Green Analytical Chemistry 7 (2023) 100077

Contents lists available at ScienceDirect

Green Analytical Chemistry

journal homepage: www.elsevier.com/locate/greeac

Cyclodextrins-based sorbents for sustainable sample preparation focusing on food analysis

Edvaldo Vasconcelos Soares Maciel [a,b], Natalia Gabrielly Pereira dos Santos [a], Deyber Arley Vargas Medina [a], Fernando Mauro Lanças [a,*]

[a] Institute of Chemistry of São Carlos, University of São Paulo, São Carlos, SP, Brazil
[b] Department of Chemistry, Clemens Schöpf Institute, Technical University of Darmstadt, Darmstadt 64287, Germany

ARTICLE INFO

Keywords:
Cyclodextrin
Sample preparation
Chromatography
Microextraction
Sorbent
New materials
Food analysis
Food surveillance

ABSTRACT

Food analysis is critical for ensuring human health and safety, as it involves the detection of contaminants such as pesticides, heavy metals, mycotoxins, allergens, and microbial contaminants. Effective extraction and preconcentration of these analytes are crucial to achieve accurate analysis and comply with regulatory standards. However, food matrices are complex, including solid, semi-solid, and liquid components, fats, proteins, carbohydrates, vitamins, minerals, and other organic and inorganic compounds. Therefore, isolation of target analytes is a challenging task. Developing efficient sample preparation techniques is essential to overcome such a downside. Exploring new and improved sorbent materials is one of the advanced strategies for developing selective and greener sample preparation approaches. Cyclodextrins (CDs) play a significant role in this topic. CDs can interact with various compounds with their external hydrophilic structure and central hydrophobic cavity. The functionalization of CDs' external hydroxyl groups allows for modifications in solubility, cavity opening, and bonding with other sorbent materials. This review discusses the current status of CDs as a robust sorbent material in food- and nutraceutical analysis. It covers the principles of CD-based sorbent preparation. It explores combining them with other materials, creating customized sorbents for solid-phase extraction techniques, including dispersive, packed devices-based, and coated devices-based methods. Moreover, we offer insights into relevant applications focusing on food surveillance and nutraceutical analysis.

Introduction

The significant advancements achieved in analytical instrumentation during the last decades have pushed forward the capabilities of the existing methods for food analysis. Monitoring and ensuring regulatory compliance in nutraceutical products is of great concern. However, this is always challenging, mainly because sample preparation of such matrices is still a bottleneck in many cases. This is primarily attributed to this procedure's labor-intensive and time-consuming nature, which makes the analytical methods susceptible to errors [1]. Sample preparation can account for approximately 70% of the total analysis time, including the entire analytical workflow [2]. It is often the most expensive and environmentally impactful step [3]. Traditional methods such as liquid-liquid extraction (LLE) and solid-phase extraction (SPE) remain prevalent in the industry sector [3]. However, analytical chemists are actively developing greener and high-efficient approaches consistent with the principles of Green Analytical Chemistry (GAC) [4, 5].

Green sample preparation involves using safe solvents, reagents, and renewable, recycled, and reusable materials. This approach minimizes

Abbreviations: ATP, attapulgite; CD, cyclodextrin; CNTS, carbon nanotubes; COF, covalent organic framework; DAN, danofloxacin; DLLME, dispersive liquid-liquid microextraction; EPI, epichlorohydrin; HF-LPME, hollow fiber liquid phase microextraction; IL, ionic liquid; GAC, green analytical chemistry; GO, graphene oxide; LLE, liquid-liquid extraction; MEPS, microextraction by packed sorbent; MIM, molecularly imprinted monolith; MIP, molecularly imprinted polymer; MNPs, magnetic nanoparticles; MOF, metal-organic framework; MSPD, matrix solid-phase dispersion; MWCNTs, multiple-walled carbon nanotubes; NC, nanocellulose; NP, nanoparticle; NS, nanosponge; PAHs, polycyclic aromatic hydrocarbons; PANI, polyaniline; PISA, polymerization-induced self-assembly; RAM, restricted access media; SBSE, stir bar sorptive extraction; SDME, single-drop microextraction; SMs, supramolecular macrocycles; SPME, solid-phase microextraction; SPE, solid-phase extraction; TFME, thin film microextraction.

* Corresponding author.
E-mail address: flancas@iqsc.usp.br (F.M. Lanças).

https://doi.org/10.1016/j.greeac.2023.100077
Received 25 May 2023; Received in revised form 25 July 2023; Accepted 28 August 2023
Available online 7 September 2023

waste generation and reduces energy demand [6]. While a rigorous evaluation is necessary to assess the actual environmental impact of new sample preparation developments, specific approaches are generally recognized for contributing positively towards more sustainable methods. Among these approaches, miniaturization, simplification/automation of techniques, and developing new efficient and sustainable extraction phases are key factors [7,8].

The miniaturization of sorbent-based techniques initiated by introducing solid-phase microextraction (SPME) in the early 1990s revolutionized sample preparation in analytical chemistry [9]. In short, SPME is based on the same principles as its predecessor SPE but focuses on reducing the use of toxic organic solvents and the sample amount [10]. The advent of SPME has encouraged the development of other miniaturized sorbent-based techniques over the past three decades, including μ-SPE, microextraction by packed sorbent (MEPS), stir bar sorptive extraction (SBSE), thin film microextraction (TFME), and more [11]. In addition, sorbent-based sample preparation microtechniques currently include sorbent-coated and packed extraction devices and dispersive-based approaches [10].

While this review primarily focuses on sorbent-based techniques, mentioning the modernization of solvent-based techniques derived from LLE is essential. Modern examples include dispersive liquid-liquid microextraction (DLLME), single-drop microextraction (SDME), and hollow fiber liquid phase microextraction (HF-LPME), among others [11]. All these miniaturized techniques have found extensive applications in food and nutraceutical analysis, contributing significantly to developing more sustainable methods. Furthermore, these techniques are aligned with green and sustainable principles, always focusing on less consumption of chemicals and reduced generation of toxic waste. Similarly, the automation of the analytical workflow has become crucial for developing modern sample preparation procedures [8,12]. Automating this procedure offers several advantages, including improved precision, enhanced reproducibility, increased analytical frequency, and faster analysis. Automated sample preparation techniques can run with significantly reduced human intervention, producing results less prone to analytical errors. Also, the analyst is less frequently exposed to hazardous chemicals, promoting a safer working environment [13]. Automating and integrating it with other analytical techniques is pivotal in the progress of analytical chemistry, including the food sector.

Although both miniaturization and automation have been keystones in this field, the possibility of obtaining even more sensitive methods depends highly on new, more selective, and efficient extraction materials [14]. Developing new sorbents is an attractive research area, and different classes are constantly springing up around the literature [15,16]. Widely known examples of them include molecularly imprinted polymers and monoliths (MIPs and MIMs), carbon-based compounds, ionic liquids (ILs), metal and covalent organic frameworks (MOFs and COFs), restricted access media (RAM), aptamer-based materials, immunosorbents, and supramolecular macrocycles (SMs) [7,17]. For more details about them, a series of excellent reviews are cited herein [18–25].

Among them, cyclodextrins (CDs) have a particular interest because of their selectivity, capability to interact with polar and non-polar compounds, as well as the possibility of being derivatized, supported, or chemically functionalized to obtain sorbents with customized properties [26]. Furthermore, CDs are supramolecular compounds (Fig. 1), i.e., they can be used to obtain nanoscopic solids without covalent bonds between them [24]. In this case, the main interactions emerge from host-guest principles (inclusion composites). In addition, CDs have large recognition cavities performing an excellent role as host molecules [26]. Due to their uniqueness, CDs can extract and pre-concentrate target analytes from matrices with several endogenous and exogenous compounds.

This review will primarily focus on samples related to food analysis, as they hold significant relevance due to their direct impact on human health. Developing and implementing analytical methods in this field is a complex task that requires careful consideration [28]. Usually, food-derived products are susceptible to contamination with external compounds (e.g., pharmaceutical drugs, pathogens, mycotoxins), mostly during production, transportation, or storage [29]. For this reason, international regulatory agencies and governments have strict laws to keep those residues and contaminants below harmful levels to humans and other animals [30]. However, these toxic compounds are often in lower concentrations than matrix substances, requiring very efficient sample preparation methods capable of extracting target analytes selectively and pre-concentrating them [31]. Here, cyclodextrin-based sorbents and their application in modern sample preparation methods for food analysis will be discussed, highlighting the most critical features. Relevant selected applications will be reviewed, mainly covering the last ten years.

Cyclodextrin-based sorbents

CDs are non-reducing oligosaccharides formed by linking glucopyranose units in a truncated cone shape [32]. These molecules possess a hydrophobic cavity that enables the formation of inclusion complexes with various analytes of interest in food analysis [33], including veterinary drugs, polycyclic aromatic hydrocarbons, dyes, aromatic derivatives, and volatile organic compounds [24]. From a purely analytical viewpoint, the above characteristics should be enough to give CDs the title of a "good" sorbent. What is not so obvious is that cyclodextrins are naturally occurring members of the cyclic oligosaccharides family of nontoxic compounds, usually possessing a -OCCO- binding motif. CDs can easily interact with metals from IA and IIA groups, forming customized materials even in an aqueous solution [34]. For example, metal-organic frameworks can be prepared under ambient conditions using just aqueous media [35]; or members of the apatite family can easily interact with CDs to form cross-linked nanocomposites [36]. Moreover, when it is necessary to produce CDs synthetically, especially in low amounts, some processes can further use the waste as raw material for producing other active substances, for example, alcohol [37]. In short, employing CD-based sorbents is often an environmentally friendly idea.

Among macrocyclic molecules, cyclodextrins offer notable advantages due to their relatively simple synthesis methodology and the ability to customize their properties for specific applications [38].

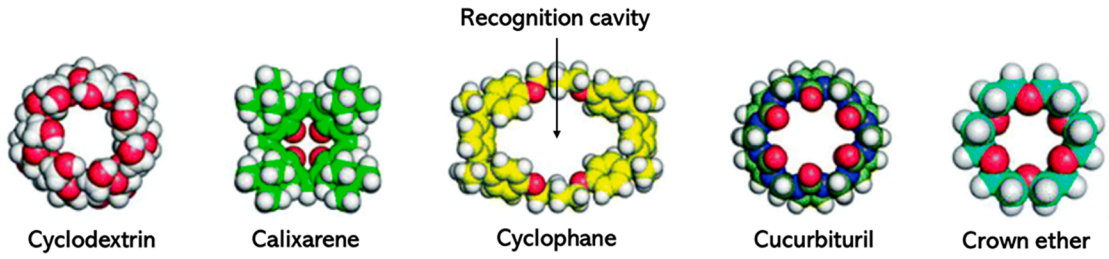

Fig. 1. Representative structures of common supramolecular macrocycles with potential for sample preparation use. Adapted from [27] with permission of Royal Chemistry Society, 2012.

Cyclodextrins are enzymatically derived from starch degradation, and the most commonly used homologs are α-CD, β-CD, and γ-CD, consisting of six, seven, and eight glucopyranose units, respectively [32]. However, β-CD is widely used in sample preparation due to its unique characteristics, including an intermediate-sized molecular cavity compared to α- and γ-CD, reduced solubility in water based-solutions resulting from favorable hydrogen bond localization, excellent complexation ability, and inherent crystal stability [39].

CDs have limited solubility in water, which restricts their use as standalone sorbents in sample preparation [40]. Aqueous CD solutions have been previously used to remove interfering compounds and extract target analytes. For example, Zhu et al. employed an aqueous β-CD solution to extract and quantify eight phenolic compounds from jujube fruit tissues [41]. The procedure involved adding dry pulp, seeds, and peel powders to a B-CD solution, followed by agitation, centrifugation, and filtration. The resulting clear liquid was then subjected to chromatographic analysis.

CDs are primarily used as sorbents in solid-phase extractions. However, their grade of solubility in water demands their covalent attachment to solid supports to enhance stability and enable their application in sorbent-based extraction methods [42]. CDs-based sorbents are typically achieved through three main approaches: (i) immobilization onto inert supports, (ii) combination with various nanomaterials (such as magnetic nanoparticles, carbon nanomaterials, carbonaceous nanomaterials, and polymer-based sorbents), and (iii) formation of nanosponges (NSs) by polymerizing CDs (monomeric units) with a suitable cross-linking agent [43].

Among these approaches, immobilizing CDs onto inert materials or combining them with nanomaterials often leads to sorbents with a low proportion of CDs. In contrast, NSs are regarded as auspicious materials. This approach allows the production of materials with diverse physical textures, mechanical properties, and shapes while maintaining a balanced presence of hydrophilic and hydrophobic groups. Furthermore, the swelling properties and amorphous nature of NSs facilitate analyte diffusion within the polymer network and simplify the sorption process. In recent developments, the focus has been on producing even more efficient materials. Efforts are underway to prepare CDs-based sorbents functionalized with diverse ionic and neutral groups, enabling simultaneous organic compounds, metals, and anions adsorption. Additionally, there is interest in creating materials capable of operating over a wide pH range [43].

However, CDs are primarily utilized as sorbents in solid-phase extractions. Due to their solubility in water, the covalent attachment of CDs to solid supports is essential to enhance their stability and make them suitable for sorbent-based extraction methods. These hybrid CD-based sorbents involve the incorporation of organic, inorganic, or polymeric supports into the hydroxyl groups of cyclodextrins [42].

Preparation of cyclodextrin-based sorbents

Cyclodextrins anchored to inert supports

Attapulgite (ATP) and silica are the more commonly used inert materials for immobilizing CDs [43]. Attapulgite is a hydrated magnesium aluminum silicate, $[(OH_2)_4(Mg, Al, Fe)_5(OH).2Si_8O_{20}]\cdot 4H_2O$, and it is typically coupled with CDs using KH-560 ((3-Glycidoxypropyl)trimethoxysilane) as a coupling agent. The coupling agent reacts with the OH groups of ATP through its methoxy silane groups, allowing the subsequent anchoring of CDs by reaction with the oxirane moiety in the presence of NaH and using dimethylformamide as the solvent (Fig. 2) [44]. For instance, Cui and coworkers prepared a β-CD/ATP sorbent for DSPE of fluoroquinolones in honey samples, achieving recoveries between 74% and 103% with relative standard deviations (RSD) of less than 7.4% [44].

Silica is widely employed as a material for functionalizing CDs due to its controlled composition, morphology, and porosity. CD-silica

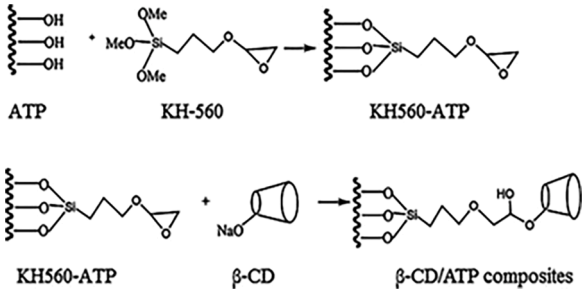

Fig. 2. Schematic representation of the synthetic route for the obtention of β-CD/ATP Composites [44].

materials can be categorized into two main classes: cyclodextrin-functionalized silicas prepared through grafting or coating reactions and cyclodextrin-silica hybrid systems prepared through sol-gel or self-assembly methods [45]. The first approach yields grafted matrices (Fig. 3a) and coated materials (Fig. 3b). These materials offer improved access to binding sites and enhanced thermal, mechanical, and chemical stability. However, they may suffer from uneven distribution of cyclodextrin molecules and low cyclodextrin loading, which can limit their adsorption capacities. In the second approach, nanoporous frameworks are obtained (Fig. 3c). These hybrid systems exhibit high cyclodextrin group loadings and robust structures, improving their adsorption capacity.

The literature comprehensively covers cyclodextrin-based silica materials' preparation, characterization, properties, and applications [43,45]. In this section, we have highlighted a few notable examples. However, it is relevant to note that numerous other silica-CD sorbents will be discussed in subsequent sections, particularly concerning different modalities of sorbent-based extractions for the treatment of food and beverage samples. For example, Zhang et al. [46] developed a sorbent from silica core-shell particles containing a magnetic core, followed by functionalization with mesoporous silica and cyclodextrin (Fe_3O_4@SiO_2@mSiO_2-β-CD), which was used for the extraction of doxycycline, an antibiotic of the tetracycline class. Langmuir isotherm models demonstrated a maximum adsorption capacity of 78 mg/g compared to 34 mg/g for the reference sorbent without cyclodextrin (Fe_3O_4@SiO_2@mSiO_2). In another study [47], they functionalized mesoporous silica with β-CD (SiO_2-β-CD) using the sol-gel method to remove methylene blue dye. The Toth isotherm model was used in this case, revealing a maximum absorption capacity of 60.55 mg/g. In this case, De Carvalho et al. [48] also dedicated efforts to removing methylene blue dye; however, the sorbent was developed from silica gel. The results showed a maximum adsorption capacity of 212 mg/g using the Langmuir isoform method. CDs immobilized onto silica particles also have demonstrated significant relevance in food analysis. In a recent study, a large pore hybrid mesoporous silica functionalized with β-cyclodextrins (LP-MS-β-CD) was utilized for the extraction of polyphenols from strawberry tree fruits, including arbutin and catechins. Both SPE and DSPE were employed. Remarkably, the DSPE technique using CD sorbents exhibited the most favorable extraction outcomes, with recoveries ranging from 104 to 113%.[49].

Cyclodextrin nanocomposites

CDs can also be attached to other nanomaterials to obtain hybrid sorbents with enhanced properties. For instance, carbon allotropes such as graphene oxide (GO) and carbon nanotubes (CNTs) functionalized with cyclodextrins have shown excellent extraction performance in various applications. [33]. These carbon allotropes stand out due to their high surface area, which in association with the CD adsorption capability, results in sorbent material with enhanced extraction characteristics. In the case of GO, the high aggregation of nanosheets hinders

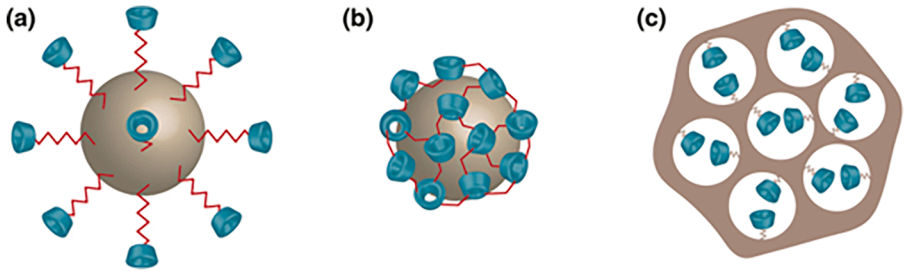

Fig. 3. Schematic representations of cyclodextrin-containing silica networks: (a) Grafted matrices, (b) Coated materials, and (c) Nanoporous frameworks [45].

its dispersion in an aqueous solution, making challenging applications in this medium. However, such limitations can be overcome through CD-GO anchoring. Song et al. [50] prepared β-CD-GO via in situ polymerization by sorption of Co(II) from aqueous solutions. The results showed that the ions' complexation occurs due to many functional groups containing oxygen on the surface of β-CD-GO, obtaining sorption of 72.73 mg/g under pH 6.0 ± 0.1 and $T = 303$ K.

Focusing on food analysis, Lança's research group recently introduced a β-CD-GO@SiO2 composite for the MEPS of isoflavones from juice samples [51]. The extractions were performed using only 1.0 mg of the sorbent material, resulting in excellent selectivity and enrichment capability while minimizing matrix effects. Additionally, this same material was utilized as an extractant in the automated online coupling of SPME with liquid chromatography [52]. We developed innovative coated needle sleeve devices attached to the endpoint of a syringe needle on a lab-made robot. This automated system performed the entire extraction procedure, including injecting the enriched extract into the chromatographic system.

Like GO, CNTs also possess low dispersivity in an aqueous solution. However, this material has excellent characteristics such as hollow and porous cylindrical structure and low mass density. In this sense, cyclodextrin can be used to increase the dispersion of this material [33]. As an example, He et al. [53] developed a sorbent based on cyclodextrin grafted on multiple-walled carbon nanotubes (MWCNTs/β-CD) to remove Cr(IV) and phenol. The material's adsorption capacity was determined by the Langmuir isoform method and compared with carbon nanotubes (MWCNTs-COOH). The data demonstrated that MWCNTs/β-CD showed adsorption of 9.74 mg/g for Cr(VI) due to the complexation of ions with hydroxyl groups on the outer surface of beta-CD, compared to 6.76 mg/g of MWCNTs-COOH. This adsorption was 100.27 mg/g for phenol and 77.66 mg/g, respectively. In an illustrative application of this type of material in food analysis, Chen and colleagues devised a carbon nanotube (CNT) nanocomposite incorporated with β-cyclodextrins (CNT-β-CD), which was subsequently immobilized within the pores of a hollow fiber using sol-gel technology. This composite material was employed for the trace analysis of tomato pesticides, yielding satisfactory recoveries ranging from 84.2 to 108.9% [54].

As illustrated in subsequent sections, combining CDs with magnetic nanoparticles (MNPs) is one of the more notable current trends in developing new CD-based sorbents for sample preparation methods. Among nanoparticles, iron oxide (Fe_3O_4) stands out as the primary magnetic carrier for CD functionalization, primarily due to its easy preparation and its excellent magnetic properties that facilitate efficient sorbent uptake using an external magnetic field. Some recent examples of this kind of sorbent involve the functionalization of β-cyclodextrin with ionic liquids and immobilized on magnetic nanoparticles (Fe_3O_4@βCD-Vinyl-TDT) to analyze polycyclic aromatic hydrocarbons (PAHs) in rice samples [55]. In addition, Ansari et al. [56] described the synthesis of hydroxyapatite-β-cyclodextrin (Fe_3O_4@HA-β-CD) used to remove heavy metals. More recently, Liu and coworkers [57] developed an N, N'-carbonyldiimidazole-β-cyclodextrin sorbent (Fe_3O_4@β-CD-CDI) for sorption and degradation of bisphenol A.

Cyclodextrin nanoporous frameworks (Nanoesponges)

Cyclodextrin-based nanosponges are a term used to define a family of insoluble organic and inorganic polymers which possess voids, internal cavities, and a porous network of nanoscale dimensions [58]. Usually, they formed colloidal dispersions in a solution that could encapsulate small molecules inside its irregular lattice [59]. Therefore, CD-based nanosponges have been found applicability as sorbent for sample preparation. So far, there are applications of them covering: decontamination of drinking water [60], bisphenols from water and juices [61], PAHs from rice [55], and pesticides from cow milk [62], among other water-related applications [63]. These polymers are obtained by polymerizing a cyclodextrin derivative as a monomer or by polycondensing cyclodextrin monomers with cross-linking agents (bi- or multifunctional molecules) [33]. The latter approach is most commonly used for synthesizing CD-based sorbents. For instance, epichlorohydrin (EPI) is a widely used cross-linker due to its high efficiency but is not environmentally friendly [64]. Other examples of cross-linkers are diisocyanates (e.g., hexamethylene diisocyanate, toluene diisocyanate), which require organic solvents in the reaction, or more eco-friendly alternatives such as carbonyls (e.g., diphenyl carbonate, N, N-carbonyldiimidazole), polycarboxylic acids, halides, and anhydride derivatives [65].

Another example is ethylenediaminetetraacetic acid (EDTA) [66], which synthesized the EDTA-β-CD polymer with a high sorption performance in removing metals. It is worth remembering that nanosponges are distinct from other CD-based sorbents, especially regarding the adsorption mechanism [43]. The characteristic cone shape-like of cyclodextrins is just partially available because they are primarily blocked throughout the nanoporous 3D structure of the solid material [43]. This means that in addition to host-guest interactions, CD-based nanosponges can trap analytes by other mechanisms that are still not fully understood [43,67]. This would explain the less popularity of this material compared to the other CD-based sorbets and the necessity of developing more greener nanosponges without using toxic cross-linkers and solvents.

Applications of cyclodextrins-based sorbents in food and nutraceutical analysis

CDs have become pivotal in advancing sorbent-based extractions from food and beverage samples. This encompasses diverse extraction techniques involving various CD-based sorbents, devices, and modalities. However, it is essential to note that food constitutes a collection of distinct matrices rather than a singular entity. The origin of the food, whether animal or plant-based, introduces a vast spectrum of samples characterized by substantial variations in physical attributes (solid, semi-solid, liquid, and viscous materials) and chemical composition. Such diversity poses challenges and necessitates food analysts to employ cutting-edge science and technology.

The physical characteristics of food samples contribute to significant variation due to uneven analyte distribution and interfering matrix components. Consequently, sample pretreatment is necessary to ensure

homogenization, particularly for solid and semi-solid food samples. Techniques such as dry grinding, wet grinding-slurry mixing, or cryogenic grinding are commonly employed to achieve uniformity in solid samples [68]. While Matrix Solid-Phase Dispersion (MSPD) and QuEChERS enable direct treatment of solid samples, most cases involve suspension, centrifugation, and filtration to transfer analytes into a liquid medium suitable for CD-based sorbent microextraction. After these operations, the homogenized solid sample can be extracted with a suitable solvent, resulting in an extract that can be further processed as a liquid sample [69]. The choice of suspension solvent and specific sample pretreatment details vary depending on the application and sample characteristics.

Even after sample pretreatment, food extracts remain complex matrices due to the presence of diverse compounds, including proteins, fats, sugars, salts, vitamins, additives, and more, each possessing distinct polarity, size, and chemical properties. These matrix interferences adversely affect critical analytical parameters such as limits of detection and quantification, accuracy, and precision, leading to reduced sensitivity and selectivity during analysis [70]. Therefore, direct analysis of food samples is generally impractical, and an appropriate extraction procedure must precede instrumental analysis. In this context, CD-based sorbents play a pivotal role by offering numerous opportunities for combining with other materials to create sorbents with enhanced selectivity. As discussed further in the subsequent section, these sorbents have demonstrated outstanding performance in a wide range of applications, encompassing diverse embodiments of sorbent-based extraction and addressing various analytes and matrices.

CDs in packed devices-based micro extractions

The efficacy of cyclodextrin-functionalized composites as extraction media has also been substantiated in various packed-device-based micro extractions, with offline approaches especially prevalent in recent years. Compared with SPME or SBSE, sorbent-packed-based techniques can offer some advantages, such as easier preparation of the extractant devices and a more significant number of accessible active sites for analyte/sorbent interaction. The packed-devices micro techniques rely on extraction microcolumns through which samples and solvents are percolated. With the appropriate sequence of column conditioning, sampling, washing, and elution, analytes can be selectively enriched, and the matrix interferents eliminated.

In recent years, cyclodextrin-functionalized sorbents have gained considerable attention in the development of packed devices for various techniques, including conventional solid-phase extraction (SPE) and its miniaturized counterparts such as μ-SPE, Disposable pipette tip microextraction (DPX), and MEPS. Table 1 provides a concise summary of selected examples highlighting the application of cyclodextrin-functionalized sorbents in analyzing food and beverage samples using packed devices-based techniques. The table showcases the versatility of these techniques, in conjunction with a diverse range of cyclodextrin-based sorbents, for the extraction of a wide array of volatile and non-volatile organic compounds, including pesticides, mycotoxins, flavonoids, and hormones, among many others. These compounds have been successfully extracted from various matrices, including vegetables, meat, feeds, juices, and wine. Additionally, it includes details regarding the quantity of sorbent utilized in each case, the analytical system employed, and the limits of detection (LODs) obtained. These comprehensive insights provide the reader with a clear understanding of the efficacy of cyclodextrin-based sorbents in these applications.

Conventional solid-phase extraction (SPE) is a simple approach for testing functionalized sorbents. It has been used to assess materials such as cyclodextrins@silica nanocomposites [80], β-cyclodextrin polymers [61], β-cyclodextrin based MIPs [81], polymers grafted with allotropic forms of carbon [82], β-cyclodextrin- nanosponges [73], and Cyclodextrin-metal–organic framework (CD-MOF) composites [35], among many others. In most cases, between 50 and 100 mg of sorbent are packed into a reusable SPE device (or a polypropylene syringe) and retained between two porous frits. Although incredibly convenient for testing particulate cyclodextrins functionalized materials, SPE has also been employed with other sorbents, such as cyclodextrins functionalized sponges. For example, Hou et al. prepared a covalently β-Cyclodextrin modified three-dimensional graphene oxide-wrapped melamine foam (MF) [72]. In this case, once prepared, the functionalized MF was packed into a 3 mL propylene SPE cartridge, compressed by two sieve plates, washed, and conditioned for further SPE of flavonoids from a *Lycium barbarum* extract (Fig. 4a). The β-CD/GO-wrapped MF exhibited an interconnected framework with high porosity and some lamellar structure, providing excellent extraction efficiency through π-π, hydrogen bonding, and host-guest interactions. Afterward, the same research group introduced a similar approach for the SPE of green malachite from seafood samples [76]. After preparation, a cube of novel β-CD-GO/MF was transferred into a 2.5 mL syringe and stuck between 0.22 μm filters. This approach proved to be a fast and efficient sample preparation strategy, with satisfactory recoveries and lower

Table 1
Selected applications of cyclodextrins-functionalized sorbents in packed-devices-based techniques for the treatment of food and beverage samples.

Analytes	Matrix	technique	Sorbent	Sorbent amount (mg)	analysis	LOD	Refs.
Food and beverage samples							
Methyl parathion and fenthion	Lettuce	DPX	Acryloyl β-CD-silica hybrid monolithic column		HPLC-DAD	4.5 −6.0 μg kg^{-1}	[71]
Sulfonamides	Chicken, pork, liver, and fish	SPE	β-CD/MOF	40	HPLC-UV	0.32–1.7 μg L^{-1}	[35]
Flavonoids	Chinese herbal medicine	SPE	β-CD/GO/MF		HPLC–UV	0.5–2 μg L^{-1}	[72]
Ochratoxin A	Grape juice and Wine	SPE	polyurethane/βCD composite nanosponge	300	HPLC-FLD	0.2 μg L^{-1}	[73]
Carbendazim and carbaryl	Leafy vegetables	DPX	Acryloyl β-CD-silica hybrid monolithic column		HPLC-DAD	1.0 and 1.5 μg kg^{-1}	[74]
Phenolic compounds	Tea beverages	SPE	Poly (glycidyl-co-ethylene dimethacrylate) nanohybrid modified with β-CD	100	HPLC-FD GC–MS	0.7–17 μg L^{-1},	[75]
Malachite Green	Seafood	SPE	β-CD/GO/MF	–	HPLC-UV	0.21 mg L^{-1}	[76]
Plant growth regulators	Plant-derived tissues and Foods	SPE	β-CD/MAA-MIPs	200	GC-FID	0.012–0.023 μg L^{-1}	[77]
Isoflavones	Soy Juices	MEPS	β-CD/GO@SiO_2	–	HPLC/MS/MS	0.5–1.0 μg L^{-1}	[51]
Aflatoxins	Maize and animal feeds	μ-SPE	β-CD/porous graphene (β-CDPG)	15	HPLC-FLD	0.025–100 μg kg^{-1}	[78]
Sanshool acid amide compounds	Pepper oil resin	SPE	β-CD/MIP	–	HPLC-UV GC-MS	–	[79]

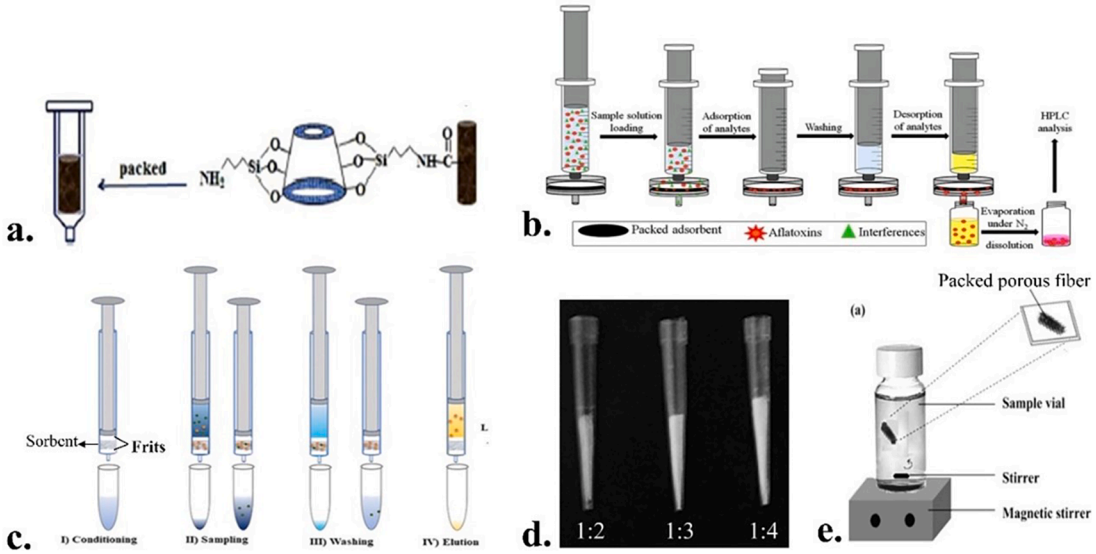

Fig. 4. Different formats of packed sorbent microextraction, employing cyclodextrin-functionalized extraction phases: **a.** SPE device packed with a β -Cyclodextrin-modified three-dimensional graphene oxide-wrapped melamine foam for extraction of flavonoids [72]; b. reusable syringe filter packed with a β-cyclodextrin decorated porous graphene nanohybrid to extract aflatoxins [78]; c. MEPS device adapted by the Lanças research group [83] and packed with β-Cyclodextrin, coupled to graphene oxide, supported the aminopropyl silica to extract isoflavones [51]; d. Pipette tips device packed with a β-cyclodextrin-silica hybrid monolithic column for the extraction of pesticides; e., a packed device developed by the Lee research group [84] and packed with cyclodextrin-based polymer to extract steroids [85].

consumption of sorbent and solvents than those based on commercial SPE cartridges.

Some alternative sorbent-packed devices have been proposed to reduce the amount of sorbent consumed and provide miniaturized, environmentally friendly sample preparation methods. For example, Tezerji and coworkers developed a β-CD supported on porous graphene nanohybrid (β-CDPG) based μ-SPE setup [78], packing 15 mg of the supramolecular nanohybrid composite into a reusable filter holder (Fig. 4b). In the μ-SPE of aflatoxins from maize and animal feed samples, this setup allowed exploiting of the advantages of the recognition and enrichment capability of β-CD and the high specific surface area of the porous graphene, providing faster sample loading capacity than those possible with conventional SPE cartridges.

Da Silva et al. developed a cyclodextrin coupled to graphene oxide supported on an aminopropyl silica composite for the MEPS of isoflavones in soy beverages [51]. In this case, less than 4.0 mg of the β-CD/GO@SiO_2 sorbent was packed into a 1.0 mL polyethylene syringe and between two polypropylene frits (Fig. 4c). Despite the very low sorbent employed, this setup exhibits LODs comparable to those reported by previous SPE methods for isoflavones determination. Moreover, the setup allowed very profitable sorbent reuse (over 50 times) and speedy sample preparation, requiring less than 5 min for the whole sample preparation process.

DPX has also been particularly useful in testing cyclodextrin-functionalized monolithic extraction media. Chen and coworkers prepared hybrid monolithic columns by directly polymerizing the acryloyl β-CD as the monomer into pre-treated 200 μL pipette tips (Fig. 4d). [74]. The monolith retained the β-CD molecular recognition capacity, and the developed pipette-tip setup allowed the sensitive determination of carbendazim and carbaryl from just 3.0 mL of extracts of leafy vegetables. The same research group recently described the preparation of acryloyl β-cyclodextrin-silica (A-β-CD-silica) hybrid monolithic columns through a sol-gel approach [71]. Sample preparation was performed by connecting the packed tip to a 5 mL gastight syringe to promote condition, sampling, washing, and elution with the syringe plunger. Assessed in the extraction of methyl parathion and fenthion in lettuce samples, this setup provided high enrichment factors and suitable sensitivity.

Another interesting cyclodextrin sorbent-packed approach combined the packed-bed format and SBSE. Manaf and coworkers developed a porous fiber-packed to extract steroids from human urine, employing polymeric β-cyclodextrin [85]. First, sorbents were prepared by cross-linking β-cyclodextrin (β-CD) using two cross-linker units at variable reactant mole ratios. Subsequently, 5 mg of sorbent was packed into a folded porous membrane, and the extractions were performed by the suspension of the extractant device in the sample solution under stirring conditions (Fig. 4e). The developed setup demonstrated suitable extraction capabilities and outstanding selectivity due to the combination of the large molecule's exclusion properties of the porous membrane and the variable hydrophilic-lipophilic balance and accessible binding sites for forming an inclusion complex of the β-CD polymer sorbents.

CDs in coated devices-based techniques

SPME is undoubtedly the most widely adopted technique for utilizing extractive devices coated with a thin layer of sorbent [86]. The predominant approach involves using metallic or silica fibers with diameters below 500 μm. Nonetheless, the emergence of SPME has also spurred the advancement of other coated-device-based techniques, such as in-tube SPME and SBSE. These alternatives replace the SPME fiber with open tubular columns or magnetic stir bars as extraction media (Fig. 5).

A recent study introduced a β-CD-functionalized silica-based SPME fiber (CDS) to enrich phenols [87]. Scanning electron microscopy analysis revealed the porous surface of CDS, resulting in increased extraction capacity. Additionally, this novel material exhibited shorter extraction and desorption times than commercial polydimethylsiloxane (PDMS) and polyacrylate (PA) fibers, leading to faster and more efficient analysis. The CD-fiber demonstrated superior enrichment of phenols, particularly for the target analyte 4-methyl phenol (4-MP), suggesting that phenols with sizes and shapes compatible with the β-CD cavity yield improved enrichment results.

Other examples of the application of cyclodextrins in SPME include their functionalization with carbon nanotubes (CNTs) in hollow fiber devices [88] for the extraction of plant hormones - 1-naphthalene acetic acid (NAA) and 2-naphthoxyacetic acid (2-NOA)- in tomato samples.

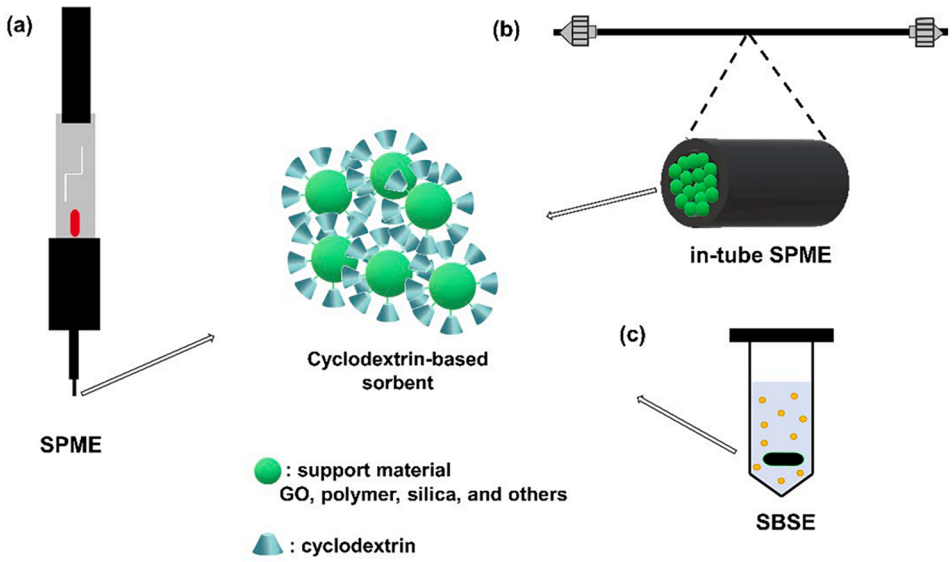

Fig. 5. Schematic representation of coated devices-based microextraction. (a) holder of SPME; (b) fiber in-tube SPME; (c) SBSE.

The results demonstrate that the enrichment factor for CNTs-β-CD was much higher (EF = 275 and 283 for NAA and 2-NOA, respectively) than that presented by a conventional hollow fiber (EF = 34 and 95) and another of CNTs (EF = 153 and 118).

Further examples include the modification of nanocellulose with β-cyclodextrin (CD-NC) [89], employing an amidation reaction (Fig. 6a) for the extraction of veterinary antibiotic danofloxacin (DAN) in milk samples. According to the authors, the interactions that lead to the inclusion complex's formation are hydrogen bonds, Van der Waals forces, and hydrophobic interactions. Pre-concentration data for DAN were generated to compare the new sorbent CD-NC with carboxylated and amidated nanocellulose, obtaining a value of 98.97%, 0.16%, and 0.12%, respectively (Fig. 6b). These results demonstrate the effectiveness of CD-NC in extracting the antibiotic and presenting a recovery rate of 76.40%.

Open tubular columns coated with cyclodextrin-based sorbents offer another coated devices-based sample preparation option. This technique, known as in-tube solid-phase microextraction (in-tube SPME), involves switching an extractive column to an analytical column through a commutative valve. This configuration allows direct loading of raw samples into the extraction column, washing out matrix interferents, and transferring analytes to the analytical column in an online and automated setup [90]. In-tube SPME is a versatile and advantageous approach for the automated treatment of complex samples. However, after consulting the literature, no reports were found regarding using cyclodextrin-based sorbents in-tube SPME for food analysis. It is worth noting that there are no practical barriers to preparing capillary open tubular columns coated with cyclodextrin-based phases. Such devices have been previously developed for analytical [91] and extractive purposes [92]. Considering the exceptional selectivity of cyclodextrins, the development of open tubular columns for the online treatment of beverage and food extracts represents an intriguing research area. Given the outstanding selectivity of cyclodextrins, This could bring new insights into food surveillance and nutraceutical analysis.

Cyclodextrins have also been reported using the SBSE technique in another approach. Lei and coworkers [93] created a stir bar coated with polyaniline and α-cyclodextrin (PANI/α-CD) for the enrichment of polychlorinated bisphenol (PCBs). The extraction performance of PANI-α-CD was compared with a commercial PDMS and a PANI stir bar through the peak area for each analyte. A good performance of the authors' sorbent was observed due to the material's hydrophobic interactions, inclusion complex, and π-π electron conjugation. In another report, Hu et al. [94] developed a PDMS/β-CD stir bar for extracting bisphenol A and estrogens (estriol, 17β-estradiol, 17α-ethynylestradiol, and estrone) in samples of drinking water. Before applying the sorbent to the actual samples, the authors sought to understand the selectivity of the PDMS/β-CD. For this, the new material's extraction capacity was compared with a conventional PDMS stir bar, using estrogens and PAHs

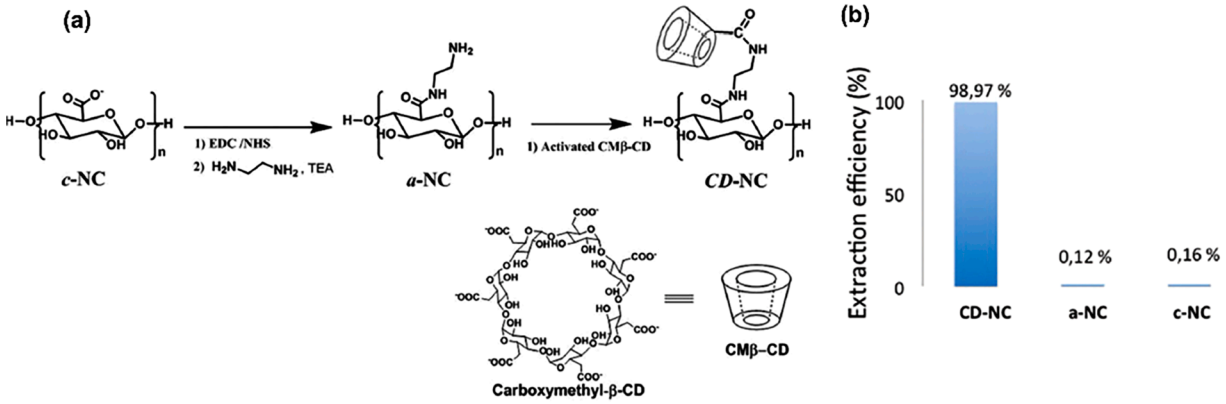

Fig. 6. (a) Synthesis of the CD-NC through the amidation reaction. (b) The extraction efficiency of CD-NC compared to amidated nanocellulose (a-NC) and carboxylated nanocellulose (c-NC). Adapted from [89] with permission of the Royal Society of Chemistry, 2015.

(fluoranthene and pyrene) standards PDMS/β-CD provided enhanced extraction of estrogens, for instance, about three times for estriol. However, it showed a slight decrease in the extraction of PHAs (e.g., 185 ng of fluoranthene were extracted by PDMS/β-CD compared to 186 ng for the PDMS stir bar). Therefore, the presence of β-CD in the sorbent increases the selectivity for polar compounds (estrogens and bisphenol A) more than for non-polar compounds.

Hu et al. [94] observed that cyclodextrin-based sorbents increase selectivity for polar compounds. This conclusion was also observed by Faraji et al. [95]. The authors used the silica functionalized with β-CD) to enrich phenolic compounds via SBSE [87]. The CDS stir bar was compared with the conventional PDMS stir bar. The results showed a higher extraction capacity of the CDS than the PDMS precisely because of its porous surface that increases enrichment and cyclodextrins' presence, making the material more polar. This CDS stir bar was tested on spiked drinking water samples with 15 μg/L of each analyte, obtaining excellent extraction repeatability with RSDs of 3.1- 6.5% for seven replicates.

Functionalized membranes represent another type of coated device extensively employed in current applications. A notable example is the work by Hu et al. [96], where they devised a polydimethylsiloxane-cyclodextrin membrane (PDMS/β-CD) via the sol-gel approach. This membrane was explicitly designed to enrich PAHs and phenols. In contrast, PDMS membranes have a higher sorption capacity (due to the high surface area) than conventional SPME fiber with the same material. In this study, the PDMS/β-CD membrane showed a good capacity for enriching PAHs compared to the PDMS membrane, mainly for naphthalene, once it has an adequate size and shape to form a complex of inclusion with β-CD. Furthermore, this membrane also showed promising results for the extraction of phenols, under low pH conditions (where they are in neutral form) and high salt concentration, through the formation of hydrogen bonds or inclusion complexes. Therefore, the PDMS/β-CD membrane proved versatile in enriching non-polar and polar compounds.

CDs in dispersive solid phase extractions

One of the most remarkable trends in exploiting CDs functionalized sorbents is their use in DSPE, particularly with magnetic material (MSPE). DSPE is a fast and efficient technique based on the dispersion of the extractant material into the sample solution under stirring conditions (or ultrasonic force convection). DSPE overcomes the drawbacks of the clogging and high backpressures that limit the sorbent-packed devices' lifetime and provide more effective interaction between the sorbent and the analytes than the coated devices-based techniques, resulting in fast and efficient extractions. Nevertheless, DSPE procedures typically involve centrifugation and filtration stages for sorbent separation. Therefore, MSPE has become a profitable alternative to exploit the advantages of the DSPE while excluding the filtration or centrifugation steps once an external magnetic field can easily retrieve the sorbent. Table 2 summarizes some selected recent publications describing applications of cyclodextrin functionalized sorbent for the treatment of food samples employing both DSPE and MSPE techniques.

Dispersive solid-phase extraction

In recent years, DSPE with cyclodextrin functionalized sorbents has been used in the treatment of food/beverage samples to effectively extract different analytes such as natural products [99], hormones [111], pollutants [112], and enzymes [103]. DSPE is a simple technique, easily implementable with raw cyclodextrin materials. For example, Zhang et al. extracted anthocyanins plant materials by mixing milled material with an extraction solvent and an aqueous solution containing β-CD [99]. A 1.65% β-CD solution and a liquid/solid ratio of 15:1 were enough to produce excellent extraction, providing a sustainable and reliable approach.

Cyclodextrin-based DSPE has also been utilized employing diverse polymeric materials, including carboxyl-functionalized porous β-cyclodextrin polymer (P-CDP-COO−) [103], MIPs [112], monodisperse restricted access media-molecularly - imprinted polymers (RAM-MIP)

Table 2
Selected applications of dispersive sorbent-based extraction using CDs-based sorbents.

Analytes *Food and beverage samples*	Matrix	Technique	Sorbent	mg	analysis	LOD	Refs.
Plant growth regulators	Fresh vegetables	MSPE	IL/Fe_3O_4@SiO_2/GO/β-CD	60	HPLC-MS	0.01 −0.018 μg kg^{-1}	[97]
Antioxidant ingredients	*Mori fructus*	MSPE	β-CD	75	HPLC-UV	30.0 ng ml^{-1}	[98]
Anthocyanins	L. Ruthenicum fruit	DSPE	β-CD	5	UPLC-DAD	0.117 −0.390 μg L^{-1}	[99]
Pyrethroids	Juice	MSPE	MNP@PAMAM@CD@IL)	50	HPLC-DAD	0.36 - 1.3 μg L^{-1}	[100]
Phthalic acid esters	Water, milk, and wine	MSPE	MIP@mSiO_2-β-CD@Fe_3O_4	30	GC–MS	1.0∼5.0 μg L^{-1}	[101]
Tetracyclines	Bovine milk	MSPE	Fe_3O_4@SiO_2@GO-β-CD	10	HPLC-UV	1.8 - 2.9 μg L^{-1}	[102]
Lysozyme	Egg white	DSPE	Carboxyl-functionalized porous β-CD polymer P-CDP-COO−	30	HPLC-UV	–	[103]
Catechins	Green tea	DSPE	Fe_3O_4/Amino-chitosan/β-CD	–	HPLC-UV	0.22 - 0.18 μg g^{-1}	[104]
Phenolic compounds	Red beet extract	DSPE	β-CD	–	UV-VIs		[105]
Beta-carotene	Carrots	MSPE	Fe_3O_4/Chitosan/β-CD	60	HPLC-UV	0.21 μg mL^{-1}	[106]
Polycyclic aromatic hydrocarbons	Rice	MSPE	Fe_3O_4/poly(β-cyclodextrin-ionic liquid) nanocomposites	20	GC-MS	0.01 - 0.18 μg kg^{-1}	[55]
Sudan dyes	Foodstuffs and environmental water	MSPE	Fe_3O_4/ porous β-CD polymers (PCDPs)	4–8	HPLC-DAD	0.025 −0.054 μg L^{-1}	[107]
Carbaryl and carbofuran	Apple	MSPE	Fe_3O_4@polyhedral oligomeric silsesquioxanes/β-CD	15	HPLC-UV-VIs	0.5 - 0.7 μg kg^{-1}	[108]
Sulfonamides	Meat samples	MSPE	Fe_3O_4@COF@Au-β-CD	20	HPLC-MS/MS	0.8 - 1.6 μg kg^{-1}	[109]
Phytohormones	Oilseeds	MSPE	Ti_3C_2 MXene/β-CD/Fe_3O_4 Fe_3O_4@Ti_3C_2@β-CD	5	UPLC-MS/MS	0.89 −13.62 ng L^{-1}	[110]
17β-estradiol	Milk	DSPE	β-CD/monodisperse RAM/ MIP	100	HPLC-UV	2.08 μg L^{-1}	[111]
Carbendazim	Fruits	DSPE	β-CD/MIP	20	HPLC-UV	0.03 mg L^{-1}	[112]
Plant growth regulators	Vegetables	MSPE	Fe_3O_4@SiO_2/GO/β-CD	100	GC-MS	0.04 - 0.28 μg kg^{-1}	[113]
Benzoylurea insecticides	Honey, tomato, and water samples	MSPE	β-CD polymer@Fe_3O_4	16	HPLC-UV	0.02 - 0.8 μg kg^{-1}	[114]
Ofplant growth regulators	Fresh vegetable	MSPE	Fe_3O_4@SiO_2/GO/β-CD	80	UHPLC-QTrap-MS/MS	0.04 - 0.29 μg kg^{-1}	[115]

[111], and some natural polymers derived sorbent such as amino-based chitosan cyclodextrin derivatives [104]. An alternative DSPE extraction with a cyclodextrin sorbent was reported by Yang and coworkers [116], who prepared effervescent tablets with the β-CD/ATP sorbent to extract pyrethroids without an external force such as vortex, stirring, or ultrasonication. The effervescence works as a dispersive mechanism so that this setup could be suitable for in-field environmental extractions. However, a centrifuge could be required to retrieve the extract sorbent.

Magnetic solid-phase extraction

MSPE is currently considered the preferred technique for evaluating innovative cyclodextrin-functionalized sorbents. Fe_3O_4 nanoparticles (NPs) are widely used to synthesize magnetic cyclodextrin-functionalized sorbents among magnetic carriers. These NPs can be directly functionalized with cyclodextrins or coated on silica or other polymers and then grafted with cyclodextrins and additional functionalized moieties.

An example of magnetic sorbent prepared by direct co-precipitation of MNPs in the presence of CDs was introduced by Wang et al. [117]. The

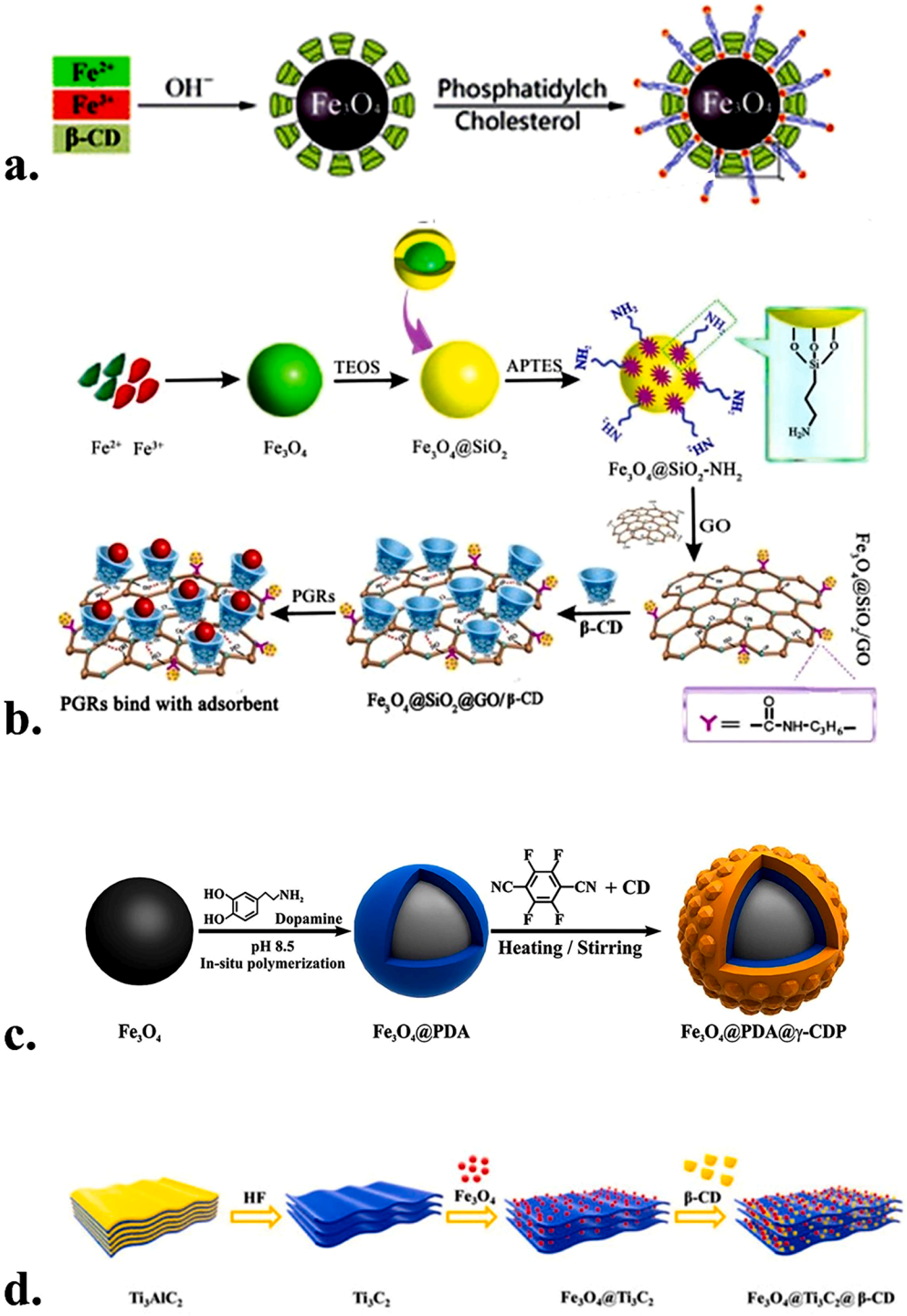

Fig. 7. Some examples of magnetic cyclodextrin functionalized sorbents. (a) cyclodextrin–lipid bilayer (β-CD–LB) magnetic nanocomposite [117]; (b) Magnetic β-CD modified graphene oxide adsorbent [115]; (c) PDA/β-CD magnetic composite [118]; (d) magnetic Ti_3C_2 MXene sorbent functionalized with β-cyclodextrin [119].

authors reported the preparation of a cyclodextrin-lipid bilayer (β-CD-LB) magnetic nanocomposite by co-precipitation of a mixture of Fe^{2+} and Fe^{3+} in the presence of a NaOH solution containing β-CD (Fig. 7a) [117]. The Fe_3O_4@β-CD–LB nanocomposite was assessed by extracting nine organochlorine pesticides (OCPs), exhibiting suitable stability and reusability.

Another common approach to prepare magnetic cyclodextrin-functionalized sorbents is to coat Fe_3O_4 NPs with a porous layer of silica and subsequently covalently bond cyclodextrins to the coated NPs. For example, Shahrebabak and coworkers reported the preparation of a poly(β-cyclodextrin-ester)-functionalized silica-coated magnetic nanoparticles (MNPs-CDP) for MSPE of the malachite green (MG) and crystal violet (CV) from water samples [120]. The synthesis of Fe_3O_4 NPs was followed by salinization, amination, and treatment with (3-glycidyloxypropyl) trimethoxy silane (EPO). To graft the poly(β-cyclodextrin-ester) (β-CDP) to the magnetic NPs surface, 0.5 g Fe_3O_4@SiO_2-GP was added to a mechanically stirred solution of 7 mL dry DMF containing 2.0 g β-CDP at 80 °C under reflux condition for 24 h under N_2 atmosphere. Then, the separation of the mixture was done with a magnet. The resulting Fe_3O_4@SiO_2/CDP sorbent performed excellently in extracting MG and CV. Chen's research group has employed a similar strategy to synthesize magnetic β-CD modified graphene oxide adsorbents [113,115]. In this case, the Fe_3O_4 NPs were coated with tetraethoxysilane (TEOS) and posteriorly derivatized with aminopropyl silica (APTES, (3-Aminopropyl) triethoxysilane) to obtain Fe_3O_4@-SiO_2–NH_2 (Fig. 7b). GO was then covalently anchored to the amino groups, and the Fe_3O_4@SiO_2/GO/β-CD sorbent was obtained through hydrogen bonding between oxygen functional groups of GO and hydroxyl of β-CD. Due to the synergy between β-CD and GO, the synthesized sorbent exhibits the ability to retain compounds, particularly those with aromatic structures, through π-π and hydrophobic interactions and the formation of host-guest inclusion complexes. As a result, it demonstrates excellent performance in the MSPE of plant growth regulators [113,115] and tetracyclines from bovine milk [102].

Another innovative sorbent was developed by Xu and coworkers, who incorporated a deep eutectic solvent (DES) composed of trifluoroacetamide and benzyl trimethylammonium chloride into β-CD previously grafted onto magnetic beads [15]. In this case, Fe_3O_4 NPs were first coated with APTES, then functionalized with β-CD, and finally impregnated with DES. The MB-NH2@β-CD@DES sorbent demonstrated suitable performance in the extraction of trypsin from bovine pancreas crude extract, attributed to the diverse interaction mechanisms provided by the cyclodextrin moieties and the DES. β-CD can form an inclusion complex with trypsin's hydrophobic and aromatic residues, while its hydrophilic outer wall provides hydrogen bond binding sites. Additionally, the DES contributed to the extraction through dipole-dipole interactions, hydrophobic interactions, and π-π stacking interactions.

Alternatively to the coating with silica, Fe_3O_4 NPs can also be coated with polymers and further functionalized with cyclodextrins. For instance, Huang and coworkers initially coated the magnetic NPs with polydopamine (PDA) and then subjected them to a reaction with γ-CD, tetrafluoroterephthalonitrile, and K_2CO_3 (Fig. 7c) [118]. The resulting Fe_3O_4@PDA@γ-CDP sorbent exhibits good hydrophilicity, aqueous dispersibility, chemical stability, and a suitable mesoporous structure with a large specific surface area. Similarly, Ma et al. [108] coated Fe_3O_4 nanoparticles with a combination of polyhedral oligomeric silsesquioxanes (POSS) and β-cyclodextrin through surface polymerization. This resulted in forming a porous sandwich structure over the Fe_3O_4, and the introduction of octa vinyl-POSS increased the polymers' specific surface area and long-term stability. The β-CD@POSS@Fe3O4 composite excellently extracted carbaryl and carbofuran from apple samples. In another outstanding example, Boon et al. [55] prepared magnetic nanoparticles coated with poly(β-cyclodextrin functionalized ionic liquid) as a sorbent for MSPE polycyclic aromatic hydrocarbons (PAHs) in rice samples. The β-CD-Vinyl-TDI was grafted on the surface of Fe_3O_4 nanoparticles using the polymerization-induced self-assembly (PISA) method. The obtained sorbent showed an adequate extraction capability due to the combined merits of β-CD-IL, TDI, and MNP, allowing the development of a method with relatively lower consumption of sorbent and desorption volume compared to other similar studies.

Natural polymers have also been utilized in the preparation of magnetic cyclodextrin-functionalized sorbents. For instance, Dai and Row extracted carotenes from carrot samples using an eco-friendly magnetic chitosan β-CD biopolymer [106]. The magnetic chitosan composite was synthesized by the in situ chemical precipitation of Fe_2^+ and Fe_3^+ in an alkaline solution with chitosan. Subsequently, it was functionalized through β-CD esterification and amidation reactions. This sorbent exhibited higher extraction recovery than β-cyclodextrin, chitosan, and other commercial sorbents.

Other magnetic cyclodextrin-based sorbents have been obtained by integrating MNPs, CDs, and modern hyper porous materials, such as COFs. For example, Guoliang et al. prepared a β-Cyclodextrin-functionalized magnetic covalent organic framework (Fe_3O_4@COF@Au-β-CD) [109]. Fe_3O_4 NPs were coated with a covalent organic framework (COF) through a solvothermal method using benzidine 1,3,5-triformylphloroglucinol in two sequential stages. Gold NPs were first immobilized onto the Fe_3O_4@COF surface, followed by functionalized with thiolated-β-CD through Au-S bonding. By combining the properties of COF and the recognition ability of β-CD, the developed sorbent exhibited excellent extraction capabilities in the MSPE of sulfonamides from meat samples.

Another approach for preparing cyclodextrin magnetic sorbents does not involve coating Fe_3O_4 NPs with a specific material. Instead, it relies on the physical immobilization of the MNPs onto the surface of 2D materials. For example, Lou et al. prepared a magnetic Ti_3C_2 MXene sorbent functionalized with β-CD [110]. Firstly, Fe_3O_4 was immobilized over the Ti_3C_2, and the Fe_3O_4@Ti_3C_2 was grafted with β-CD, obtaining a highly selective sorbent for the extraction of phytohormones from oil seeds (Fig. 7d). Yazdanpanah and Nojavan employed a similar approach to synthesize a magnetic β-CD-carbon nanotube composite [119]. This composite was prepared by reacting oxidized carbon nanotubes with cyclodextrin in the presence of hydrazine hydrate and subsequent attachment to the Fe_3O_4 NPs via chemical co-precipitation of Fe^{2+} and Fe^{3+}. The magnetic CNT-CD composite performed better than the M-CNT in extracting PAHs from aqueous media.

Matrix solid-phase dispersion extraction

Matrix solid-phase dispersion extraction technique (MSPD) is a commonly used dispersive technique for directly treating solid samples. It can be particularly beneficial in analyzing food samples, which often exist in solid form and undergo cryogenic drying and grinding during sample pretreatment. For instance, Du et al. [98] ground a portion of dried Mori Fructus powders and β-CD into a mortar at room temperature to extract multiple antioxidants. Afterward, the mixture was put into an MSPD column and eluted with an ionic liquid solution. Compared with other methods, the extraction by ionic liquid-assisted trace β-CD matrix solid-phase dispersion extraction method was more straightforward and environment-friendly due to shorter extraction time, less reagent, and less sample consumption.

Concluding remarks

Cyclodextrin-based sorbents play a relevant role in modern sample preparation techniques because of their interesting physicochemical properties. An external hydrophilic surface and an internal hydrophobic one form them. This distinct characteristic allows CDs to form inclusion complexes in a host-guest-like mechanism with many targets in food analysis. This means that CDs can interact with a broad range of compounds, from hydrophobic lipids to very polar food additives or contaminants. In addition, cyclodextrins have been combined with other

classes of sorbents, including MIPs, MOFs, COFs, and carbon-based materials [7,17]. This review discussed different preparation procedures, highlighting the range of highly selective CD-based sorbents that can be produced. We also pointed out the possibility of adapting them to various sample preparation devices such as fibers, membranes, particles, monoliths, nanocomposites, and magnetic materials [28].

In most cases, chemically-modified or hybrid CD-based materials exhibit superior mechanical and chemical resistance compared to unmodified materials. Within such a context, applications herein discussed comprised various sorbent-based sample preparation techniques, such as DSPE, MSPE, SPE, μ-SPE, SPME, and SDBS [28]. On one hand, packed and coated-based approaches (e.g., SPME or MEPS) report great accuracy, precision, and pre-concentration factors. However, the complex coating or packing process and specific hardware requirements can be challenging. On the other hand, dispersive-based approaches (i.e., DSPE and MSPE) offer a straightforward procedure, requiring only the dispersion of the sorbent in a solution. That being said, CD-based sorbents extract a very decent range of targets, including pesticides, mycotoxins, other harmful substances, and bioactive compounds such as flavonoids, vitamins, and antioxidants from food and dietary supplements.

Despite the abovementioned attractive properties, cyclodextrins are still considered an environmentally friendly class of sorbent. This comes mainly from the fact that they are naturally occurring compounds, or when it is necessary to produce them synthetically, byproducts of reaction or waste can be further used, creating a sustainable chain. Some works also report their functionalization with other materials in aqueous media without using toxic chemicals. Therefore, the combination of cyclodextrins with other compounds to generate hybrid and greener materials is a trend expected to keep increasing soon. Though, we still need more attention to this field as cyclodextrins are not so applied when compared, for example, to more traditional, not-greener materials such as C18 or other commercially available ones. Finally, integrating such sorbents in miniaturized and automated techniques holds promise for the future of sample preparation, enabling high-throughput and environmentally-friendly analytical methods that require minimal sample amounts.

Author statement

The authors declare that this manuscript has not been (and is not) submitted to any other journal. The authors agree with its publication if accepted and have no conflict of interest.

Availability of data and materials

Not applicable.

CRediT authorship contribution statement

Edvaldo Vasconcelos Soares Maciel: Conceptualization, Writing – original draft. **Natalia Gabrielly Pereira dos Santos:** Conceptualization, Writing – original draft. **Deyber Arley Vargas Medina:** Conceptualization, Writing – original draft. **Fernando Mauro Lanças:** Funding acquisition, Conceptualization, Supervision, Writing – original draft.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

Acknowledgments

The São Paulo Research Foundation supported this work, FAPESP [Grants 2017/02147-0; 2017/21984-0 – EMU; 2017/21985-6 – EMU]; the National Council for Scientific and Technological Development, CNPq [Grant 308843/ 2019-3]; the Coordination for the Improvement of Higher Education Personnel – Brazil, CAPES [Finance Code 001], and the Alexander von Humboldt Foundation – Germany.

References

[1] S. Armenta, F.A. Esteve-Turrillas, S. Garrigues, M. de la Guardia, Alternative green solvents in sample preparation, Green Anal. Chem. 1 (2022), 100007, https://doi.org/10.1016/j.greeac.2022.100007.
[2] S. Armenta, F.A. Esteve-Turrillas, S. Garrigues, M. de la Guardia, Smart materials for sample preparation in bioanalysis: a green overview, Sustain. Chem. Pharm. 21 (2021), 100411, https://doi.org/10.1016/j.scp.2021.100411.
[3] N.H. Godage, E. Gionfriddo, Use of natural sorbents as alternative and green extractive materials: a critical review, Anal. Chim. Acta 1125 (2020) 187–200, https://doi.org/10.1016/j.aca.2020.05.045.
[4] F. Pena-Pereira, I. Lavilla, C. Bendicho, Greenning Sample Preparation: an overview of cutting edge contributions, Curr. Opin. Green Sustain. Chem. (2021), 100481, https://doi.org/10.1016/j.cogsc.2021.100481.
[5] Á.I. López-Lorente, F. Pena-Pereira, S. Pedersen-Bjergaard, V.G. Zuin, S.A. Ozkan, E. Psillakis, The ten principles of green sample preparation, TrAC Trends Anal. Chem. 148 (2022), 116530, https://doi.org/10.1016/j.trac.2022.116530.
[6] W. Alahmad, S.I. Kaya, A. Cetinkaya, P. Varanusupakul, S.A. Ozkan, Green chemistry methods for food analysis: overview of sample preparation and determination, Adv. Sample Prep. 5 (2023), 100053, https://doi.org/10.1016/j.sampre.2023.100053.
[7] D.A. Vargas Medina, A.T. Cardoso, E.V.S. Maciel, F.M. Lanças, Current materials for miniaturized sample preparation: recent advances and future trends, TrAC Trends Anal. Chem. 165 (2023), https://doi.org/10.1016/j.trac.2023.117120.
[8] D.M. Sartore, D.A. Vargas, M.D. Bocelli, M. Jordan, Modern automated microextraction procedures for bioanalytical, environmental and food analyses, (2023). 10.1002/jssc.202300215.
[9] C.L. Arthur, J. Pawliszyn, Solid phase microextraction with thermal desorption using fused silica optical fibers, Anal. Chem. 62 (1990) 2145–2148, https://doi.org/10.1021/ac00218a019.
[10] N. Manousi, V. Samanidou, Green sample preparation of alternative biosamples in forensic toxicology, Sustain. Chem. Pharm. 20 (2021), 100388, https://doi.org/10.1016/j.scp.2021.100388.
[11] J.M. Kokosa, A. Przyjazny, Green microextraction methodologies for sample preparations, Green Anal. Chem. 3 (2022), 100023, https://doi.org/10.1016/j.greeac.2022.100023.
[12] D. Arley, V. Medina, E. Vasconcelos, S. Maciel, F. Mauro, Trends in analytical chemistry modern automated sample preparation for the determination of organic compounds : a review on robotic and on- fl ow systems, Trends Anal. Chem. 166 (2023), 117171, https://doi.org/10.1016/j.trac.2023.117171.
[13] D.A.V. Medina, L.F. Rodriguez Cabal, F.M. Lanças, Á.J. Santos-Neto, Sample treatment platform for automated integration of microextraction techniques and liquid chromatography analysis, HardwareX 5 (2019) e00056, https://doi.org/10.1016/j.ohx.2019.e00056.
[14] A.L. de Toffoli, E.V.S. Maciel, B.H. Fumes, F.M. Lanças, The role of graphene-based sorbents in modern sample preparation techniques, J. Sep. Sci. 41 (2018) 288–302, https://doi.org/10.1002/jssc.201700870.
[15] F. Xu, Y. Wang, Z. Liu, X. Wei, J. Chen, X. He, H. Li, Y. Zhou, A deep eutectic solvent modified magnetic β-cyclodextrin particle for solid-phase extraction of trypsin, Anal. Chim. Acta 1137 (2020) 125–135, https://doi.org/10.1016/j.aca.2020.09.005.
[16] Y. Chen, L. Xia, R. Liang, Z. Lu, L. Li, B. Huo, G. Li, Y. Hu, Advanced materials for sample preparation in recent decade, TrAC Trends Anal. Chem. 120 (2019), 115652, https://doi.org/10.1016/j.trac.2019.115652.
[17] G. Mastellone, A. Marengo, B. Sgorbini, P. Rubiolo, C. Cagliero, New phases for analytical scale extraction from plants: current and future trends, TrAC Trends Anal. Chem. 141 (2021), 116288, https://doi.org/10.1016/j.trac.2021.116288.
[18] X. Kou, L. Tong, S. Huang, G. Chen, F. Zhu, G. Ouyang, Recent advances of covalent organic frameworks and their application in sample preparation of biological analysis, TrAC Trends Anal. Chem. 136 (2021), 116182, https://doi.org/10.1016/j.trac.2021.116182.
[19] E.V.S. Maciel, A.L. de Toffoli, E.S. Neto, C.E.D. Nazario, F.M. Lanças, New materials in sample preparation: recent advances and future trends, TrAC Trends Anal. Chem. 119 (2019), 115633, https://doi.org/10.1016/j.trac.2019.115633.
[20] K.D. Clark, M.N. Emaus, M. Varona, A.N. Bowers, J.L. Anderson, Ionic liquids: solvents and sorbents in sample preparation, J. Sep. Sci. 41 (2018) 209–235, https://doi.org/10.1002/jssc.201700864.
[21] Z. Wei, L. Mu, Y. Huang, Z. Liu, Imprinted monoliths: recent significant progress in analysis field, TrAC Trends Anal. Chem. 86 (2017) 84–92, https://doi.org/10.1016/j.trac.2016.10.009.
[22] T. Khezeli, A. Daneshfar, Development of dispersive micro-solid phase extraction based on micro and nano sorbents, TrAC Trends Anal. Chem. 89 (2017) 99–118, https://doi.org/10.1016/j.trac.2017.01.004.

[23] C.E.D. Nazario, B.H. Fumes, M.R. da Silva, F.M. Lanças, New materials for sample preparation techniques in bioanalysis, J. Chromatogr. B 1043 (2017) 81–95, https://doi.org/10.1016/j.jchromb.2016.10.041.

[24] J. Ma, Y. Zhang, B. Zhao, Q. Jia, Supramolecular adsorbents in extraction and separation techniques - a review, Anal. Chim. Acta 1122 (2020) 97–113, https://doi.org/10.1016/j.aca.2020.04.054.

[25] M. Saura-Cayuela, S. Lara-Torres, I. Pacheco-Fernández, M.J. Trujillo-Rodríguez, J.H. Ayala, V. Pino, Green materials for greener food sample preparation: a review, Green Anal. Chem. 4 (2023), 100053, https://doi.org/10.1016/j.greeac.2023.100053.

[26] A. Cid-Samamed, J. Rakmai, J.C. Mejuto, J. Simal-Gandara, G. Astray, Cyclodextrins inclusion complex: preparation methods, analytical techniques and food industry applications, Food Chem. 384 (2022), 132467, https://doi.org/10.1016/j.foodchem.2022.132467.

[27] Z. Dong, Q. Luo, J. Liu, Artificial enzymes based on supramolecular scaffolds, Chem. Soc. Rev. 41 (2012) 7890, https://doi.org/10.1039/c2cs35207a.

[28] M.S. Jagirani, M. Soylak, Review: microextraction technique based new trends in food analysis, Crit. Rev. Anal. Chem. 52 (2022) 968–999, https://doi.org/10.1080/10408347.2020.1846491.

[29] E.D. van Asselt, A. Arrizabalaga-Larrañaga, M. Focker, B.J.A. Berendsen, M.G. M. van de Schans, HJ van der Fels-Klerx, chemical food safety hazards in circular food systems: a review, Crit. Rev. Food Sci. Nutr. 0 (2022) 1–13, https://doi.org/10.1080/10408398.2022.2078784.

[30] E.F. Fiorentini, M. Llaver, M.N. Oviedo, P.Y. Quintas, R.G. Wuilloud, Green analytical chemistry state-of-the-art analytical methods based on ionic liquids for food and beverage analysis, Green Anal. Chem. 1 (2022), 100002, https://doi.org/10.1016/j.greeac.2022.100002.

[31] P. Hajeb, L. Zhu, R. Bossi, K. Vorkamp, Sample preparation techniques for suspect and non-target screening of emerging contaminants, Chemosphere 287 (2022), 132306, https://doi.org/10.1016/j.chemosphere.2021.132306.

[32] S.K. Upadhyay, G. Kumar, NMR and molecular modelling studies on the interaction of fluconazole with β-cyclodextrin, Chem. Cent. J. 3 (2009) 1–9, https://doi.org/10.1186/1752-153X-3-9.

[33] Y. Fei, C. Dexian, M. Jie, Synthesis of cyclodextrin-based adsorbents and its application for organic pollutant removal from water, Curr. Org. Chem. 21 (2017) 1976–1990, https://doi.org/10.2174/1385272821666170503110023.

[34] Y. Furukawa, T. Ishiwata, K. Sugikawa, K. Kokado, K. Sada, Nano- and microsized cubic gel particles from cyclodextrin metal-organic frameworks, Angew. Chem. Int. Ed. 51 (2012) 10566–10569, https://doi.org/10.1002/anie.201204919.

[35] Y. Li, N. Zhu, T. Chen, Y. Ma, Q. Li, A green cyclodextrin metal-organic framework as solid-phase extraction medium for enrichment of sulfonamides before their HPLC determination, Microchem. J. 138 (2018) 401–407, https://doi.org/10.1016/j.microc.2018.01.038.

[36] M.R. Bayatloo, S. Nojavan, Rapid and simple magnetic solid-phase extraction of bisphenol A from bottled water, baby bottle, and urine samples using green magnetic hydroxyapatite/β-cyclodextrin polymer nanocomposite, Microchem. J. 175 (2022), 107180, https://doi.org/10.1016/j.microc.2022.107180.

[37] L. Jicsinszky, F. Rossi, R. Solarino, G. Cravotto, Comparison of the conventional and mechanochemical syntheses of cyclodextrin derivatives, Molecules 28 (2023) 467, https://doi.org/10.3390/molecules28020467.

[38] E.V.S. Maciel, K. Mejía-Carmona, M. Jordan-Sinisterra, L.F. da Silva, D.A. Vargas Medina, F.M. Lanças, The current role of graphene-based nanomaterials in the sample preparation arena, Front. Chem. 8 (2020) 664, https://doi.org/10.3389/fchem.2020.00664.

[39] M.N.H. Rozaini, B. Saad, M.R. Ramachandran, E. Abdul Kadir, Advanced materials as adsorbents in microextractions for the determination of contaminants: a mini review, Int. J. Technol. 10 (2019) 1157, https://doi.org/10.14716/ijtech.v10i6.3282.

[40] C. Belenguer-Sapiña, E. Pellicer-Castell, A.R. Mauri-Aucejo, E.F. Simó-Alfonso, P. Amorós, Cyclodextrins as a key piece in nanostructured materials: quantitation and remediation of pollutants, Nanomaterials 11 (2021) 1–28, https://doi.org/10.3390/nano11010007.

[41] Q.Y. Zhu, Q.Y. Zhang, J. Cao, W. Cao, J.J. Xu, L.Q. Peng, Cyclodextrin-assisted liquid-solid extraction for determination of the composition of jujube fruit using ultrahigh performance liquid chromatography with electrochemical detection and quadrupole time-of-flight tandem mass spectrometry, Food Chem. 213 (2016) 485–493, https://doi.org/10.1016/j.foodchem.2016.06.115.

[42] T.F.G.G. Cova, D. Murtinho, A.A.C.C. Pais, A.J.M. Valente, Cyclodextrin-based materials for removing micropollutants from wastewater, 2018. 10.2174/1385272822666181019125315.

[43] A. Gentili, Cyclodextrin-based sorbents for solid phase extraction, J. Chromatogr. A. 1609 (2020), 460654, https://doi.org/10.1016/j.chroma.2019.460654.

[44] X. Cui, P. Zhang, X. Yang, M. Yang, W. Zhou, S. Zhang, H. Gao, R. Lu, β-CD/ATP composite materials for use in dispersive solid-phase extraction to measure (fluoro)quinolone antibiotics in honey samples, Anal. Chim. Acta 878 (2015) 131–139, https://doi.org/10.1016/j.aca.2015.03.056.

[45] N. Morin-Crini, M. Fourmentin, S. Fourmentin, G. Torri, G. Crini, Synthesis of silica materials containing cyclodextrin and their applications in wastewater treatment, Environ. Chem. Lett. 17 (2019) 683–696, https://doi.org/10.1007/s10311-018-00818-0.

[46] Y. Zhang, F. Jiang, D. Huang, S. Hou, H. Wang, M. Wang, Y. Chi, Z. Zhao, A facile route to magnetic mesoporous core-shell structured silicas containing covalently bound cyclodextrins for the removal of the antibiotic doxycycline from water, RSC Adv. 8 (2018) 31348–31357, https://doi.org/10.1039/c8ra05781h.

[47] A. Ebadi, A.A. Rafati, Preparation of silica mesoporous nanoparticles functionalized with β-cyclodextrin and its application for methylene blue removal, J. Mol. Liq. 209 (2015) 239–245, https://doi.org/10.1016/j.molliq.2015.06.009.

[48] L.B. De Carvalho, T.G. Carvalho, Z.M. Magriotis, T.D.C. Ramalho, L.D.M.A. Pinto, Cyclodextrin/silica hybrid adsorbent for removal of methylene blue in aqueous media, J. Incl. Phenom. Macrocycl. Chem. 78 (2014) 77–87, https://doi.org/10.1007/s10847-012-0272-z.

[49] S. Izcara, S. Morante-Zarcero, D. Pérez-Quintanilla, I. Sierra, Application of a hybrid large pore mesoporous silica functionalized with β-cyclodextrin as sorbent in dispersive solid-phase extraction. Toward sustainable sample preparation protocols to determine polyphenolic compounds in Arbutus unedo L. fruits by UHPL, J. Food Compos. Anal. 118 (2023), 105191, https://doi.org/10.1016/j.jfca.2023.105191.

[50] W. Song, J. Hu, Y. Zhao, D. Shao, J. Li, Efficient removal of cobalt from aqueous solution using β-cyclodextrin modified graphene oxide, RSC Adv. 3 (2013) 9514–9521, https://doi.org/10.1039/c3ra41434e.

[51] F.M. LF da Silva, Lanças, β-Cyclodextrin coupled to graphene oxide supported on aminopropyl silica as a sorbent material for determination of isoflavones, J. Sep. Sci. 43 (2020) 4347–4355, https://doi.org/10.1002/jssc.202000598.

[52] L.F. da Silva, D.A. Vargas Medina, F.M. Lanças, Automated needle-sleeve based online hyphenation of solid-phase microextraction and liquid chromatography, Talanta 221 (2021), 121608, https://doi.org/10.1016/j.talanta.2020.121608.

[53] Y. He, Z. Xu, F. Wu, Q. Yang, J. Zhang, Preparation and adsorption studies of β-cyclodextrin grafted onto multi-walled carbon nanotube, J. Chem. Technol. Biotechnol. 90 (2015) 2257–2264, https://doi.org/10.1002/jctb.4541.

[54] Y. Ding, X. Song, J. Chen, Analysis of pesticide residue in tomatoes by carbon nanotubes/β-cyclodextrin nanocomposite reinforced hollow fiber coupled with HPLC, J. Food Sci. 84 (2019) 1651–1659, https://doi.org/10.1111/1750-3841.14640.

[55] Y.H. Boon, N.N. Mohamad Zain, S. Mohamad, H. Osman, M. Raoov, Magnetic poly(β-cyclodextrin-ionic liquid) nanocomposites for micro-solid phase extraction of selected polycyclic aromatic hydrocarbons in rice samples prior to GC-FID analysis, Food Chem. 278 (2019) 322–332, https://doi.org/10.1016/j.foodchem.2018.10.145.

[56] A. Ansari, S. Vahedi, O. Tavakoli, M. Khoobi, M.A. Faramarzi, Novel Fe3O4/hydroxyapatite/β-cyclodextrin nanocomposite adsorbent: synthesis and application in heavy metal removal from aqueous solution, Appl. Organomet. Chem. 33 (2019) 1–11, https://doi.org/10.1002/aoc.4634.

[57] D. Liu, Z. Huang, M. Li, X. Li, P. Sun, L. Zhou, Construction of magnetic bifunctional β-cyclodextrin nanocomposites for adsorption and degradation of persistent organic pollutants, Carbohydr. Polym. 230 (2020), 115564, https://doi.org/10.1016/j.carbpol.2019.115564.

[58] G. Utzeri, P.M.C. Matias, D. Murtinho, A.J.M. Valente, Cyclodextrin-based nanosponges: overview and opportunities, Front. Chem. 10 (2022), https://doi.org/10.3389/fchem.2022.859406.

[59] I. Krabicová, S.L. Appleton, M. Tannous, G. Hoti, F. Caldera, A.Rubin Pedrazzo, C. Cecone, R. Cavalli, F. Trotta, History of cyclodextrin nanosponges, Polymers 12 (2020) 1122, https://doi.org/10.3390/polym12051122 (Basel).

[60] J.M. Anne, Y.H. Boon, B. Saad, M. Miskam, M.M. Yusoff, M.S. Shahriman, N.N. M. Zain, V. Lim, M. Raoov, β-Cyclodextrin conjugated bifunctional isocyanate linker polymer for enhanced removal of 2,4-dinitrophenol from environmental waters, R. Soc. Open Sci. 5 (2018), 180942, https://doi.org/10.1098/rsos.180942.

[61] Y. Li, P. Lu, J. Cheng, X. Zhu, W. Guo, L. Liu, Q. Wang, C. He, S. Liu, Novel microporous β-cyclodextrin polymer as sorbent for solid-phase extraction of bisphenols in water samples and orange juice, Talanta 187 (2018) 207–215, https://doi.org/10.1016/j.talanta.2018.05.030.

[62] K. Yongfeng, D. Wuping, L. Yan, K. Junxia, X. Jing, Molecularly imprinted polymers of allyl-β-cyclodextrin and methacrylic acid for the solid-phase extraction of phthalate, Carbohydr. Polym. 88 (2012) 459–464, https://doi.org/10.1016/j.carbpol.2011.12.027.

[63] S. Iravani, R.S. Varma, Nanosponges for water treatment: progress and challenges, Appl. Sci. 12 (2022) 4182, https://doi.org/10.3390/app12094182.

[64] N. Morin-Crini, G. Crini, Environmental applications of water-insoluble β-cyclodextrin- epichlorohydrin polymers, Prog. Polym. Sci. 38 (2013) 344–368, https://doi.org/10.1016/j.progpolymsci.2012.06.005.

[65] J. Morales-Sanfrutos, F.J. Lopez-Jaramillo, M.A.A. Elremaily, F. Hernández-Mateo, F. Santoyo-Gonzalez, Divinyl sulfone cross-linked cyclodextrin-based polymeric materials: synthesis and applications as sorbents and encapsulating agents, Molecules 20 (2015) 3565–3581, https://doi.org/10.3390/molecules20033565.

[66] M. Yao, Y. Ding, Z. Wang, Y. Deng, F. Zhao, E. Repo, D. Yin, Y. Meng, S. Jafari, M. Sillanpää, EDTA-cross-linked β-cyclodextrin: an environmentally friendly bifunctional adsorbent for simultaneous adsorption of metals and cationic dyes, Environ. Sci. Technol. 49 (2015) 10570–10580.

[67] S. Allahyari, F. Trotta, H. Valizadeh, M. Jelvehgari, P. Zakeri-Milani, Cyclodextrin-based nanosponges as promising carriers for active agents, Expert Opin. Drug Deliv. 16 (2019) 467–479, https://doi.org/10.1080/17425247.2019.1591365.

[68] A. Schincaglia, J. Aspromonte, F.A. Franchina, T. Chenet, L. Pasti, A. Cavazzini, G. Purcaro, M. Beccaria, Current developments of analytical methodologies for aflatoxins' determination in food during the last decade (2013–2022), with a particular focus on nuts and nut products, Foods 12 (2023), https://doi.org/10.3390/foods12030527.

[69] J.A.M. Pereira, N. Casado, P. Porto-Figueira, J.S. Câmara, The potential of microextraction techniques for the analysis of bioactive compounds in food, Front. Nutr. 9 (2022) 1–20, https://doi.org/10.3389/fnut.2022.825519.

[70] C.V. Berenguer, L. Garc, S. C., J.A.M. Pereira, Applied sciences exploring the potential of microextraction in the survey of food fruits and vegetable safety, (2023).

[71] L. Chen, X. Dang, Y. Ai, H. Chen, Preparation of an acryloyl β-cyclodextrin-silica hybrid monolithic column and its application in pipette tip solid-phase extraction and HPLC analysis of methyl parathion and fenthion, J. Sep. Sci. 41 (2018) 3508–3514, https://doi.org/10.1002/jssc.201701273.

[72] X. Hou, X. Lu, P. Niu, S. Tang, L. Wang, Y. Guo, β-Cyclodextrin-modified three-dimensional graphene oxide-wrapped melamine foam for the solid-phase extraction of flavonoids, J. Sep. Sci. 41 (2018) 2207–2213, https://doi.org/10.1002/jssc.201701322.

[73] M. Appell, K.O. Evans, M.A. Jackson, D.L. Compton, Determination of ochratoxin A in grape juice and wine using nanosponge solid phase extraction clean-up and liquid chromatography with fluorescence detection, J. Liq. Chromatogr. Relat. Technol. 41 (2018) 949–954, https://doi.org/10.1080/10826076.2018.1544148.

[74] L. Chen, M. Li, Y. Ai, X. Dang, J. Huang, H. Chen, One-pot preparation of an acryloyled β-cyclodextrin-silica hybrid monolithic column and its application for determination of carbendazim and carbaryl, Food Chem. 269 (2018) 181–186, https://doi.org/10.1016/j.foodchem.2018.07.006.

[75] C. Belenguer-Sapiña, E. Pellicer-Castell, C. Vila, E.F. Simó-Alfonso, P. Amorós, A. R. Mauri-Aucejo, A poly(glycidyl-co-ethylene dimethacrylate) nanohybrid modified with β-cyclodextrin as a sorbent for solid-phase extraction of phenolic compounds, Microchim. Acta. 186 (2019), https://doi.org/10.1007/s00604-019-3739-4.

[76] Z. Gao, Y. Li, Y. Ma, W. Ji, T. Chen, X. Ma, H. Xu, Functionalized melamine sponge based on β-cyclodextrin-graphene oxide as solid-phase extraction material for rapidly pre-enrichment of malachite green in seafood, Microchem. J. 150 (2019), 104167, https://doi.org/10.1016/j.microc.2019.104167.

[77] C. Wang, C. Ding, Q. Wu, X. Xiong, Molecularly imprinted polymers with dual template and bifunctional monomers for selective and simultaneous solid-phase extraction and gas chromatographic determination of four plant growth regulators in plant-derived tissues and foods, Food Anal. Methods 12 (2019) 1160–1169, https://doi.org/10.1007/s12161-019-01455-1.

[78] N.S. Tezerji, M.M. Foroughi, R.R. Bezenjani, N. Jandaghi, E. Rezaeipour, F. Rezvani, A facile one-pot green synthesis of β-cyclodextrin decorated porous graphene nanohybrid as a highly efficient adsorbent for extracting aflatoxins from maize and animal feeds, Food Chem. 311 (2020), 125747, https://doi.org/10.1016/j.foodchem.2019.125747.

[79] X. Chen, X. Jin, Y. Li, G. Chen, K. Chen, J. Kan, Preparation and characterization of molecularly-imprinted polymers for extraction of sanshool acid amide compounds followed by their separation from pepper oil resin derived from Chinese prickly ash (Zanthoxylum bungeanum), J. Sep. Sci. 41 (2018) 590–601, https://doi.org/10.1002/jssc.201701014.

[80] C. Belenguer-Sapiña, E. Pellicer-Castell, J. El Haskouri, C. Guillem, E.F. Simó-Alfonso, P. Amorós, A. Mauri-Aucejo, Design, characterization and comparison of materials based on β and γ cyclodextrin covalently connected to microporous silica for environmental analysis, J. Chromatogr. A 1563 (2018) 10–19, https://doi.org/10.1016/j.chroma.2018.05.070.

[81] C. He, S. Lay, H. Yu, S. Shen, Synthesis and application of selective adsorbent for pirimicarb pesticides in aqueous media using allyl-β-cyclodextrin based binary functional monomers, J. Sci. Food Agric. 98 (2018) 2089–2097, https://doi.org/10.1002/jsfa.8690.

[82] C. Wang, L. Cheng, L. Zhang, Y. Zuo, Graphene oxide based molecularly imprinted polymers modified with β-cyclodextrin for selective extraction of di(2-ethylhexyl) phthalate in environmental waters, J. Sep. Sci. 42 (2019) 1248–1256, https://doi.org/10.1002/jssc.201801171.

[83] E.V. Soares Maciel, A.L. de Toffoli, F.M. Lanças, Recent trends in sorption-based sample preparation and liquid chromatography techniques for food analysis, Electrophoresis 39 (2018) 1582–1596, https://doi.org/10.1002/elps.201800009.

[84] C. Basheer, A.A. Alnedhary, B.S.M. Rao, S. Valliyaveettil, H.K. Lee, Development and application of porous membrane-protected carbon nanotube micro-solid-phase extraction combined with gas chromatography/mass spectrometry, Anal. Chem. 78 (2006) 2853–2858, https://doi.org/10.1021/ac060240i.

[85] N.A. Manaf, B. Saad, M.H. Mohamed, L.D. Wilson, A.A. Latiff, Cyclodextrin based polymer sorbents for micro-solid phase extraction followed by liquid chromatography tandem mass spectrometry in determination of endogenous steroids, J. Chromatogr. A 1543 (2018) 23–33, https://doi.org/10.1016/j.chroma.2018.02.032.

[86] V. Jalili, A. Barkhordari, A. Ghiasvand, A comprehensive look at solid-phase microextraction technique: a review of reviews, Microchem. J. 152 (2020), 104319, https://doi.org/10.1016/j.microc.2019.104319.

[87] Y. Hu, Y. Zheng, G. Li, Solid-phase microextraction of phenol compounds using a fused-silica fiber coated with β-cyclodextrin-bonded silica particles, Anal. Sci. 20 (2004) 667–671, https://doi.org/10.2116/analsci.20.667.

[88] X.Y. Song, W. Ha, J. Chen, Y.P. Shi, Application of β-cyclodextrin-modified, carbon nanotube-reinforced hollow fiber to solid-phase microextraction of plant hormones, J. Chromatogr. A 1374 (2014) 23–30, https://doi.org/10.1016/j.chroma.2014.11.029.

[89] C. Ruiz-Palomero, M.L. Soriano, M. Valcárcel, β-Cyclodextrin decorated nanocellulose: a smart approach towards the selective fluorimetric determination of danofloxacin in milk samples, Analyst 140 (2015) 3431–3438, https://doi.org/10.1039/c4an01967a.

[90] E.V.S. Maciel, D.A. Vargas Medina, J.V.B. Borsatto, F.M. Lanças, Towards a universal automated and miniaturized sample preparation approach, Sustain. Chem. Pharm. 21 (2021), https://doi.org/10.1016/j.scp.2021.100427.

[91] M.A. Ahmed, R.B. Yu, J.P. Quirino, Recent developments in open tubular liquid chromatography and electrochromatography from 2019 to 2021, TrAC Trends Anal. Chem. 164 (2023), 117045, https://doi.org/10.1016/j.trac.2023.117045.

[92] Y. Fan, Y.Q. Feng, S.L. Da, Z.H. Wang, In-tube solid phase microextraction using a β-cyclodextrin coated capillary coupled to high performance liquid chromatography for determination of non-steroidal anti-inflammatory drugs in urine samples, Talanta 65 (2005) 111–117, https://doi.org/10.1016/j.talanta.2004.05.040.

[93] Y. Lei, M. He, B. Chen, B. Hu, Polyaniline/cyclodextrin composite coated stir bar sorptive extraction combined with high performance liquid chromatography-ultraviolet detection for the analysis of trace polychlorinated biphenyls in environmental waters, Talanta 150 (2016) 310–318, https://doi.org/10.1016/j.talanta.2015.12.025.

[94] Y. Hu, Y. Zheng, F. Zhu, G. Li, Sol-gel coated polydimethylsiloxane/β-cyclodextrin as novel stationary phase for stir bar sorptive extraction and its application to analysis of estrogens and bisphenol A, J. Chromatogr. A 1148 (2007) 16–22, https://doi.org/10.1016/j.chroma.2007.02.101.

[95] H. Faraji, S.W. Husain, M. Helalizadeh, Bcyclodextrin-bonded silica particles as novel sorbent for stir bar sorptive extraction of phenolic compounds, J. Chromatogr. Sci. 49 (2011) 482–487, https://doi.org/10.1093/chrsci/49.6.482.

[96] Y. Hu, Y. Yang, J. Huang, G. Li, Preparation and application of poly (dimethylsiloxane)/β-cyclodextrin solid-phase microextraction membrane, Anal. Chim. Acta 543 (2005) 17–24, https://doi.org/10.1016/j.aca.2005.04.050.

[97] S. Cao, J. Chen, G. Lai, C. Xi, X. Li, L. Zhang, G. Wang, Z. Chen, A high efficient adsorbent for plant growth regulators based on ionic liquid and β-cyclodextrin functionalized magnetic graphene oxide, Talanta 194 (2019) 14–25, https://doi.org/10.1016/j.talanta.2018.10.013.

[98] K. Du, Y. Chen, J. Li, F. Tian, X. mei Gao, Y. xu Chang, Determination of antioxidant ingredients in Mori Fructus employing ionic liquid-assisted miniaturized matrix solid-phase dispersion extraction via ultra-performance liquid chromatography, J. Food Biochem. 43 (2019) 1–10, https://doi.org/10.1111/jfbc.12807.

[99] Y. Zhang, F. fang Chen, J. Sang, Green approach for sample preparation and determination of anthocyanins from lycium ruthenicum murr. Using a β-cyclodextrin-based extraction method coupled with UPLC-DAD analysis, Food Anal. Methodss 11 (2018) 2141–2148, https://doi.org/10.1007/s12161-018-1191-4.

[100] F. Liu, X. Yang, X. Wu, X. Xi, H. Gao, S. Zhang, W. Zhou, R. Lu, A dispersive magnetic solid phase microextraction based on ionic liquid-coated and cyclodextrin-functionalized magnetic core dendrimer nanocomposites for the determination of pyrethroids in juice samples, Food Chem. 268 (2018) 485–491, https://doi.org/10.1016/j.foodchem.2018.06.105.

[101] S.L. Wei, W.T. Liu, X.C. Huang, J.K. Ma, Preparation and application of a magnetic plasticizer as a molecularly imprinted polymer adsorbing material for the determination of phthalic acid esters in aqueous samples, J. Sep. Sci. 41 (2018) 3806–3814, https://doi.org/10.1002/jssc.201800535.

[102] N. Al-Afy, H. Sereshti, A. Hijazi, H.Rashidi Nodeh, Determination of three tetracyclines in bovine milk using magnetic solid phase extraction in tandem with dispersive liquid-liquid microextraction coupled with HPLC, J. Chromatogr. B Anal. Technol. Biomed. Life Sci. 1092 (2018) 480–488, https://doi.org/10.1016/j.jchromb.2018.06.049.

[103] H.L. Duan, Q.Le Niu, J. Wang, S.Y. Ma, J. Zhang, Z.Q. Zhang, High uptake carboxyl-functionalized porous β-cyclodextrin polymer for selective extraction of lysozyme from egg white, J. Chromatogr. A 1600 (2019) 80–86, https://doi.org/10.1016/j.chroma.2019.04.056.

[104] Y. Dai, K.H. Row, Application of amino-based chitosan cyclodextrin derivatives for the extraction of catechins in green tea with high-performance liquid chromatography, J. Sep. Sci. 42 (2019) 2660–2667, https://doi.org/10.1002/jssc.201900427.

[105] P. Tutunchi, L. Roufegarinejad, H. Hamishehkar, A. Alizadeh, Extraction of red beet extract with β-cyclodextrin-enhanced ultrasound assisted extraction: a strategy for enhancing the extraction efficacy of bioactive compounds and their stability in food models, Food Chem. 297 (2019), 124994, https://doi.org/10.1016/j.foodchem.2019.124994.

[106] Y. Dai, K.H. Row, Isolation and determination of beta-carotene in carrots by magnetic chitosan beta-cyclodextrin extraction and high-performance liquid chromatography (HPLC), Anal. Lett. 52 (2019) 1828–1843, https://doi.org/10.1080/00032719.2019.1570245.

[107] H.L. Duan, Z.L. Mou, J. Wang, S.Y. Ma, H.Y. Zhan, Z.Q. Zhang, Magnetically modified porous β-cyclodextrin polymers for dispersive solid-phase extraction high-performance liquid chromatography analysis of sudan dyes, Food Anal. Methods 12 (2019) 1429–1438, https://doi.org/10.1007/s12161-019-01476-w.

[108] Q. Ma, X. Liu, Y. Zhang, L. Chen, X. Dang, Y. Ai, H. Chen, Fe_3O_4 nanoparticles coated with polyhedral oligomeric silsesquioxanes and β-cyclodextrin for magnetic solid-phase extraction of carbaryl and carbofuran, J. Sep. Sci. 43 (2020) 1514–1522, https://doi.org/10.1002/jssc.201900896.

[109] Y. Yang, G. Li, D. Wu, A. Wen, Y. Wu, X. Zhou, β-Cyclodextrin-/AuNPs-functionalized covalent organic framework-based magnetic sorbent for solid phase extraction and determination of sulfonamides, Microchim. Acta 187 (2020), https://doi.org/10.1007/s00604-020-04257-z.

[110] Z. Luo, M. Xu, R. Wang, X. Liu, Y. Huang, L. Xiao, Magnetic Ti3C2 MXene functionalized with β-cyclodextrin as magnetic solid-phase extraction and *in situ* derivatization for determining 12 phytohormones in oilseeds by ultra-performance liquid chromatography-tandem mass spectrometry, Phytochemistry 183 (2021), 112611, https://doi.org/10.1016/j.phytochem.2020.112611.

[111] X. Wang, H. Liu, Z. Sun, S. Zhao, Y. Zhou, J. Li, T. Cai, B. Gong, Monodisperse restricted access material with molecularly imprinted surface for selective solid-phase extraction of 17β-estradiol from milk, J. Sep. Sci. 43 (2020) 3520–3533, https://doi.org/10.1002/jssc.202000449.

[112] S. Farooq, J. Nie, Y. Cheng, S.A.S. Bacha, W. Chang, Selective extraction of fungicide carbendazim in fruits using β-cyclodextrin based molecularly imprinted polymers, J. Sep. Sci. 43 (2020) 1145–1153, https://doi.org/10.1002/jssc.201901029.

[113] J.Y. Chen, S.R. Cao, C.X. Xi, Y. Chen, X.L. Li, L. Zhang, G.M. Wang, Y.L. Chen, Z. Q. Chen, A novel magnetic β-cyclodextrin modified graphene oxide adsorbent with high recognition capability for 5 plant growth regulators, Food Chem. 239 (2018) 911–919, https://doi.org/10.1016/j.foodchem.2017.07.013.

[114] X. Liang, R. Ma, L. Hao, C. Wang, Q. Wu, Z. Wang, β-Cyclodextrin polymer@ Fe_3O_4 based magnetic solid-phase extraction coupled with HPLC for the determination of benzoylurea insecticides from honey, tomato, and environmental water samples, J. Sep. Sci. 41 (2018) 1539–1547, https://doi.org/10.1002/jssc.201701197.

[115] J. Chen, S. Cao, M. Zhu, C. Xi, L. Zhang, X. Li, G. Wang, Y. Zhou, Z. Chen, Fabrication of a high selectivity magnetic solid phase extraction adsorbent based on β-cyclodextrin and application for recognition of plant growth regulators, J. Chromatogr. A 1547 (2018) 1–13, https://doi.org/10.1016/j.chroma.2018.03.004.

[116] X. Yang, P. Zhang, X. Li, L. Hu, H. Gao, S. Zhang, W. Zhou, R. Lu, Talanta effervescence-assisted β -cyclodextrin /attapulgite composite for the in- syringe dispersive solid-phase extraction of pyrethroids in environmental water samples, 153 (2016) 353–359. 10.1016/j.talanta.2016.03.007.

[117] H. Wang, S. Yan, B. Qu, H. Liu, J. Ding, N. Ren, Magnetic solid phase extraction using Fe_3O_4@β-cyclodextrin-lipid bilayers as adsorbents followed by GC-QTOF-MS for the analysis of nine pesticides, New J. Chem. 44 (2020) 7727–7739, https://doi.org/10.1039/d0nj01191f.

[118] C. Huang, Y. Wang, Q. Huang, Y. He, L. Zhang, Magnetic γ-cyclodextrin polymer with compatible cavity promote the magnetic solid-phase extraction of microcystins in water samples, Anal. Chim. Acta. 1054 (2019) 38–46, https://doi.org/10.1016/j.aca.2018.12.028.

[119] M. Yazdanpanah, S. Nojavan, Micro-solid phase extraction of some polycyclic aromatic hydrocarbons from environmental water samples using magnetic β-cyclodextrin-carbon nanotube composite as a sorbent, J. Chromatogr. A 1585 (2019) 34–45, https://doi.org/10.1016/j.chroma.2018.11.066.

[120] S. Moradi Shahrebabak, M. Saber-Tehrani, M. Faraji, M. Shabanian, P. Aberoomand-Azar, Magnetic solid phase extraction based on poly (β-cyclodextrin-ester) functionalized silica-coated magnetic nanoparticles (NPs) for simultaneous extraction of the malachite green and crystal violet from aqueous samples, Environ. Monit. Assess. 192 (2020), https://doi.org/10.1007/s10661-020-8185-6.