in our review study, these materials exhibit significant potential for modification, allowing for improving their physicochemical properties to create new and enhanced hybrid materials. These hybrid materials have demonstrated great versatility by proposing novel synthesis routes to address the limitations of the individual materials. Despite these advancements in traditional and hybrid material synthesis, the non-environmentally friendly synthesis approaches remain a significant drawback. Many of these procedures still consume large quantities of organic solvents and require considerable time to perform, thereby increasing the health risks due to exposure. From the authors' point of view, adopting eco-friendly synthesis strategies is crucial for the future of sorbent materials in MEPS applications. Implementing these environmentally sustainable strategies can bring new perspectives to green analytical practices and promote the development of sustainable methods. This shift can potentially lead the field of microextraction sample preparation toward new and promising horizons.

4. Greening Sample Preparation: Natural Biosorbents for MEPS Enhancement

Despite the numerous advantages of synthetic sorbent materials in microextraction methods, particularly in MEPS protocols, these materials continue to face challenges concerning their environmental impact. Specifically, their synthesis processes often conflict with fundamental GAC principles [21,22]. A notable concern regarding these sorbents is that their synthesis often involves non-environmentally friendly protocols, requiring substantial quantities of reagents and solvents, thus increasing the amount of chemical waste. Such a drawback increases the environmental impact and elevates scientists' exposure to harmful chemicals [90,91]. Moreover, a recent trend has been the introduction of renewable and biodegradable sorbents [92]. These materials often exhibit remarkable physicochemical properties and represent a greener alternative to traditional synthetic materials in microextraction methods [92,93]. However, hybrid sorbents are typically created by combining synthetic materials such as MIPs, MOFs, GBMs, and MNPs with biopolymers to address the potential lack of selectivity in these materials [22]. Incorporating biopolymers into synthetic materials reduces the environmental impact compared to synthetic sorbents alone,

thus providing new directions for their use in microextraction methods [21,22]. This section will overview the hybrid biosorbent materials developed over the past six years (July 2018 to July 2024) and their advantages as sorbents in MEPS applications (Figure 3).

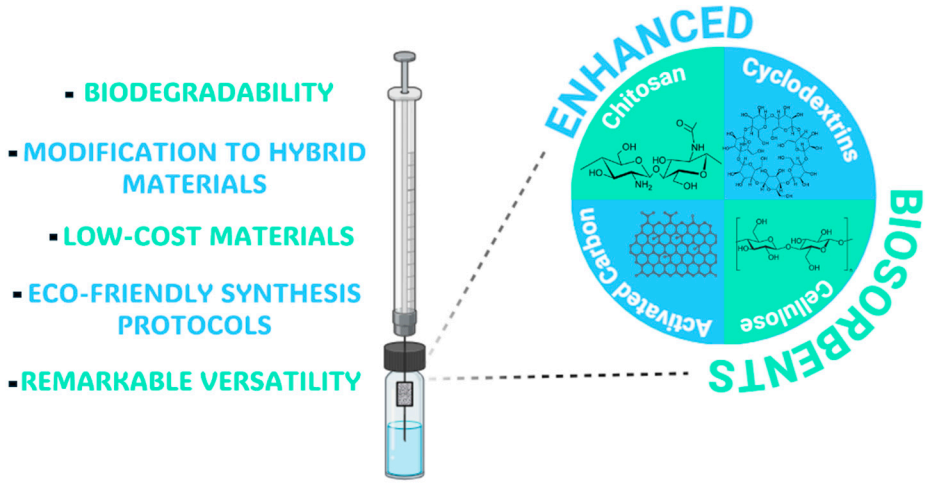

Figure 3. Schematic illustration of some of the biopolymers used in MEPS applications and their advantages. Created with BioRender https://www.biorender.com (assessed on 20 October 2024).

4.1. Cyclodextrins (CDs)

Cyclodextrins (CDs) are supramolecular compounds typically defined as non-reducing oligosaccharides formed by the linkage of glucopyranose units into a distinctive truncated cone shape [94,95]. The primary advantages of this biopolymer include its high selectivity and exceptional ability to interact with compounds of varying polarity. Additionally, their application in sample preparation methods is facilitated by large recognition cavities capable of accommodating diverse molecules, thereby preconcentrating target analytes within their polymeric network [96,97]. Furthermore, given their great potential in the scientific field of sample preparation, the abundance of hydroxyl groups within their structure makes cyclodextrins highly amenable to functionalization [22]. Such an advantage grants them the title of suitable biopolymers for anchoring various materials to create hybrid and enhanced sorbent phases for MEPS extraction.

Da Silva and Lanças [63] described the coupling of β-cyclodextrin (β-CD) to graphene oxide supported on aminopropyl silica (β-CD@GO@Si) as the sorbent phase for MEPS extraction of isoflavones in soy-based juice, followed by liquid chromatography–tandem mass spectrometry analysis (LC-MS/MS). The synthesis procedure first involved obtaining the GO phase using the traditional Hummers method under optimized conditions. Subsequently, a GO aqueous solution was treated with a mixture of 1-ethyl-3-(3-dimethylamino propyl)carbodiimide (EDC) and N-hydroxysuccinimide (NHS), followed by the addition of aminopropyl silica into the reaction medium. The resulting biopolymer was then separated and washed several times before use. An interesting finding emerged from comparing the extraction efficiency of graphene oxide-silica (GO@Si) with the synthesized β-CD@GO@Si sorbent. According to their main findings, although GO@Si exhibited higher extraction recovery compared to β-CD@GO@Si, matrix effect studies indicated that β-CD@GO@Si was less influenced by the matrix, suggesting the material's selectivity through β-cyclodextrin anchoring to the polymeric network. The optimal conditions for MEPS highlighted that the washing and desorption cycles were critical variables. Moreover, the method achieved LODs and LOQs ranging from 0.5–1.0 μg L^{-1} and 0.5 to 1.5 μg L^{-1}, respectively. Application to local samples successfully detected four isoflavones, demonstrating the sorbent's potential and the MEPS method's effectiveness in trace-level isoflavone analysis.

García-Valverde et al. [98] proposed an in-syringe MEPS approach utilizing β-CD grafted onto cotton fibers for the extraction of cocaine and methamphetamine from saliva samples, followed by direct mass spectrometry analysis (DI-MS). The sorbent synthesis involved three main steps: activating the carboxylic groups on the cotton fibers, introducing superficial amine groups, and finally immobilizing carboxylated β-CD. The main findings highlighted the importance of optimizing the size, shape, and hydrophobic nature of the β-CD to ensure the best possible interaction between the sorbent and the target drugs. The authors highlighted that using the sorbent in the proposed MEPS approach facilitates the direct infusion of the extract into the MS instrument, significantly enhancing the analytical throughput for drug analysis in complex biological samples, such as saliva.

4.2. Chitosan (CS)

CS, a biopolymer derived primarily from chitin found in organisms such as arthropods, green algae, and mollusks, has garnered significant attention for its application as a sorbent phase in microextraction protocols [22,99]. One key advantage of this biopolymer that underscores its considerable potential is the abundant presence of organic functional groups, particularly amino (NH_2) and hydroxyl (OH) groups. These functional groups facilitate chelation and electrostatic interactions with various compounds, including organic and inorganic pollutants [100]. Furthermore, the amino and hydroxyl groups in the CS structure allow for its modification or anchoring with other materials, creating hybrid biopolymers with enhanced properties [101,102]. This versatility has led to notable advancements in microextraction, with numerous studies demonstrating the efficacy of CS-based hybrid biopolymers in microextraction strategies [103]. This shows the great potential of CS as a valuable component in advanced microextraction techniques, such as MEPS.

Zhu et al. [104] proposed fabricating tailor-made CS fiber for MEPS to extract petroleum acids (PAs) from crude oils, followed by two-dimensional gas chromatography–mass spectrometry (GC×GC-MS) analysis. The CS fibers were produced through a simple hydrothermal reaction of the fiber with acetic acid at 120 °C for 6 h. The resulting fibers, with a diameter of about 10 μm and a length of a few centimeters, were packed (15 mg) into the middle of a glass pipette. Under optimal conditions, the MEPS method involved 15 sampling cycles and 10 eluting cycles completed in just 5 min, demonstrating high analytical throughput. The authors highlighted the sorbent's potential to provide low back-pressure in the MEPS system, addressing a significant challenge in evaluating PAs in crude oil samples due to their viscosity. Furthermore, compared to traditional sorbents, the developed CS fiber was considered cheaper and more eco-friendly. The LOD values ranged from 0.7 ng g^{-1} to 5.4 ng g^{-1}, with recovery values between 79 and 117%, showcasing the sorbent's capability to analyze trace-level concentrations.

A hyper-crosslinked polymer composed of graphene oxide and chitosan cryogel (HCP-GO/CS) was employed in a packed syringe apparatus for the extraction of furfural and 5-hydroxymethylfurfural (HMF) from cellulosic biomass hydrolysate, followed by analysis using liquid chromatography coupled with a photodiode array detector (LC-PDA) [105]. The biosorbent preparation began with the synthesis of hyper-crosslinked graphene oxide (HCP-GO) using dichloroethane and an $FeCl_3$ solution. Subsequently, CS was dissolved in a 0.50% v/v acetic acid solution. The two solutions were mixed, and glutaraldehyde was added to facilitate the interaction between HCP-GO and CS. Figure 4 illustrates the synthesis process for the biopolymer. The developed packed protocol achieved an LOD and LOQ of 0.25 ng L^{-1} and 1.0 ng L^{-1} for furfural, and 0.20 ng L^{-1} and 0.50 ng L^{-1} for HMF, respectively. Furthermore, the authors highlighted that the developed HCP-GO/CS biopolymer could be used for 20 extractions without losing its

analytical efficiency, demonstrating the high applicability of the MEPS in-syringe method in real-world scenarios.

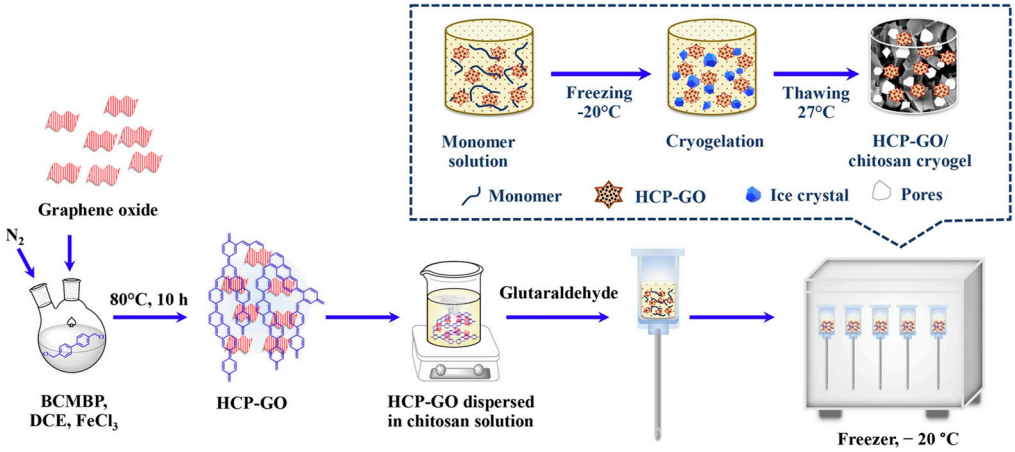

Figure 4. Schematic illustration of the synthesis methodology for the HCP-GO/CS biopolymer obtention. Reproduced with permission from Elsevier, published initially in *Microchemical Journal* [105]. Copyright 2022 ELSEVIER.

Most recently, Samadifar and Yamini [56] reported the synthesis of a chitosan@MOF-199 bio-composite and its application in MEPS for extracting β-blocker drugs from biological matrices, followed by liquid chromatography with ultraviolet–visible detection (LC-UV). The synthesis procedure was divided into two main parts: the synthesis of MOF-199 and then the dispersion of CS in an aqueous solution containing 1% acetic acid. The resulting mixture was freeze-dried, and the sorbent (7 mg) was then packed into the MEPS system. Under optimal conditions, applying the biosorbent in the MEPS protocol ensured LODs ranging from 1.5 to 4.5 μg L^{-1}, with recovery values between 77% and 112%. Additionally, the authors noted that the proposed MEPS protocol could be reused more than 60 times to extract β-blocker drugs from biological samples.

4.3. Other Bio-Based Materials

Besides the biopolymers derived from CDs and CS, other versatile biomaterials have shown significant potential as sorbent phases for MEPS due to their remarkable adsorption capacities [22]. One such material is AC and biomass, which has been extensively investigated due to its distinct physicochemical properties [56]. AC is a porous, amorphous solid material with a large surface area and abundant oxygenated functional groups, such as carboxylic acids, phenols, and carbonyls [56]. These exceptional characteristics make AC an ideal material for sample preparation methods [106,107]. Conventional methods for obtaining AC typically involve non-renewable sources, such as coal, lignite, and petroleum by-products. In addition to being finite, these resources entail high costs and pose significant environmental and human health risks [56].

Consequently, there is a growing demand for economically viable and environmentally friendly methods to produce AC. Biomass, including eco-friendly sources such as agricultural waste, industrial waste, sewage, and forestry residues, has emerged as a sustainable alternative over traditional sorbents, besides their potential as green sources of AC obtention [108,109]. Moreover, hybrid AC materials based on biopolymers have also been demonstrated as green alternatives to conventional AC [22]. The remarkable physicochemical characteristics of this material derived from these sources have expanded its potential applications in microextraction methods, particularly in MEPS protocols.

An in-syringe MEPS approach was demonstrated by Mashile, Mpupa, and Nomngongo [110], utilizing a chitosan-activated carbon (CAC) sorbent to extract parabens from

environmental waters. The extracted samples were then analyzed using LC-PDA. The authors reported immersing AC and CS in an oxalic acid solution for the synthesis process, maintaining constant stirring until a viscous gel formed. After subsequent steps, the resulting biopolymer was dried at 50 °C and then packed into the syringe apparatus. Characterization assays demonstrated that the CAC sorbent exhibited a superior surface area (1181 m^2/g) compared to its precursor AC (1075 m^2/g), confirming the effectiveness of the modification.

Additionally, the optimization of the method revealed a strong dependence on the pH and eluent solvent volume for the extraction of parabens, impacting the analytical performance. The method's analytical evaluation showed an adsorption capacity ranging from 227 to 256 mg g^{-1}. Furthermore, the LOD and LOQ were found to be 6–15 ng L^{-1} and 20–50 ng L^{-1}, respectively, with recovery values ranging from 96.7% to 107%. These results indicate the method's capability to preconcentrate and accurately assess the presence of parabens in real environmental matrices.

An innovative biomass-based MEPS approach was proposed by Rasolzadeh et al. [111], who reported using green microalgae (*Chlorella vulgaris*) as a sorbent for nitrofurantoin in urine samples for the first time. Unlike traditional MEPS methods, where the sorbent is typically synthesized, the authors cultivated and then applied dried algae (4 mg) packed into the MEPS apparatus. Among the usual parameters evaluated in MEPS protocols, this study specifically assessed the particle size of the algae. Larger particles (125 to 200 μm) were found to be more effective, as smaller particles substantially increased the back pressure of the microextraction apparatus. The analytical performance of the method showed an LOD of 0.039 mg L^{-1} and a recovery rate of 91.1%. The process was then applied to urine samples, demonstrating its effectiveness in determining nitrofurantoin in biological samples. The study presented by the authors represented a new direction for using biomass from green sources, expanding the range of potential sorbents for MEPS applications.

Cellulose is a polysaccharide with a long chain of β-D-glucose units linked by β-(1–4)-glycosidic bonds [112]. This natural material is a promising biodegradable and versatile polymeric precursor for hybrid and enhanced materials, which have potential applications in microextraction methods [113]. Due to its natural abundance, cellulose is considered a cheap and eco-friendly material for synthesizing and producing novel bio-sorbents for MEPS extraction [113]. Having this in mind, Matin, Ayazi, and Jamshidi-Ghaleh [114] proposed using cellulose filter paper coated with montmorillonite in polystyrene (MMT/PS) for the MEPS extraction of fluoxetine from water samples. They reported depositing the MMT/PS onto the filter paper for the cellulose modification using the phase separation method. The resulting films were cut, and several were placed inside the syringe barrel to create the final layered structure of the MEPS syringe. Characterization assays of the sorbent revealed a porous structure characteristic of cellulose materials.

Additionally, MEPS optimization indicated that the number of sorbent layers was the most influential parameter. A higher number of sorbent layers increased the specific surface area and provided more adsorptive sites for interaction with fluoxetine. The analytical application of the sorbent in the MEPS protocol achieved LODs as low as 2 ng mL^{-1}, with the recoveries of fluoxetine ranging from 76.4% to 107.2% in wastewater, river, and dam water samples. The study presented by the authors highlights the potential of cellulose as an eco-friendly sorbent, offering a green alternative to traditional, expensive, and non-environmentally friendly materials commonly used in MEPS extraction.

Despite the still-emerging trend of using biopolymers in MEPS extraction within the scientific community, researchers are continuously working to develop new bio-alternatives and sources for improved materials [13,22]. Gelatin is one of these materials with unexplored potential as a sorbent phase for microextraction methods, particularly in MEPS

approaches [115]. This natural and biodegradable material is derived from the hydrolysis of collagen, with the structural formula (NH_2COOH–CH–R), in which R represents an amino acid [116]. Its outstanding advantages include biocompatibility, low cost, non-toxicity, and high availability, making it highly desirable for proposing new environmentally friendly alternatives for microextraction methods [115,116]. Recognizing this potential, Moradi, Mehrani, and Ebrahimzadeh [117] demonstrated the fabrication of a gelatin/sodium triphosphate hydrogel nanofiber mat (GT/STP/HNFM) for the preconcentration of La^{3+} and Tb^{3+} in MEPS before their detection in environmental water using inductively coupled plasma optical emission spectroscopy (ICP-OES). For sorbent production, the authors utilized a spinning method in which a voltage of 12 kV was applied between two electrodes for 2 h. In the MEPS protocol, 12 mg of the sorbent was packed into the MEPS apparatus. This approach achieved LOD values of 0.1–0.2 ng mL^{-1}, with recoveries ranging from 85% to 102%. The authors also highlighted that the sorbent could be reused more than 25 times without losing its analytical performance.

Biomaterials have been highlighted in the literature as versatile alternatives to traditional sorbent phases commonly used in MEPS methods. This trend is driven by their unique physicochemical properties, including biodegradability, non-toxicity, availability, and low cost. Considering the critical principles of GAC, using biomaterials in microextraction protocols enhances the environmental sustainability of this emerging green analytical trend. It safeguards human health by promoting eco-friendly synthesis methods for obtaining these materials. When selecting the ideal sorbent phase for MEPS extraction in solid-based microextraction methods, aligning with the analysis's primary objectives is crucial while weighing each biomaterial's potential advantages and drawbacks. Table 2 highlights the benefits and disadvantages of the biomaterials discussed in this section.

Table 2. Advantages and drawbacks of biopolymers for use as sorbents in microextraction protocols.

Biopolymer	Advantages	Drawbacks	Ref.
Chitosan	Biodegradability, non-toxicity, high adsorption capability, easily modified.	Low solubility in neutral and alkaline pH; poor thermal and mechanical stability.	[118,119]
Cyclodextrins	Biodegradability, non-toxicity, host–guest chemistry, enhanced selectivity due to e large recognition cavities.	Partial solubility in water.	[118–120]
Cellulose	Biodegradability, non-toxicity, excellent mechanical proprieties, remarkable porosity, low density, high adsorption capacity, and low-cost material.	Hydrophobic matrix.	[121,122]
Natural Activated Carbon	Biodegradability, non-toxicity, high porous material, low-cost material, excellent mechanical proprieties.	Impurities from the biomass, pore size distribution, and the activation process can involve using chemicals and be energy-consuming.	[123]
Gelatin	Biodegradability, non-toxicity, low-cost material, and a high abundance of organic functional groups allow its modification and combination with different materials.	Poor thermal stability and chemical resistance, considerable fast degradability in water.	[116,124]

Although Table 2 illustrates the main advantages and drawbacks of biopolymers as sorbent phases in microextraction methods, researchers should focus on the drawbacks

of each material to select the ideal one. While biopolymers share common advantages, such as biodegradability and non-toxicity, evaluating their drawbacks can clarify the challenges researchers might face when applying these materials in MEPS protocols across different applications.

Although we have selected only a few biopolymers as sorbents to exemplify their potential in packed MEPS approaches, the continuous advancements in this scientific field remain largely unexplored. Many other biopolymers have been investigated for their application in microextraction strategies, though they have yet to be applied to MEPS methodologies. Biomaterials such as agarose, starch, alginate, and casein, among others, are derived from natural sources and possess adequate physicochemical properties for functionalization and modification. These enhancements could yield sorbent materials that are well suited for MEPS applications. From the authors' critical perspective, much effort is still needed to introduce new research focusing on the application of biosorbents in MEPS methodologies. These strategies can address common drawbacks, particularly the environmental impact of traditional and synthetic sorbent phases. Moreover, an updated literature review is necessary to expand the application of these sorbents in MEPS, as the current usage is still limited to the materials discussed in this study.

5. Insights into Semi and Automated MEPS Approaches: Current Applications

The automation of sample preparation techniques is a critical factor in improving high-throughput analytical workflows [125]. Manual sample handling is one of the major causes of errors in chemical analysis, which can be mitigated through automation [126]. Although equipment issues are also a crucial cause of errors in analytical methods, implementing systematic procedures for continuous verification, such as calibration, can maximize equipment reliability and reduce errors. The automation of MEPS has already been explored in the first decade of this century [127–129] but remains relevant today, alongside the automation of other sample preparation techniques [125,130–132].

A recently explored way to automatize MEPS sampling preparation is using a semi-automatic syringe controller. The semi-automatic MEPS is usually performed using a small semi-automatic syringe controller that can be manually moved through the sample's recipient. For example, this strategy has been employed by Xiong and Zhang [133] to determine catecholamines and metanephrines in urine. The semi-automatic syringe controller allows for the reduction of the sample preparation time. Combined with the LC-MS/MS approach, the method presented an LOQ below 1.53 ng mL^{-1} and accuracies between 88.4% and 112.0% intra-analysis and 89.0% and 109.5% inter-analysis [133]. Moreover, since MEPS material can be reused, it has the potential to significantly reduce the costs compared to non-reusable MEPS devices [133].

In another study, an MEPS method using a semi-automatic syringe controller could successfully determine vanillylmandelic acid in urine [134]. Parabens in cosmetics were also determined by a similar approach, with a semi-automatic syringe controller [135]. After optimization, the method resulted in a linear range between 0.05 and 4 μg mL^{-1} and an LOD below 5 ng mL^{-1} [135]. MEPS performed on semi-automatic syringe controllers has also been applied to metabolomic analysis. An MEPS extraction method was developed for simultaneous qualitative and quantitative analysis of forty-one compounds from brain-derived cell cultures in LC-MS, resulting in quantification limits lower than 10 ng mL^{-1} [136]. Fully automated commercial platforms have also been employed for MEPS. In general, the automation of MEPS in fully automatic equipment is performed in a multipurpose platform containing a moving arm with a syringe holder that can move above the sample recipients. As a recent example, a rapid and fully automated method has

been developed to quantify monohydroxy polycyclic aromatic hydrocarbons in human urine using MEPS coupled with gas chromatography–mass spectrometry (GC-MS) [137]. This approach enabled efficient analysis with reasonable LOD values below 19.4 μg L^{-1} in urine, accuracy between 88 and 110%, and precision between 5.1 and 19.0% in urine [137]. Likewise, in another study using commercial automatized MEPS, polyamines and related compounds were analyzed in saliva using in situ derivatization and MEPS coupled with GC-MS [138]. The automation was also performed in a fully automatized sampler that ensured an LOQ lower than 112.5 μg L^{-1} and accuracy between 74% and 109% [138].

Though commercial equipment is an option, lab-made equipment has also been successfully used for automated MEPS sample preparation. Medina et al. [139] developed a sample treatment platform that integrates various microextraction techniques with liquid chromatography, highlighting the advantages of automation in analytical procedures (Figure 5A). This platform consists of an Arduino-controlled XYZ Cartesian robot comprising a micro-syringe driver capable of loading, dispensing, and transferring sample aliquots. The robot moves on the lateral, horizontal, and vertical axes, and stepper motors move it. The platform can accommodate vial racks, stirring/heating mantles, and other laboratory instruments [139]. Furthermore, the syringe driver can accommodate a valve for integration with separation and detection systems such as LC. This equipment has been used for other applications such as needle–sleeve solid-phase microextraction coupled to LC [140], hollow fiber liquid-phase hyphenated to LC [141], and single-drop microextraction [142] coupled to LC [143].

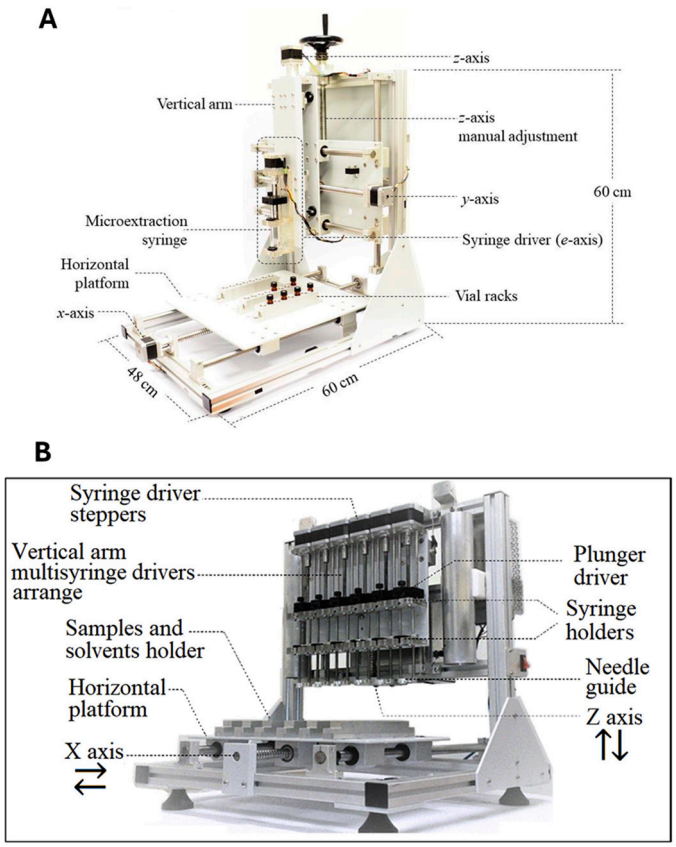

Figure 5. (**A**) Lab-made multitask sample treatment platform. Reproduced with permission from Elsevier and published initially in *HardwareX* [139] Copyright 2019 ELSEVIER. (**B**) Six-arm lab-made multitask sample treatment platform. Reproduced with permission from Elsevier and published initially in *Talanta* [19]. Copyright 2020 ELSEVIER.

A modification of this equipment, presenting six syringe holders, has been developed (Figure 5B). The presence of six syringe holders allows the equipment to prepare six samples simultaneously, improving the high-throughput capability of the MEPS sample preparation method. This device was successfully used for forensic and clinical analysis. Sartore et al. [19] developed an automated process for extracting cannabinoids from human urine using a lab-made device packed with an MIP polymer. This sampling preparation method demonstrates good linearity between 5 and 250 ng mL^{-1}, with the LOD and LOQ lower than 5.0 ng mL^{-1} and 20.0 ng mL^{-1}, respectively. The same automated robot was effectively employed in environmental analysis. Bocelli et al. [144] developed a microextraction by the packed sorbent–liquid chromatography–tandem mass spectrometry (MEPS-LC-MS/MS) method for determining parabens, benzophenones, and synthetic phenolic antioxidants in wastewater. This study demonstrated LODs ranging from 0.15 to 0.30 ng L^{-1}; the intra-day and inter-day relative standard deviations were between 3 and 21%. Contaminating compounds in drugs have also been monitored using the system. Dos Santos et al. [145] employed the six-arm robots to analyze N-nitrosamines in losartan tablets. The extractions were performed using a carboxylic acid-modified polystyrene divinylbenzene copolymer-packed MEPS cartridge. The automated MEPS presented a low LOD at 50 ng g^{-1}, with accuracy between 80% and 136%.

In short, the automation of MEPS, whether through semi-automatic syringe controllers or fully automated commercial platforms, is a modern and robust strategy for performing MEPS. Both approaches have demonstrated interesting analytical capabilities with low LOD and LOQ levels (Table 3). Semi-automated MEPS offers intrinsic advantages, such as lower costs and simpler instrumentation, enabling precise extraction cycles. However, these methods still require some level of manual handling, including the manual insertion and holding of the syringe in the sample container. In contrast, fully automated MEPS systems can process samples without manual intervention but require more expensive and specialized instrumentation. Commercial equipment is a simple and effective device that performs automatized (or semi-automated) MEPS with good reliability. Additionally, lab-made automated equipment, such as Arduino-controlled robots, further extends these advantages by integrating various microextraction techniques with high-throughput capabilities. Thus, the automation of MEPS not only streamlines analytical workflows but also ensures high sensitivity and reliability in detecting and quantifying target analytes across various matrices.

Despite all these advantages, the semi and complete automation of MEPS procedures still faces challenges that hinder its full potential in analytical applications. One major challenge is fully integrating MEPS with LC-MS methods in analytical procedures. This integration still requires significant effort to develop interfaces that provide such integration. Moreover, the implementation of semi- and fully automated MEPS instrumentation remains inaccessible to most laboratories or research groups due to the high costs and the need for a skilled operator. Therefore, for widespread implementation of these strategies in laboratories, the instrumentation needs to be more affordable and accompanied by easy-to-learn platforms for operation.

On the other hand, an option that still needs to be explored is the development of lab-made prototypes of semi- and fully automated MEPS. In these scenarios, researchers must ensure the reproducibility of these instruments to provide adequate analytical performance. Implementing new lab-made MEPS instrumentation is a potential approach to overcome the high costs of industrial versions. This is the future for more accessible and enhanced automated procedures, leading to improved analytical applications.

Table 3. Summarization of recent applications of semi-automatic and automatic MEPS.

Type	Sorbent	Analytes	Matrix	LOQ	LOD	Year	Ref.
Semi-automated	C18	Catecholamines, metanephrines	Urine	0.167–1.53 ng mL^{-1}	0.0800–0.440 ng mL^{-1}	2020	[133]
Semi-automated	AX	Vanillylmandelic acid	Urine	0.5 µg mL^{-1}	-	2020	[134]
Semi-automated	C18	Parabens	Cosmetics	0.05 µg mL^{-1}	2–5 ng mL^{-1}	2021	[135]
Semi-automated	C8, C18, and M1 mixed-mode sorbent containing 80% C8 and 20% SCX strong cationic exchange	Forty-one compounds from brain-derived cell cultures	Cell cultures	0.1–10 ng mL^{-1}	-	2023	[136]
Fully automated (commercial)	C18	Monohydroxy polycyclic aromatic hydrocarbons	Urine	1.5–65.6 µg L^{-1}	0.6–19.4 µg L^{-1}	2022	[137]
Fully automated (commercial)	C18	Polyamines and related compounds	Saliva	8.68–23.8 µg L^{-1}	1.83–33.8 µg L^{-1}	2019	[138]
Lab-made fully automated	MIP	Cannabinoids	Urine	5.0–20 g mL^{-1}	1.0–5.0 ng mL^{-1}	2020	[19]
Lab-made fully automated	Strata-X	Parabens, benzophenones, synthetic phenolic antioxidants	Wastewater	0.15–0.6 ng L^{-1}	0.15–0.30 ng L^{-1}	2023	[144]
Lab-made fully automated	Carboxylic acid-modified polystyrene divinylbenzene copolymer	N-nitrosamines	Drug tablets	80 ng g^{-1}	50 ng g^{-1}	2023	[145]

AX: anion exchange; SCX: strong cation exchange; MIP: molecularly imprinted polymer.

6. Conclusions

In this review, we have highlighted the application of traditional synthetic polymers and bio-based approaches for synthesizing enhanced sorbent materials for MEPS applications. The literature has emphasized the superior physicochemical properties of synthetic materials, including improved selectivity, high surface area, remarkable adsorption capability, and excellent thermal and mechanical properties. These attributes have been effectively utilized in MEPS applications and applied to complex matrices. The appropriate selection of synthetic sorbent materials has enabled MEPS protocols to outperform traditional sorbent phases, such as C18 and C8, by enhancing the analytical performance. These improved properties of synthetic materials have demonstrated their capability for trace-level analysis with high analytical throughput in MEPS methods.

Furthermore, implementing different materials to create hybrid sorbents has been explored as a potential approach to overcoming the common drawbacks of individual materials. Despite these advantages, the major drawback of synthetic materials remains the use of environmentally harmful synthesis protocols, which typically consume large amounts of organic solvents and generate significant chemical waste. There is a pressing

need for deeper insights into new and eco-friendly synthesis approaches to increase the potential of synthetic materials for green analytical practices.

On the other hand, there has been an increasing trend toward the introduction of bio-based sorbents. These materials offer key ecological benefits, such as green synthesis protocols and biodegradability, resulting in minimal or no harmful conditions for their production. A significant advantage of these materials lies in their rich abundance of functional groups, such as NH_2 and OH, which enable the modification of biopolymers with various materials to create enhanced biosorbents. Despite their extraordinary potential, our review noted a lack of applications for their use in MEPS protocols. This may be due to challenges associated with using packed biosorbents in MEPS strategies, such as the back pressure in MEPS syringes. However, there is still a need for considerable effort from the scientific community to propose new applications for biosorbents in MEPS, fully exploring their potential in this microextraction approach for diverse applications.

We have presented the current applications of semi- and fully automated MEPS instrumentation. As demonstrated, these approaches offer higher precision and accuracy in various analytical applications. One significant advantage of industrial versions is their reproducibility, which reduces the potential for human error in sample handling. Proper application of these strategies enables researchers to achieve low detection and quantification concentration levels with satisfactory recovery values across different applications. However, the implementation of automated and semi-automated MEPS systems continues to face challenges, primarily due to the high cost of these instruments and the requirement for skilled operators, who often need specialized training. This demand for training incurs additional costs and requires a significant investment of time. These factors hinder the widespread adoption of industrial versions in laboratories. To address these challenges, the fabrication of lab-made prototypes appears to mitigate cost-related issues.

Developing new, user-friendly interfaces can also enhance the application of semi- and fully automated MEPS strategies. However, significant scientific effort is still required to fully integrate MEPS with LC-MS. This integration has the potential to offer superior alternatives to traditional sample preparation methods in LC-MS applications, paving the way for new and improved analytical strategies.

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