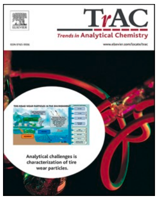
Trends in Analytical Chemistry 193 (2025) 118486

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

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



Sustainable materials for sorptive extraction techniques

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ARTICLE INFO

Keywords:
Sustainable materials
Natural sorbents
Biopolymers
Green synthesis
Environmental samples
Food samples
Biological samples

ABSTRACT

Interest in sustainable materials for sorptive extraction techniques has grown significantly in recent years, in line with the principles of Green Analytical Chemistry. This review discusses the increasing use of natural materials—such as cellulose-based materials, cork, or wood—as well as innovative strategies to tailor their properties in order to achieve the sensitivity and selectivity required for analytical applications.

Sustainable materials can also be developed through green synthetic approaches applied to widely used materials, including molecularly imprinted polymers, carbon-based materials, and metal-organic frameworks, among others. These approaches often involve the use of monomers derived from natural sources, environmentally friendly solvents such as water or deep eutectic solvents, or energy-efficient synthetic techniques.

The incorporation of these sustainable materials into extraction techniques—especially microextraction—contributes to the development of more environmentally responsible analytical methods. This article highlights recent applications of such materials in the analysis of environmental, food, and biological samples.

1. Introduction

New challenges are continuously emerging in analytical chemistry to make the analytical process more sustainable. A key step in this evolution is without doubt the sample preparation, that typically involves sample clean-up and analyte preconcentration. It should be also emphasized that sample preparation uses solvents/reagents that can be toxic, generates hazardous laboratory waste, involves between 60 % and 80 % of the total analysis time, and, in some cases, demands high energy. Therefore, any attempt to minimize these negative effects will significantly contribute to increasing the sustainability of the whole analytical method.

Although the first principle of Green Analytical Chemistry (GAC) states that sample treatment should be avoided, this is still playing a pivotal role in the analysis of complex samples [1]. New cutting-edge determination techniques improve the sensitivity required for determining the low concentration at which the analytes can be present in the sample and can also minimize the matrix-related problems of the complex samples. However, the analysis of complex biological, food and environmental samples still require a previous sample preparation step.

Most GAC principles are directly or indirectly related to sample preparation and it should be emphasized that, in recent years, new approaches have significantly improved its greenness. In this sense, the ten principles of Green Sample Preparation (GSP) were defined in order to establish a road map for the development of overall greener analytical methods [2]. Two principles of GSP refer to the minimization of sample, chemical and material amounts and waste. They can be achieved by miniaturization of the sample preparation step, and in the last years, significant efforts have been devoted to miniaturize extraction techniques [3,4].

As it is well-known, most used sample extraction techniques can be classified as solvent-based or sorptive-based extraction techniques. Regarding solvent-based techniques, liquid-liquid extraction (LLE), widely used in the past, has been substituted by miniaturized techniques that involve the use of lower volume of solvent and are therefore more respectful with the environment. Examples of liquid-liquid microextraction techniques are: single drop microextraction (SDME), dispersive liquid-liquid microextraction (DLLME) or hollow-fiber liquid phase

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https://doi.org/10.1016/j.trac.2025.118486
Received 12 June 2025; Received in revised form 1 October 2025; Accepted 4 October 2025

microextraction (HF-LPME) [4].

In addition, in LLE, the GSP principle referring to the use of safer solvents can also be applied by using more benign solvents or biobased-solvents, such as d-limonene, or water, to replace potentially mutagenic and carcinogenic solvents [5]. New solvents have also emerged in liquid-based extraction techniques, such as ionic liquids (ILs) or deep eutectic solvents (DESs), although not all of them directly contribute to the greenness of the method [2,6].

ILs formed by organic salts present excellent properties such as chemical and thermal stability, low volatility which results in low emissions, tuneable polarity, hydrophobicity and selectivity. An interesting modification of ILs is the magnetic ILs (MILs) that enable the recovery of the solvent using an external magnet, avoiding the step of centrifugation or evaporation for the enrichment before the analysis. Both ILS and MILs have been used in the extraction of a variety of analytes in different liquid-based microextraction techniques [7].

In the recent years, in the search for biodegradable and less toxic solvents than ILs, DESs have emerged, not only in the extraction field but also in the catalysis, synthesis, among others. DESs are mixture of two or three generally safe and cost-effective components associated through hydrogen bounding interaction, resulting in a eutectic mixture with a lower melting point. For instance, they have been satisfactory applied in the DLLME for the extraction of gliflozins from river water [8]. The recent use of natural-based DESs (NADES), namely organic acids, amino acids, sugars and organic bases has increased their interest, and, for example, they have been applied for the DLLME of sulfonamides from water samples [9].

Although the improvement in the solvent-based extraction as regards greener solvents and miniaturization, sorptive-based extraction is still the preferred alternative for sample preparation. Although solid-phase extraction (SPE) is the most used technique in a wide range of applications, it uses significant solvent volume and contributes to solid waste, mainly when the cartridges are single-use. Therefore, with the aim of miniaturization, several techniques have been developed, such as solid-phase microextraction (SPME) with the clear advantage of being solvent-free. Other modalities such as sorptive bar extraction technique (SBSE), dispersive SPE (DSPE), magnetic SPE (MSPE), matrix solid-phase dispersion (MSPD), pipette tip SPE (PT-SPE), microextraction in packed sorbent (MEPS) have also been developed and applied to several fields [4] with the aim of miniaturization and therefore reducing not only the amounts of solvent, sample and chemicals but also the waste, following the principals of GSP.

A large diversity of materials with different characteristics is available for sorptive-based extraction that enables the successful extraction of a wide variety of compounds from diverse types of samples [10]. The different interactions that can be exploited between the analyte and the material depending on their characteristics have enlarged the diversity of materials available for the different sorptive-extraction techniques. Typical materials can be grouped in silica-based, polymer-based and carbon-based, but improvements on the features of these materials and new materials such as metal-organic frameworks (MOFs), covalent organic framework (COFs), among others, have been developed and successfully applied to different fields [11]. However, following the trends of the GSP, many efforts have been focused in the last years on the development of greener materials to achieve sustainable analytical methods [4,12,13]. The use of natural sorbents obtained from natural sources are of increasing interest because of their biodegradability, renewability and ease of access. Another option to make the materials more sustainable is the use of greener synthesis of materials, such as the selection of more sustainable reagents for the synthesis and also more environmentally friendly synthetic process [12].

In addition, different metrics have been developed to evaluate to greenness, sustainability or efficiency of the whole analytical methods [4] and in the recent years, metrics devoted to evaluate sample preparation protocols have been developed, such as AGREEprep [14] and sample preparation metric of sustainability (SPMS) [15].

In this review, the different options to prepare greener materials will be discussed as well as their application to different fields, focusing on studies published between 2018 and 2025 to isolate organic compounds from different samples. The studies were selected in order to provide a wide overview of the different types of materials and their applications.

2. Sustainable materials

2.1. Natural materials

The use of natural materials for analytes' isolation is clearly in line with the concepts of sustainability [6] and circular analytical chemistry, where reusing, repairing, refurbishing and recycling are key terms [16]. However, the systematic consideration of the value they provide in terms of the analytical properties of the method (sensitivity, selectivity, precision) is mandatory. Reaching a balance between sustainability and analytical performance is a clear objective when designing an analytical process. Regarding the use of natural materials, this fact would eventually involve their modification to adequate their performance to the expected analytical behaviour. For this purpose, introducing specific functional groups results in improved extraction. Moreover, this modification will entail a combination of interaction mechanisms that consequently increase the number of analytes that can be isolated from the sample matrix in a single step. In this section, the natural sorbents most used for sample preparation will be discussed.

2.1.1. Cellulose-based materials

Cellulose is the most abundant biopolymer in nature. The wide presence of hydroxyl groups on the surface gives it a high hydrophilicity. The main representatives of this family of natural materials are paper and cotton. Although structurally related, in paper, the cellulose fibers are mechanically compressed, resulting in a planar geometry, while cotton is a soft, fluffy fiber. This results in differences in their use in microextraction techniques. On the one hand, paper is normally used under the thin film microextraction formats with a higher active surface as both sides can be used for analytes' interactions [17]. On the other hand, cotton exhibits higher versatility as it can be used in dispersive techniques or packed in different elements such as pipette tips or needles, among others. Both share favourable features as regards their use in sample preparation, such as wide availability, cost-effectiveness, wase-to-use and versatility as the free hydroxyl groups on the surface facilitate the chemical modification to tailor the interactions with the target family of compounds.

Unmodified paper can be used to isolate analytes from simple matrices if they are present at relatively high concentration [18]. In other scenarios, a modification of the paper surface is recommended to increase the selectivity and efficiency of the extraction step. The simplest modification involves the physical deposition of a thin film of the sorptive-phase via dip-coating or drop-casting although in this case, the leaching of the sorbent can eventually occur during the extraction step. Different phases have been deposited following this procedure. The thin-film can be polymeric, using either a single phase [19] or a combination of two [20], providing different extraction domains to increase the number of analytes that can be extracted in a single step, e.g. including those belonging to the same family by with different polarity as it is the case of UV filters, where the most polar ones are more difficult to isolate from environmental waters. Nanoparticles (NPs) have also been used, being necessary to prepare a dispersion of the nanomaterial in a proper solvent. After evaporation a thin film of the NPs is formed over the paper surface. This combination is interesting as the NPs aggregation is prevented while the extraction efficiency is maintained [21]. A nanocomposite can also be used as sorbent by adding the selected NPs to a polymer solution. The synergic mixture combines the extraction capacity of the sorbent with the additional properties that the NPs can confer on to the sorbent phase that ranges from magnetism [22] to photocatalytic behaviour [23]. These modifications are in line with a minimum environmental impact as only the dissolution of the polymer into few milliliters (ca. less than five) of the appropriate organic solvent is needed. Moreover, once prepared, the solution/dispersion can be reused to prepare a large number of extraction units. The described materials have been used in the clinical/toxicological and environmental fields. Paper can also be combined with MOF as sportive phase [24]. In this case, the synthetic procedure is based on an in-situ synthesis approach in which the MOF precursors are added to the cellulose scaffolds. This avoids the problems of homogeneous distribution in the ex-situ approach and also increase the greenness of the whole procedure, evaluated with AGREprep and SPMS. The prepared MIL-53(Al) @cellulose was used for the extraction of neonicotinoid insecticides form environmental waters.

The sorbent phase used to isolate the target compounds can also be sustainable as it is the case of the modification of cellulose paper with humic acids [25]. The thin film is generated under mild conditions, as after dipping the paper in the humic acid solution, heating with a hot air gun for 30 s and left stand overnight at room temperature. As an advantage, the modified paper exhibits cation-exchange properties which expand the range of analytes that can be extracted with this phase, and permits the isolation of basic drugs (cocaine, codeine and methadone) from saliva samples.

The applicability of cotton in sample preparation also includes raw and modified cotton, the latter one being the most interesting in the sample preparation realm. Modification of the cotton fibers involves the coverage with a thin film of the sorbent by dip coating or drop casting as described above. The materials used as sorbents includes polymers [26], NPs [27], or selective recognition moieties as cyclodextrins [28]. In contrast to paper, the fibrous nature of cotton makes it compatible with different extraction formats. For example, the dispersive format is very common as in this modality, the kinetics of the extraction is favoured due to the maximized contact between the sorbent and the target analytes. If the process is carried out inside the body of a syringe, the different cycles (analytes retention and elution) can be implemented in the same device. Moreover, it can be hosted in the hub Luer of a needle, using a syringe to flow the sample and eluent through the sorbent. In the gauge of the needle is high enough, the cotton can be packed inside, which allows the use of large amounts of sorbent phase, thus increasing the efficiency of the extraction process [29]. The materials have been mainly applied to isolate drugs from biological samples. Covalent functionalization of cotton usually involves the inclusion of amine groups [30]. This confers on the cotton surface a positive charge, being possible the retention of negatively charged compounds (e.g. dye contaminants), in contrast to the behaviour of the previously described approaches.

Interestingly, cotton can be also modified by thermal treatment. The carbonization process renders carbon fibers whose polarity can be fine-tuned by selecting the proper pyrolysis conditions, viz. temperature (200–700°C) and time (0.5–4 h) under an inert atmosphere [31]. It was observed that more aggressive conditions were needed to retain the more hydrophobic compounds while mild conditions (shorter times and medium temperature) were adequate to maximize the interaction with more hydrophilic compounds. Although no additional solvents or polymers are needed in this case, this approach is more energy demanding that the previously described ones.

2.1.2. Wood

Wood is a natural material mainly composed of cellulose, hemicellulose and lignin. This composition slightly modified its use in sample preparation as additional interactions (π-π, dipole-dipole or hydrogen-bonding) can be established with the target compounds. In the negative side, the abundant leaching of endogenous compounds is usually observed during the extraction step which results in a relatively high level of interferences in the instrumental analysis of the extracts [32]. Wood has been mainly used as sorbent in the wooden toothpicks (WTs) format. WTs are cheap, with a narrow shape and high mechanical stability. This last property permits, for instance, their use for direct puncturing of the sample [33]. In addition, WTs are suitable substrate for ambient ionization mass spectrometry techniques [34], in contrast to paper that exhibits problems of irreproducibility associated to the bending observed during the spray formation. Regarding the surface modification of WTs, different alternatives have been proposed in the literature. In general, the incorporation of specific functional groups [35], polymers [36] or composites [37] are aimed at boosting interaction towards the target compounds (drugs present in biological fluids). Liquid phases can also be immobilized onto the WTs taking advantage of the high porosity they exhibit [38]. In general, the modification of these substrates is compatible with the criteria established to calculate the greenness of the method as, thanks to their low dimensions, the consumption of organic solvens to prepare the polymer solution is also low.

Finally, sawdust (SWD) has been recently proposed for sample preparation [39]. In this approach, the SWD was previously carboxymethylated to reinforce the H- bonds and hydrophobic interactions with electrostatic interactions via the carboxyl groups. The reduced particle size of SWD allowed for packing into pipette tips, the amount of sorbent being limited by the back pressure created in the system by the sample flow. The sorbent was applied to the determination of antidepressants in biofluids. In this case, the carboxymethylation step penalized the method greenness.

2.1.3. Cork

Cork is a natural, biodegradable, reusable, and sustainable material composed by suberin, lignin, cellulose and hemicellulose, among other minor components such as waxes and tannins. As a result, interactions with the analytes similar to those described for the previous natural materials have been identified as well as the interferences from endogenous compounds during the instrumental analysis of the extracts. As a distinct characteristic, cork presents a microscopic honeycomb structure formed by prismatic cells. This ordered porous structure results in excellent extraction capabilities thanks to the enhanced surface area. In sample preparation, cork has been used in different formats, namely: powder, granules, disks, sheets and pellets which are compatible with different microextraction techniques and, as a rule, the surface has not been modified. The elasticity and flexibility of cork makes it compatible with microextraction devices such as SBSE [40], SPME, rotating disk microextraction (see Fig. 1) [41] or PT-SPE [42], among other approaches. Described applications are focused on the determination of emerging contaminants in environmental water samples as will be described in section 3.1.1.

Probably one of the most favourable features of cork is its high sustainability as normally it is obtained from recycled stoppers. Moreover, its easy coupling with rotating disk or pipette tip microextraction permits the development of high-throughput methodologies, with a clear contribution to reduce the time and cost of the analysis.

2.1.4. Other natural fibers and biopolymers

Natural fibers obtained both from plants (coconut, kapot, sisal) or animals (so-called natural proteins such as feather, silk or wool) have also gained popularity as sorbents as they also exhibit excellent sorbent capacity and are sustainable in nature. Among their advantages, the possibility of covering a wide range of polarity, together with the rich presence of surface functional groups can be highlighted. As it has been previously described for other materials, modification can also be implemented to boost the sensitivity and/or selectivity of the extraction [43].

In addition to this, other biopolymers can also be directly used as sorbents: chitosan, alginate or agarose can be cited among the most reported in literature [13]. Chitosan is a water soluble (pH < 7) polymer derived from quinin, predominantly presents in the shell of arthropods (viz. crab and shrimp). There are several application fields which benefit from its use, namely: medicine, cosmetic, food industry and wastewater treatment. In the field of Analytical Chemistry, its potential to retain

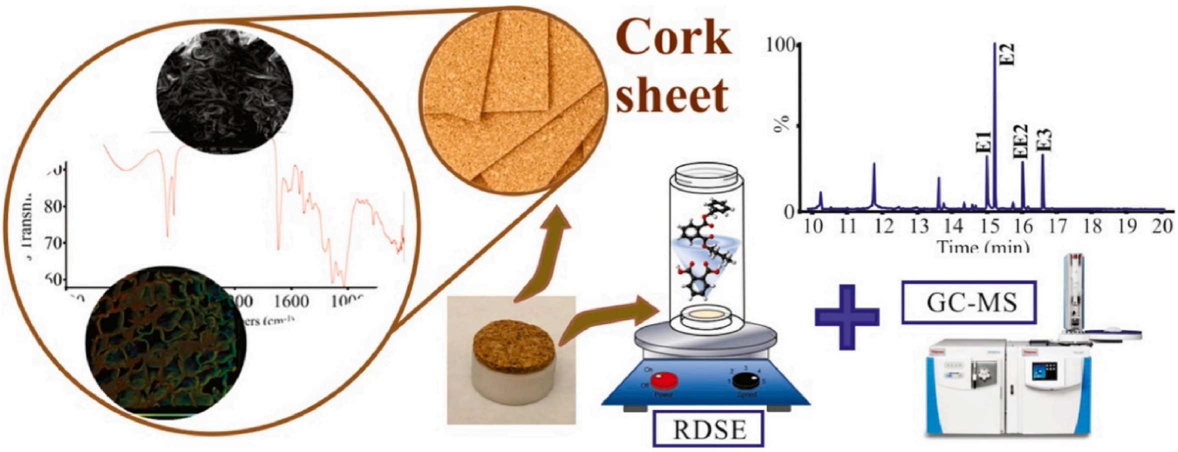

Fig. 1. Schematic representation of the incorporation of a cork sheet into a rotating disk unit to determine hormones in waters. Adapted from Ref. [41] with permission of Elsevier.

metal ions (through complexation) and organic compounds has led its use to develop sustainable microextraction approaches. Although it can be used unmodified [44], its combination with magnetic nanoparticles or other materials [45,46] has also been proposed.

Alginate is a linear, non-toxic, biodegradable and water-soluble biopolymer obtained from brown algae. As chitosan, it also has applicability in a wide variety of fields. For sample preparation, its high solubility in water hinders it direct use as sorbent. However, it can stand as scaffold or stabilizer of a second material which acts as the effective sorbent in the extraction process. The application of alginate-based sorbents in various microextraction techniques, including functionalization approaches that enhance the extraction performance has been described by Jatkowska et al. [47].

Agarose is also a linear biopolymer easily found in seaweed. It also exhibits a gelling ability and therefore, is an excellent candidate to form three-dimensional porous structure with capacity to support liquid or solid extractants [13].

2.1.5. *Materials based on biowaste*

The use of agricultural by-products (viz. peels or seed) for the development of new materials has become increasingly popular for sample preparation owing to their inherent properties including biodegradability, non-toxicity and biocompatibility. Their fibrous/porous structure together with the surficial functional groups facilitates analytes' interaction. Moreover, they clearly contribute to the circular economy as residues are directly transformed into raw materials. Biowaste residues (coffee residues, bracts and peels of various fruits) have been investigated for the extraction of a wide variety of compounds from different samples either with analytical or remediation purposes [48, 49].

The introduction of natural materials in sample preparation, despite their eventual further modification to enhance selectivity or extraction capacity, certainly improves the sustainability of this step and consequently that of the whole analytical process. We should be aware that the environmental cost associated with commercial sorbents, prepared at a large scale remains invisible for researchers and it is usually not considered in the evaluation of the method sustainability. Two limitations related to the introduction of natural sorbents in the analytical process must be, however underlined. On the one hand, normally the reusability of the material is not tested as in most of the applications, considering that the resources needed in the cleaning step override the low cost and availability of the natural sorbent. Nevertheless, if the sorbent needs to be modified, maybe the costs associated with the reusability should be compared to those derived from the synthesis. On the other hand, the homogeneity of the material is also a recurrent question as it affects the reproducibility of the analytical method. Reproducibility implies the homogeneity of the material in terms of composition and analytical performance.

2.2. *Green strategies for the preparation of materials*

Apart from using natural sorbents, which is probably the preferred choice in the last years, different strategies can also be applied in the preparation of materials that make them more sustainable. Emphasis on greener synthetic procedures would significantly contribute to overall greener sample preparation approaches [1]. These strategies can be applied to a wide diversity of sorbents and some of them will be discussed in this section.

One of the most used materials in sorptive extraction techniques are the synthetic polymers being most of them obtained from synthetic monomers from petrol. To increase their sustainability, some strategies can be applied, such as the use of polymers coming from natural sources or removable monomers (poly (lactic acid), polycaprolactone o polyhydroxybutyrate [50]) or the use of more benign solvents, water or biobased organic solvent in order to avoid the use of petrol-derived solvents. Another general strategy is to move to more environmentally friendly synthesis procedure, using for example, less energy-demanding techniques, (e.g., decreasing temperature, time), such as microwave- or ultrasound-assisted synthesis, for instance in the preparation of nanomaterials [51].

These strategies can be applied not only to synthetic polymers but also to a wide range of materials to make them greener, such as MOFs, COFs or molecularly imprinted polymers (MIPs). Nanomaterials (NMs) have also gained attention due to the wide variety that can be prepared and in case of magnetic NMs, their ability to be separated with an external magnetic field, which make them very useful in different extraction techniques [52].

As environmentally benign solvents, water is the most suitable one because it is a low cost, ecofriendly, safe and nontoxic waste free solvent, although its use in some cases is a challenge due to the poor solubility of some monomers, for instance in the preparation of porous organic polymers [53]. However, it has been successfully used in the preparation of some materials, such as green magnetic azo porous organic polymer using a diazo coupling reaction with hydroxyl-rich natural kaempferol and fuchsin as monomers [54] to be employed in MSPE of phenolic endocrine disruptors from water and fish samples. Another example is the preparation of a bio-based organic-inorganic hybrid material for the SPE of antibiotic residues from honey, milk and eggs [55]. In this case, the sorbent was based on the interaction of polyvinylalcohol (PVA) and humic acid (HA) loaded in inorganic silica (SiO_2@PVA/HA).

Other types of more environmentally friendly solvents are the ILs, supercritical fluids (SCFs) or NADESs, some of them also used in the liquid-based extraction techniques.

ILs are organic salts made from ions, and they exhibited interesting properties as previously mentioned, which make them suitable for the eco-friendly preparation of NMs [51] and MIPs [56] among others. ILs-based sorbents have been applied in different sample preparation techniques such as SPE, MSPE, SPME [4,7]. However, the greenness of ILs is not so clear considering their poor degradability and toxicity [57].

As regards SCFs, carbon dioxide is an eco-friendly solvent suitable to prepare materials, such as NMs, because of their reduced environmental impact, enhanced mass transfer, energy efficiency and reusability [51].

Regarding NADESs, which are the most increasingly used, they are produced from renewable sources and are increasingly used as extraction solvent [58] and a good alternative in the synthetic processes of different types of materials [59] for sorptive extraction techniques, including carbon-based materials [12], hydrogel-based materials [60], NMs [61], MIPs [62,63] or MOFs [64,65] among others. NADESs are not only used as green solvent but also as functional monomer in the synthetic process [61] as will be described below.

2.2.1. Carbon-based materials

Carbon-based materials are considered as green materials due to their low toxicity and cost-effective synthesis. Their interest as materials for sorptive extraction techniques has increased due to their morphology, mechanical properties and typical high surface area. They can also be regenerated and reused several times (reducing waste) and modified by covalent functionalization to tune the polarity and selectivity [66]. Examples of DESs modified with graphene, graphene oxide (GO), carbon nanotubes (CNTs) or carbon nanofibers have been described in literature [59]. For instance, a graphene-DES, using a DES of choline chloride-ethylene glycol, has been used in PT-SPE for the determination of sulfamerazine from river water [67]. Another example is based on the modification of magnetic CNTs with polymeric DES (PDES) for the magnetic SPE of bovine serum albumin (BSA) [68] and Fig. 2 shows the scheme of the preparation of M-CNT@PDES and its application where AA is acrylic acid and a novel DES of 3-acrylamidopropyul trimethylammonium chloride and xylitol (1:1) was used.

Carbon-based materials have also been modified with biopolymers to obtain materials with interesting properties and have been particularly applied in miniaturized techniques, being cellulose, alginate, agarose, starch, cyclodextrin and chitosan the most used [69].

2.2.2. Hydrogels

Hydrogels have emerged as new materials in sample preparation techniques although their use is still limited. They are polymeric three-dimensional networks of hydrophilic chains that enable them to expand in the presence of water. The hydrophilic polymer chains can be cross-linked through different types of interactions that ensure structural integrity, thermal and chemical stability [60]. The increasing interest of hydrogels is due to the use of natural precursor monomers or polymers, such as polysaccharides, agarose, carbohydrates, chitosan, among others. They can be further modified with carboxylic, amine, hydroxyl groups to change their functionality. Carbon-based materials, such GO or CNTs, can also be incorporated into hydrogel to enhance the specific surface area and specific interactions, and the inclusion of magnetic NPs allows its use in DMSPE.

Hydrogels based on DESs provide an expanded surface area and improve selectivity and capacity and several materials have been developed [70,71]. For instance, a magnetic DES based on polymeric hydrogel, synthesized using acrylic acid-menthol DES as functional monomer has been successfully applied to MSPE of pesticides from water samples [70]. In this case, ammonium persulfate was used as initiator and acrylic acid-Fe_3O_4 NPs as a crosslinking agent. Another

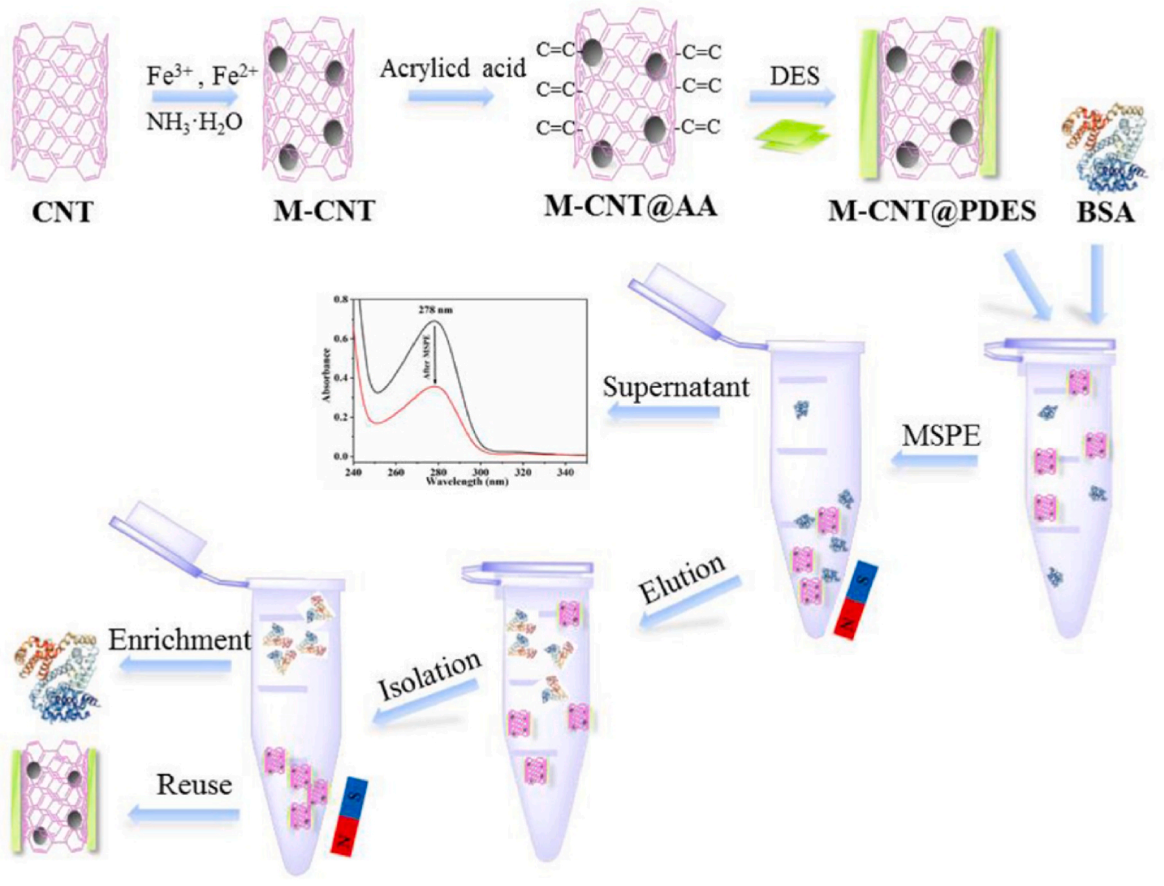

Fig. 2. Fabrication of M-CNT@PDES and its application for the extraction of bovine serum albumin [68] with permission of Elsevier.

example involves the use of a copolymeric DES gel incorporated into calcium alginate hydrogel beads that was applied in μ-SPE (20 mg) of pesticides from non-alcoholic malt beverages [72]. In this case, the NADES was obtained from thymol and methacrylic acid, that can be obtained from Roman chamomile oil. After the copolymerization using ethylene glycol methacrylate as crosslinking monomer and ammonium persulfate as initiator, the polymer was encapsulated in calcium alginate hydrogel beads. The comparison of the extraction efficiency of the new hydrogel sorbent modified with NADES with unmodified calcium alginate confirmed an increase of 1.5–3.4 times in the extraction efficiency.

2.2.3. *Molecularly imprinted polymers*

MIPs, typically designed for the selective recognition of a target molecule or a small group of structurally related molecules, are widely used in sorptive extraction techniques due to the increased selectivity they provide. Different strategies have been applied in the synthetic process of green MIPs [73]. The use of more sustainable reagents (template, functional monomers, crosslinkers and solvents), the computational approach to design and screen different monomers in order to select the best functional monomer and therefore to reduce the number of MIPs to be synthesized and evaluated, and using of more sustainable polymerization and template removal approaches, are strategies that can significantly contribute to the greenness of the MIPs [56,63]. A new methic, AGREEMIP, was developed to evaluate the greenness of MIPs synthesis procedure [74] and its application for assessing the greenness of 30 different MIP used in sample preparation is described in a recent paper [75].

As regards template, the use of a dummy molecule with similar size, shape and functionality that the template but lower toxicity is a strategy to contribute to GAC [12,76] and the use of a multi-template MIPs is also a good alternative to reduce the MIPs synthesis [12,77]. However, the most contributing strategy to greenness is the selection of porogen, functional monomers and crosslinker. As porogen, responsible for providing porous structure and promoting template-monomer interaction in the pre-polymerization mixture, to avoid toxic solvents, other more sustainable solvents such as water [62,77,78], ILs [79,80] or DESs [59,81,82] can be used. Both ILs and DESs have also been used as functional monomer, or crosslinked agent [56,80] although in the last years, DESs are increasingly used for the reasons already mentioned and examples of the use of DESs as functional monomer, porogen, crosslinker, co-solvent and modifier are extensively discussed in Madikizela et al. [63].

A recent example describes the preparation of a DES-MIP using water as porogen for the retention of bisphenol A [62]. The authors evaluated four types of DES, bisphenol A as template and polystyrene-divinylbenzene (PS-DVB) as carrier, all of them dispersed in water, and different retention conditions were evaluated in batch experiments, which demonstrated a good capacity of retention that can be further exploited in sorptive extraction techniques.

The use of biopolymers has appeared as a green alternative to produce MIPs, chitosan being the most studied one, due to its excellent biological properties and the presence of hydroxyl and amine groups in its structure, which facilitates the interaction with a wide range of templates even in aqueous media [56,80]. Chitosan has also been used in the preparation of MIPs using DES as template and functional monomer, for instance, for the enrichment of gallic acid from ginseng tea, using a NADES of mixture of choline chloride and gallic acid (1:2) [83].

2.2.4. *Metal-organic framework*

The interesting characteristics of MOFs, such as the variety of structural compositions, large surface area and chemical/thermal stability have promoted their use in several applications, such as carbon capture, catalysis, remediation, biomedical delivery, among others, and in the recent years, they have been increasingly used in sorptive extraction techniques owing to the different types of interactions they can stablished with the analytes. The interest is especially directed to the green MOFs that involve the use of nontoxic metals (such as Zr, Cu or Zn), more bening solvents (such as DESs, water, supercritical fluids, ILs), natural ligands (such as amino acids, sugars, natural biomolecules) and environment friendly and economic synthetic routes (such as synthesis at room temperature) [12,65]. When materials are prepared using nontoxic biomolecules as ligands, they are alsonamed as metal-biomolecule-frameworks (MBioFs).

The use of DESs in MOFs increase the MOFs' stability and versatility, and the integration of DES into MOFs is due to the interaction between DES and the pore surface of the MOFs, which involves the successful creation of DES@MOF composites. This type of material has been applied in different extraction techniques, such as SPE, DSPE, MSPE or SPME and examples of their application in sample preparation in food and environmental analysis have been recently reviewed [64], including the AGREEprep score of different methods, and a collection of which are also summarised in Section 3. An example is the use of a magnetic UiO-66-NH_2@DES for the MSPE of fluorotelomer alcohols (PTFOs) in edible oils, where the DES was composed of levulinic acid and trifluoromethoxylbenzene, which exhibited good recoveries [84].

A DES-Imprinted polymer based on MOFs was also used for the selective retention of the benzydamine hydrochloride, used as template, from environmental waters [81]. In this case, the use of magnetic UiO-66-NH_2 as supporter and DES as functional monomer improved the retention compared to other commercial sorbents such as HLB, PS-DVB or silica. Another interesting approach is the preparation of a fiber for SPME of amphetamines and modafinil in medicinal supplements [85]. In this case, a monolithic fiber of MOF MIL-Al(53)-DES/MIP was prepared providing good selectivity, high capacity and after optimization of the extraction conditions, excellent figures of merit were achieved.

Although much work has been done to make the synthetic process greener and more sustainable, most of materials described are in-house prepared, which means that commercial materials are still far from being green. Much work has to be done to make them available to the laboratories and to make greener their analytical methods.

3. Applications

Applications of the previously materials described in several fields will be discussed in this section, with detailed explanation of the technique, material and extraction conditions. The fields where these sustainable materials have been mainly applied are environmental, food, and biological samples and the selected examples of each field are included in Tables 1–3 respectively Regarding to the extraction techniques in which the materials are applied, they are mainly applied to SPE, but also, other emerging techniques such as dispersive solid-phase extraction (DSPE), dispersive micro-solid-phase extraction (d-μSPE), magnetic dispersive micro-solid-phase extraction (M-*d*-μSPE), pipette tip solid-phase extraction (PT-SPE) bar adsorption microextraction (BAμE), rotating disk sorptive extraction (RDSE), capsule phase microextraction (CPME), fabric phase sorptive extraction (FPSE), among others, have been also considered, although not all the materials are applied to all mentioned techniques and application fields.

3.1. *Environmental samples*

The introduction of natural materials and materials prepared using sustainable approaches has been applied for the analysis of environmental samples. In this section, these applications are covered organised by the type of material as in previous sections. In addition, Table 1 collects the more representative example of application to environmental samples of each type of material and some of them will be discussed in this section.

Table 1
Examples of applications of sustainable materials in environmental analysis.

Material (configuration)	Extraction technique	Extraction conditions	Sample	Analytes	Instrumental technique	Recovery (%)	Limits of detection	Ref.
Natural sorbents								
Cork								
Cork powder	SPE	50 mg of cork, 20 mL of sample, elution with 1 mL AcOEt	Water (river, lake, fountain, etc.)	17 fungicides	GC-MS/MS	70–118	0.3–84 ng L^{-1}	[86]
Laminar cork	RDSE 140–510 < 13	10 min for extraction using 35 mL of sample and a liquid desorption using 1 mL of MeOH: AcOEt (50:50 % v/v) for 20 min.	Water (river and lake)	20 contaminants including UV filters, pesticides and PAHs	GC-MS	80–120	0.08–1.5 μg L^{-1}	[88]
Cork pellets	BAμE	Cork pellets (10 × Ø 3 mm) 15 mL of sample 60 min of agitation, desorption with 120 μL of AcOEt for 30 min	Drinking, stream and river waters	10 organochloride pesticides	GC-ECD	49–138 drinking, 40–128 stream, 68–129 river	3–15 ng L^{-1}	[87]
Natural fibers								
Coconut	Micro-solid phase extraction	0.1 g of biosorbent, modifier (sodium dodecyl sulfate, 10 mmol L^{-1}), desorption solvent (MeOH, 150 μL), extraction time 10 min.	Environmental water, soybean milk, fruit juice and alcoholic beverage samples	Triazole fungicides	LC-UV/VIS	67–105	3 μg L^{-1}	[90]
Carbowax 20 M on cotton (fabric)	FPSE	2.5 cm × 2 cm fabric: 20 mL sample pH 6, 1000 rpm, 20 min D: 0.5 mL AcOEt, vortex, 3 min	Tap, Spring, Fountain, Rain, Runoff and River water	17 Fungicides	GC-MS/MS	72–115	1–35 ng L^{-1}	[93]
Sol–gel PDMS on cotton (fabric)	FPSE	10 mL of sample 15 min extraction by ultrasounds and 0.5 mL ofEtOH as desorption solvent (5 min)	River, sea, spring, laundry washing place, and wastewater	12 nitro-, polycyclic and macrocyclic musk	GC-MS/MS	82–110	below 8 ng L^{-1}	[95]
Silk fibers (carbonized)	In-tube SPME	60 mL of sample, sampling rate 2 mL min^{-1}, 1 % (v/v) MeOH in sample, desorption time of 2 min.	Water samples	Polycyclic aromatic hydrocarbons	LC	83–115	0.005–0.050 μg L^{-1}	[98]
Biopolymers								
Lignocellulosic natural sorbent (Araucaria angustifolia bracts)	BAμE	30 mL of sample, pH 6, NaCl concentration 30 %, extraction time 180 min, desorption time 40 min, desorption solvent ACN/H_2O 3:1	River water.	Methyl, propyl, and butylparaben, bisphenols A and F, estradiol, ethinylestradiol, benzophenone	LC- DAD	62–116	Limits of quantification, 1–10 μg L^{-1}	[99]
Chitosan crosslinked with glutaraldehyde to form thin films	RDSE	pH 4, 20 % NaCl (salting out effect), 30–45 min equilibrium time, elution MeOH: AcOEt (1:1)	Natural and residual waters	Methyl triclosan and triclosan	GC-MS	89–96	0.11 and 0.20 μg L^{-1}	[100]
Amylodextrin hydrogel	Pipette-tip micro-SPE	6.0 mg sorbent, pH 7.5, flow rate 2.0 mL/min, adsorption time: 16.5 min, volume of desorption solvent: 1.1 mL, desorption time: 11.7 min.	River and agricultural waters	Triazole fungicides	Ion mobility spectrometry	93–98	0.10–0.20 ng mL^{-1}	[71]
Biowaste								
Peanut shell-derived activated biochar	RDSE	10 mg of sorptive phase, pH 2, 70 min of extraction time, 15 mL of sample	Water	Ethyl paraben, 17-α-ethinylestradiol, bisphenol A, triclosan, diclofenac	GC-MS	16–87	0.003 and 0.73 μg L^{-1}	[48]

(*continued on next page*)

Table 1 (*continued*)

Material (configuration)	Extraction technique	Extraction conditions	Sample	Analytes	Instrumental technique	Recovery (%)	Limits of detection	Ref.
Natural sorbents								
		volume, 2000 rpm rotating velocity, and ACOEt as the elution solvent.						
Rice husk silica-carbon sol-gel nanocomposite (5–20 wt% Fe) in glycerol	µ-SPE	µ-SPE device (35 mg, ~0.5 cm × 1.0 cm) 5 mL of sample stirred at 1000 rpm for 30 min. Desorption with 300 µL solvent (ultrasonication 20 min)	Hospital wastewater	Beta blockers (atenolol, alprenolol, pindolol, acebutolol and propranolol)	LC–MS/MS	81–105	4.0–6.4 ng L^{-1}	[104]
Moringa oleifera seed powder	µ-SPE	10 mL of sample, 0.1g of biosorbent, vortex 3000 rpm 5 min, residue + 200 mL ACN vortex 15 s, then 1500 rpm 5 min, supernatant filtered with 0.45 mm.	Water	Triazole fungicides	LC-DAD	71–111	30 mg L^{-1}	[105]
Materials prepared using sustainable approaches								
Magnetic azo porous organic polymer (Mazo-POP)	MSPE	25 mg Mazo-POP into 100 mL sample solution, shaking 15 min. Mazo-POP separated from the solution by a magnet, and transferred to a glass tube. Desorption using 0.35 mL MeOH, vortex 1 min. Filtration with a 0.22 µm filter	Water	Phenolic compounds (bisphenol A (BPA), bisphenol F (BPF), bisphenol B (BPB), p-tert-butylphenol (4-t-BP))	UPLC-MS/MS	85–109	0.02–0.5 ng mL^{-1}	[54]
Metal-organic framework CIM-80(Al)	SPME	9.5 mL sample and 0.5 mL MeOH, stirring at 500 rpm, fiber immersion for 60 min. Liquid desorption with 1.5 mL MeOH at 500 rpm for 45 min. Evaporation to dryness and reconstitution 200 µL MeOH	Bottled water	14 Phtalates	UPLC-MS/MS	70–107	0.01 to 0.5 µg L^{-1}	[109]
Composite Carboxy Cotton Fiber@UiO-66-NH2@TpBD	Pipette tip solid-phase extraction (PT-SPE)	15 mg sorbent, 20 mL sample pH 7.0 flow rate 1 mL/min. Elution 300 µL of MeOH/H_2O (80:20, v/v)	Water	Bisphenols	UPLC-DAD	88–90	0.16–0.75 ng mL^{-1}	[91]
Double-layered pristine PES/DES@BC	TF-SPME	2 mL sample, pH 6.0, sorbent (1 cm × 1 cm, 2.5 mg), orbital shaker 500 rpm 5 min, adsorbent dried room temperature. Elution 100 µL MeOH	Water	12 multiclass pesticides	GC-µECD/GC–MS	75–105	0.01–0.03 µg L^{-1}	[110]
Magnetic poly (acrylic acid-menthol DES) hydrogel	SPME	0.2 g hydrogel added to 5 mL sample stirred for 15 min; hydrogel dried by argon gas, desorption 1 mL EtOH shaking for 10 min	Water	16 pesticides	GC-µECD/GC–MS	61–120	0.002–0.12 µg L^{-1}	[70]

(*continued on next page*)

Table 1 (*continued*)

Material (configuration)	Extraction technique	Extraction conditions	Sample	Analytes	Instrumental technique	Recovery (%)	Limits of detection	Ref.
Natural sorbents								
Magnetic molecularly imprinted polymer (Fe3O4@MIP) based on DES	DSPE	30 mg of Fe_3O_4@MIP-ChCl-BuIM, 10 mL H_2O shaking (200 rpm) for 15 min at room temperature	Spiked water	Naproxen	(UV/vis) spectroscopy	93–97		[111]
DES-MIP (benzyltrimethylammonium chloride: α-methylacrylic acid [TMBAC][MAA] functional monomer and water as porogenic agent	SPE	Adsorbent mass (50 mg), sample flow rates (10-, 20-, and 30-mL h^{-1})	Rain and river (spiked)	Bisphenol A	LC-UV/VIS	91–108	1 μg L^{-1}	[62]

ACN: acetonitrile; **AcOEt:** ethyl acetate; **BAμE:** bar adsorptive microextraction**; BC:** bacterial cellulose**; DAD**: diode array detection; **DES:** deep eutectic solvent; **DI:** direct infusion; **DSPE:** dispersive solid-phase extraction; **Dμ-SPE:** dispersive micro-solid phase extraction**; ECD**: electron capture detector; **ESI:** electrospray ionization; **EtOH:** ehtanol; **FLD:** fluorescence detector; **FPSE:** fabric phase sorptive extraction; **FSPE:** fabric solid-phase extraction; **GC**: gas chromatography**; LC-UV**: liquid chromatography-ultraviolet; **IT-SPE**: in-tube solid phase extraction; **LC:** liquid chromatography**; MAC:** magnetic-activated carbon; **MS**: mass spectrometry; **Mazo-POP:** magnetic azo porous organic polymer**; MCS:** magnetic chitosan; **MeOH:** methanol; **MEPS:** microextraction by packed sorbent; **MGO**: magnetic graphene oxide; **MIP**: molecularly imprinted polymer**; MOF:** metal organic framework**; μECD**: micro electron capture detector**; μ-SPE:** micro-solid phase extraction; **MSPE**: magnetic solid-phase extraction; **MS/MS**: tandem mass spectrometry; **PAHs:** polycyclic aromatic hydrocarbons; **PDA**: photo-diode array; **PDMS:** polydimethylsiloxane; **PES:** Polyethersulfone**; PT-SPE**: pipette tip solid phase extraction; **RSDE**: rotating-disk sorptive extraction; **SBSDME:** stir bar-sorptive dispersive microextraction**; SPME:** solid-phase microextraction; **TF:** Thin film; **TFME:** thin film microextraction; **UPLC**: Ultra performance liquid chromatography; **US:** ultrasound-assisted; **VIS**: visible.

3.1.1. *Natural materials*

3.1.1.1. Cork. The use of cork-based products (CBPs) is a low-cost and eco-friendly alternative to be employed as sorbent in SPE and derived techniques for the extraction of persistent and emerging pollutants from the aquatic environment.

Cork was used [86] in a SPE sustainable methodology for the extraction of 17 fungicides followed by GC-MS/MS analysis [86]. The most critical parameters affecting SPE were optimized by experimental design methodology. Under the optimal conditions, the method was successfully validated including recovery evaluation in different water samples (river, fountain, rainwater and spring water). The analysis of waters collected in vineyards areas revealed the presence of most target fungicides at concentration up to hundreds of μg L^{-1}.

Organochlorine pesticides have also been extracted using a cork pellet material [87]. In this case, the authors propose a cork pellet-based bar adsorptive microextraction methodology as a new greener alternative for the determination of organochlorine compounds. Aldrin, chlordane, dieldrin, endrin, lindane, 4,4-DDD, 4,4-DDE, 4,4-DDT, α-endosulfan and β-endosulfan were analyzed in water samples (drinking water, stream water and river water) with separation/detection by GC and electron capture detection (GC-ECD). The parameters that can affect the sample preparation efficiency such as desorption solvent and time, as well as extraction time and ionic strength were evaluated by multivariate and univariate designs. Under the optimal conditions the cork pellets (10 × Ø 3 mm) were used for the extraction of 15 mL of sample for 60 min followed by desorption with 120 μL of ethyl acetate for 30 min.

. Laminar cork was employed as extraction phase in rotating-disk sorptive extraction (RDSE), an integrated extraction/stirring technique, proposed in 2009 by Richter and co-workers, for the determination of 20 contaminants including UV filters, pesticides and PAHs from aqueous samples. The influencing parameters were carefully optimized using multivariate designs achieving satisfactory analytical performance [88].

In an innovative study, Viera et al. [89] investigated the viability of applying cork and montmorillonite clay modified with IL as biosorbents employing also the RDSE technique followed by LC-MS analysis. The target compounds included methyl paraben, ethyl paraben, propyl paraben, and isobutyl paraben. The optimal conditions comprised an extraction time of 30 min and the use of an ammonia solution (pH 10) as desorption solvent. The proposed methods showed limits of quantification of 0.8 μg L^{-1} for cork, 3.0 μg L^{-1} for montmorillonite clay and 6.0 μg L^{-1} for a classical C_{18} sorbent.

3.1.1.2. Natural fibers. Coconut husk fiber (CHF) was investigated as an eco-friendly and effective biosorbent for micro-solid phase extraction (μ-SPE) of pesticides prior to their determination by LC [90]. Fourier transform infrared spectrometry, scanning electron microscopy and transmission electron microscopy methods were used to characterize the modified biosorbent. The developed method was successfully applied to determine triazole fungicides in environmental water samples.

A cotton base biosorbent was used in pipette tip solid-phase extraction (PT-SPE) coupled with ultra-performance liquid chromatography (UPLC) for the detection of trace levels of the three bisphenols (BPs) in water using a cotton based biosorbent [91]. A hybrid material (UiO-66-NH_2@TpBD) was immobilized on cotton, through a layer-by-layer strategy. The sorbent showed great potential towards industrial applications in the field of BP adsorption and removal from water samples. A simple, sensitive and reproducible method to determine trace of three bisphenols in river, pond and tap water was developed.

Natural fabrics as cotton functionalized with different polymeric sorbents via sol-gel process has been proposed by Kabir et al. [92] for environmental analysis since its origin, using the emerging FPSE technique. A wide range of contaminants including pesticides [93] and emerging contaminants as PCPs [94,95] were extracted from environmental, agricultural and urban waters. The most critical experimental parameters affecting FPSE, such as the type and size of sol-gel coated FPSE media, sample volume, extraction time, type and volume of desorption solvent, or ionic strength effect, were optimized to obtain the highest extraction efficiency. High enrichment factors and very low LODs at the low ng L^{-1} were achieved demonstrating the suitability of this technique for environmental applications [96].

Silk fibers were carbonized to develop an adsorbent made of biomass carbon. An extraction tube packed with carbonized silk fibers was prepared for in-tube SPME followed by LC analysis. The method exhibited good extraction performance for polycyclic aromatic hydrocarbons (PAHs) from real water samples [97]. The same authors also proposed carbonized cotton fibers as sorbent with the aim of improving the material enrichment ability. The extraction process was evaluated for PAHs, oestrogens and phthalates only resulting efficient for the first family of compounds, reaching high enrichment factors for some of them [98].

3.1.1.3. Biopolymers. A lignocellulosic natural sorbent from *Araucaria angustifolia* bracts was proposed in bar adsorptive microextraction (BAμE) technique for the determination of emerging contaminants in river water. Methyl, propyl, and butylparaben, bisphenols A and F, estradiol, ethinylestradiol, and benzophenone were determined by BAμE followed by LC with diode-array detection [99].

A thin biofilm of chitosan was developed as a sorptive phase for RDSE for the determination of triclosan and methyl triclosan from water [100]. The main characteristic of this material is the presence of a high number of nitrogenous groups, which gives a high reactivity; but, on the other hand, its main disadvantage is associated with its high swelling. To prevent this problem, chitosan was crosslinked with glutaraldehyde to form thin films that were immobilized on the surface of the rotating disk. The optimal extraction conditions were pH 4, 20 % NaCl, 30–45 min of equilibrium time, and elution with a mixture of methanol:ethyl acetate (1:1). The green properties of the phase were evaluated, demonstrating its biodegradability and reusability for at least three cycles. The analysis of natural and residual waters revealed the presence of triclosan at 0.7–1.3 μg L^{-1}.

An interesting method applied for the preconcentration of triazole fungicides used melamine-based sorbent followed by LC determination [101]. The method employs a melamine sponge anchored with nickel/aluminium layered double hydroxide (Ni/Al-LDH-MS) employing micro-solid phase extraction (micro-SPE). Eco-friendliness criteria were confirmed by Analytical Eco-scale and Analytical GREEnness metric (AGREE).

In a recent study [102], Mater-Bi film, a commercially available patented blend of polybutylene-terephthalate, starch and fatty acids, was proposed for the extraction of emerging contaminants in water. The interaction among a range of contaminants and the Mater-Bi film was investigated by means of two sequential experimental designs. The method, approximating a fabric phase sorptive extraction, involved the pH and ionic strength modification of the sample, 1 h extraction and desorption in ethanol. The method allowed the quantification of pharmaceuticals and UV filters at the μg L^{-1} and ng L^{-1} levels in wastewater. The evaluation by green and white analytical chemistry metrics (0.6 evaluated with AGREE and 83.4 evaluated with RGB, respectively) highlighted the promising potential of this biodegradable polymeric film compared with conventional extraction methods.

A hydrogel-based sorbent synthesized by a combination of hydrophilic acrylic polymer and biodegradable amylodextrin was used as a green sorbent in the pipette-tip micro-solid phase extraction procedure for extraction and quantification of 3 triazole fungicides in environmental water [71]. The extraction conditions were set as follows: the amount of sorbent 6.0 mg, pH of sample solution 7.5, flow rate 2.0 mL min^{-1}, adsorption time 16.5 min, volume of desorption solvent 1.1 mL, and desorption time 11.7 min. The proposed method was successfully applied for the quantification of triazoles in river and agricultural waters.

A sustainable and innovative material made of modified clay immobilized in an agarose film is proposed for detecting trihalomethanes and other organochlorine pollutants in water using HS-SPME followed by GC-ECD, showing suitable performance for the determination of the target pollutants [103]. The IL intercalated with montmorillonite on an agarose film has been compiled by four times following the green chemistry principles. The adsorbent-holder agarose gel is biodegradable, the adsorbent montmorillonite clay is a widespread eco-material and the ILs are considered as bening solvents.

3.1.1.4. Materials based on biowaste. Peanut shell-derived activated biochar has been proposed as a low-cost, efficient sorbent for the extraction of emerging contaminants from environmental water samples using RDSE and GC–MS analysis [48]. The target compounds included ethyl paraben, diclofenac, triclosan, bisphenol A, and 17-α-ethinylestradiol, covering a wide range of polarities. The extracting capacities of the activated carbon demonstrated to be superior to those of biochar and the untreated phase. The optimal conditions for extraction consisted of using 10 mg of sorptive phase, pH 2, 70 min of extraction time, 15 mL of sample, and ethyl acetate as elution solvent. The comparison with commercial phases demonstrated that activated carbon offered comparable or higher extraction efficiencies for these five emerging contaminants.

A rice husk silica-carbon nanocomposite in glycerol material was used in an environmentally friendly micro-solid phase extraction (μ-SPE) LC–MS/MS method for determination of trace level beta blockers (β-blockers) (atenolol, alprenolol, pindolol, acebutolol and propranolol) in water [104]. The nanosorbent demonstrated suitability for the determination of trace level β-blockers in hospital wastewater and it could be re-used up to 25 times without apparent decrease in the extraction efficiencies.

Other interesting approach proposes the use of *Moringa oleifera* seeds as a green, efficient biomaterial for the selective enrichment and extraction of triazole fungicides in environmental waters followed by LC analysis [105]. This kind of seeds were shown to be an efficient material, thereby contributing to the development of low-cost analytical methodologies falling within the current concept of green chemistry.

3.1.2. Materials prepared using sustainable approaches

Porous organic polymers (POPs) are prominent sorbents for effective extraction. However, green and sustainable construction of functional POPs is still a challenge. A magnetic azo Porous Organic Polymer (Mazo-POP) was developed for the first time using hydroxy-rich natural kaempferol and low-toxic basic fuchsin as monomers through a diazo coupling reaction [54]. The magnetic sorbent was used for extracting phenolic EDCs from water and fish samples, followed by UPLC-MS detection.

Magnetic nanoparticles (MNPs) exhibit exceptional performance in extracting and enriching a wide range of pollutants due to their super-paramagnetic properties, ease of separation, and surface modification allowing selective adsorption capacity. Current research and analysis on biosynthesized green MNPs from green sources are of great interest in environmental analysis [106]. However, several hindrances remain for the practical implementation of green MNPs for environmental preconcentration. One of the main challenges focuses on the regulation of the size of MNPs to enhance super-paramagnetism and thereby enable to perform separation and recovery in low gradient magnetic fields. Another challenge consists of assessing the MNPs ecological toxicity ensuring a safer use for environmental analysis.

An original method employs a green magnetic snail shell hydroxyapatite sorbent for the SPE extraction of phenyl-N-methylcarbamate insecticides from water followed by LC-MS analysis. Magnetic extraction parameters were optimized by means of an experimental design using a Doehlert matrix showing suitable method performance [107].

Five metal-organic frameworks (MOFs), specifically HKUST-1, MOF-5(Zn), MIL-53(Al), UiO-64 and MOF-74(Zn) were synthesized, characterized and used for μSPE under dispersive mode (D-μSPE), combined with UPLC and time-of-flight (TOF) mass spectrometry detection. These MOFs were tested for the extraction of six pollutants of different families, including a PAH (fluorene), two hormones (progesterone and estrone), a drug (carbamazepine), a pesticide (atrazine) and one biocide (triclosan), from tap water and wastewater [108].

Green MOFs have also been used as a sorbent coating in SPME. The metal-organic framework CIM-80(Al) is proposed as a fiber coating (thickness 3.5 μm) to isolate and determine 14 phthalate esters in bottled water [109]. The results obtained are promising and comparable to commercial coatings. Quantification was performed by UPLC-MS/MS showing satisfactory performance.

A nanofiber double-layered biosorbent using polyethersulfone (PES) doped with a natural DES, consisting of choline chloride (ChCl) and caffeic acid (CFA), electrospun onto a bacterial cellulose (BC) substrate is proposed for extracting 12 multiclass pesticides from water showing its prospective for widespread use in environmental analysis. Method sustainability was evaluated by means of the Analytical Eco-Scale and Analytical Greenness metrics showing good score [110].

A novel magnetic DES-based polymeric hydrogel was synthesized by thermal frontal polymerization, using acrylic acid-menthol DES (as a functional monomer), ammonium persulfate (as initiator), and acrylic acid-Fe_3O_4 nanoparticles (as cross-linker). The hydrogel was characterized by FTIR and FE-SEM techniques and used in magnetic SPE followed by GC–μECD analysis for the monitoring of 16 pesticides in different environmental waters [70].

Husin et al. [111] used DES-based choline-imidazole (ChCl-BuIM) (1:1) as a co-solvent in the polymerization process of magnetic imprinted polymer (Fe_3O_4@MIP-ChCl-BuIM) for the adsorption of naproxen from wastewater. Compared to sorbents prepared without DES addition, the material exhibited higher adsorption capacity owing to the presence of π -π interactions between the aromatic and benzene rings in naproxen and imidazole structures.

Another interesting attempt combining a DES with a MIP was proposed employing a DES composed of L-menthol and formic acid (FA:L-mentholin (1:1)) used as a porogen [112]. The capacity and selectivity achieved enabled the DES-MIP application to the SPME of triazines from soil sample extracts. However, authors underline the challenge of unusually high nonspecific interactions that can affect the selectivity and efficiency of the MIPs suggesting to explore other DESs and templates that could improve the performance.

3.2. Food samples

The incorporation of sustainable materials in microextraction techniques for the analysis of different analytes in food samples will be described in this section. Sustainable materials mainly based on cellulosic materials, wood, yarn, natural fibers, biopolymers such as chitosan, cellulose, agarose, or alginate, biowaste residues, as well as other miscellaneous green materials (NPs, bioMOFs, or DES) have been described. Representative applications involving the use of these sustainable materials for food analysis are presented in Table 2, including some quality parameters of the methods. For these samples, the high number of interferences and the complexity of the matrices make it essential to develop analytical methods with high selectivity and sensibility.

3.2.1. Natural materials

3.2.1.1. Cellulose-based materials. As commented in Section 2, cellulose-based materials present favourable features that make them good candidates to be used in sample preparation. In the case of cellulose, paper without any modification has been successfully applied to the isolation of biogenic amines from beer [18]. The use of raw cellulose paper-supported hydrophobic deep eutectic solvent (HDES) has been recently reported as a sorbent for extraction of carbamates in edible insect and fruit samples [113]. In detail, the paper was functionalized with HDES, being the resulting sorbent used in DSPE of carbamates giving as a results LODs below 30 μg L^{-1} and recoveries ranged from 77 % to 158 %, with RSDs below 9 %. To assess the environmental impact of the developed extraction procedure, the AGREE tool was used obtaining a score of 0.53. The use of safer solvents (HDES) contributed to a high score, whereas the lack of automation led to a lower score. The proposed method is considered sustainable and environmentally friendly and represents an acceptable green analytical approach.

Apart from raw cellulose paper, other authors have described the preparation of cellulose-based nanosorbents. For example, a carboxymethylcellulose (CMC)/Zn-based MOF/GO was prepared taking advantage of the biocompatibility of CMC, porosity, structural adaptively and flexibility of MOF and the high surface area of GO [114]. The developed sorbent was used for the DSPE of fungicides from fruits by GC-FID with acceptable LODs and good recoveries (>91 %).

On the other hand, the use of raw and modified cotton packed in a syringe or in-tube have been also reported [115,116]. In the case of raw cotton, it was used to selectively isolate zearalenone in cereals and medicines follow by HPLC-MS/MS [115], resulting in a very simple, low-cost and time-saving analysis of this mycotoxin at low concentrations.

3.2.1.2. Wood. The use of wood as sorbent to extract compounds of interest on food has been also explored. For instance, Liu et al. [117] developed an innovative method using wooden toothpicks functionalized with a MIP for the selective SPME of antibiotics from food matrices, coupled to ambient mass spectrometry (MIP-coated wooden-tip electrospray (ESI)-MS). This approach enabled the direct enrichment of macrolide antibiotics in drinking water, honey, and milk, achieving excellent enrichment factors of 244–1604, 72–370, and 12–82, respectively. The method demonstrated high sensitivity, with LODs ranging from 1.1 to 15.8 ng g^{-1}, while recovery rates for macrolide antibiotics in honey and milk samples ranged between 73 % and 98 % (RSD below 3 %). Moreover, after a proper regeneration of the MIP-coated wooden-tip sorbent, five cycles could be carried out. The integration of MIP-coated wooden-tip SPME with ESI-MS provided a rapid, selective, and cost-effective solution for antibiotic residue analysis in food, highlighting its strong potential for food safety monitoring.

3.2.1.3. Natural fibers. In the case of natural fibers, some authors have designed permeable cellulose fabric pieces impregnated with different polymeric materials via sol-gel process for the extraction of organic contaminants from vegetables, fruit juices and wines [118–120]. Among the various polymers evaluated, highly polar containing poly(ethylene glycol) (i.e. Carbowax 20) exhibited the best extraction performance in terms of extraction recovery. The fabricated fabric disks prepared were applied to the FPSE of pesticides from different matrices, achieving recoveries above 89 % for organophosphorus pesticides in vegetables [118], 92 % for organochlorine pesticides in fruit juices [119] and 77 % for fungicides and insecticides in wines [120]. The set-up of FSPE enables its easy integration with various analytical techniques such as GC-MS [118,119] or UPLC-ESI-MS/MS [120] Moreover, FPSE offers several advantages, such as straightforward preparation, extended operational lifetime, regeneration capability, high stability, and cost-effectiveness of the extraction supports.

3.2.1.4. Biopolymers. The applications that involve the use of biopolymers as sorbent materials related to food sample preparation has experimented a great increase in the last years. In the case of chitosan, their use as the only material responsible for the extraction of target analytes from complex matrices has been scarcely investigated [121], which might be attributed to its low stability in acidic media jointly with its low adsorption capacity [122,123]. To overcome this limitation, different modification strategies have been described to enhance the chitosan adsorption capacity through the incorporation of functional materials. One of them consists of the incorporation of GO to increase its surface area, improve chemical and thermal stability, and to provide additional functional groups while ensuring excellent hydrophilicity of the resulting chitosan-based composites [46,124–127]. In this context, an interesting study evaluated the performance of a MEPS LC-MS/MS protocol for pesticide and antibiotic determination in food matrices [121]. The method provided low LODs (0.020–5 μg L^{-1}) and good recoveries (82–109 %) with RSDs values above 15 %, while also demonstrating high throughput (>10 extractions per hour) and notable green attributes. In this sense, AGREE and GAPI assessments highlighted methodological positive aspects, including the use of a biodegradable

Table 2
Application of sustainable materials for food sample analysis.

Material (configuration)	Extraction technique	Extraction conditions	Sample	Analytes	Instrumental technique	Recovery (%)	Limits of detection	Ref.
Natural sorbents								
Cellulose and cotton								
Cellulose	Raw filter paper	Paper strips (1.5 × 0.5 cm), adsorption with H_2O for 45 min, desorption with 500 µL MeOH/H_2O (6:4 v/v), 0.1 % HFor for 5 min	Beer	Biogenic amines	DI-MS	–	60–180 µg L^{-1}	[18]
DES-cellulose	Filter paper	Paper strips (3 × 1 cm), 10 mL sample, adsorption with H_2O for 10 min, desorption with 100 µL ACN for 15 min	Fruits	Carbamates	LC-UV	77–158	10–30 µg L^{-1}	[113]
Magnetic cellulose	SBSDME	10 mg sorbent, 5 mL sample, adsorption with H_2O at RT for 10 min, desorption with 3 mL n-hexane for 5 min	Fruit juices	Polychlorinated biphenyls	GC-MS	70–108	2.1–54 ng L^{-1}	[153]
Zn(BDC)-GO-CMC	DSPE	15 mg sorbent, 50 mL sample, adsorption at pH 7.0 for 4 min, desorption with 100 µL EtOH for 3 min	Fruits	Triazole fungicides	GC-FID	92–102	0.3–1.5 ng mL^{-1}	[114]
Cotton	In-syringe-SPE	200 mg sorbent, 3 mL sample, adsorption with n-hexane for 4 cycles, desorption with 100 µL ACN for 4 cycles	Cereals and medicines	Zearalenone	LC-MS/MS	94–110	0.025 ng g^{-1}	[115]
PPy-Cu-Cr-Fe-Cotton	IT-SPE	70 mg sorbent, adsorption with H_2O at pH 10.0 for 20 min, desorption with 100 µL 0.1 M NaCl in MeOH for 10 min	Honey	Chlorophenols	LC-UV	93–107	0.05–0.07 µg L^{-1}	[116]
Wood								
MIP-wooden (tip)	SPME	100 mL sample, adsorption with H_2O at pH 5.0 for 40 min at 25 °C	Honey and milk	Antibiotics	Ambient ESI-MS	73–98	1.1–15.8 ng g^{-1}	[117]
Natural fibers								
CW20 M-cellulose (fabric)	FPSE	Adsorption with ACN at pH 6.0 for 25 min, desorption with 200 µL ethyl acetate for 8 min	Vegetables	Organophosphorus pesticides	GC-MS	89–99	0.033–0.136 ng g^{-1}	[118]
PEG-PPG-PEG-cellulose (fabric)	FPSE	FPSE media (2.5 cm × 2.0 cm, 10 mL sample, adsorption with H_2O for 20 min, desorption with 500 µL acetone for 15 min	Fruit juices	Organochlorine pesticides	GC-MS	92–100	0.007–0.032 ng mL^{-1}	[119]
CW20 M-cellulose (fabric disks)	FPSE	FPSE media (1 cm × 1 cm), 10 mL sample, adsorption with MeOH overnight at RT, desorption with 300 µL ACN:MeOH (8:2, v/v) for 15 min	Wine	Fungicides and insecticides	LC-MS/MS	77–121	0.01–0.1 ng mL^{-1}	[120]
Biopolymers								
MIP-CS (particles)	PT-SPE	10 mL sample, adsorption with H_2O at pH 6.0 for 12 h, desorption with 100 µL MeOH/AcOH (9:1, v/v) 5 % NaCl	Chili powder samples	Rhodamine B	LC-UV	85–103	0.0015 mg kg^{-1}	[121]
PPY/GOx/C18-CS (cryogel)	SPE	3 mL sample, adsorption with H_2O, desorption with 3 mL ACN	Fruit juice	Carbamate pesticides	LC-UV	84–99	0.5–2.0 µg L^{-1}.	[124]
GO-MCS (particles)	MSPE	10 mg sorbent, 10 mL sample, adsorption with MeOH at pH 5.0 for 40 min, at 25 °C, desorption with $CHCl_3$/MeOH (1:1, v/v) for 20 min	Rice	Phenylurea herbicides	LC-UV	90–94	0.008–0.03 ng g^{-1}	[125]
GO-AG-CS (gel)	TFME	10 mL sample, adsorption with H_2O at pH 3.0 for 15	Honey and tea	Chlorophenols	LC-UV	90–105	0.03–0.13 µg L^{-1}	[46]

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Table 2 (*continued*)

Material (configuration)	Extraction technique	Extraction conditions	Sample	Analytes	Instrumental technique	Recovery (%)	Limits of detection	Ref.
Natural sorbents								
		min, desorption with 250 µL DES for 5 min						
MGO-AG-CS (film)	MSPE	5 mL sample, adsorption with MeOH for 30 min, desorption with 2 mL EtOH	Chicken egg	Streptomycin and gentamicin	LC-UV	92–94	0.19 µg kg^{-1}	[126]
SiGO-CS	MEPS	7 mg sorbent, 0.5 mL sample, adsorption with 0.05 M phosphate, pH 7.0; desorption with 100 µL ACN for pesticides; adsorption with McIlvaine buffer/0.05 M EDTA; desorption with 100 µL ACN for antibiotics	Corn, tomato, milk	Pesticides and antibiotics	LC-MS/MS	82–109	0.020–5 µg L^{-1}	[127]
AG-HFCS (disk)	RDSE	5 mL sample, adsorption with 2 % NaCl (w/v) at pH 2.5 for 5 min	Oil/Infant powder milk	Malondialdehyde	Spectrophotometry	88–100	1.1–1.4 ng mL^{-1}	[149]
p(St-Co-AC)/Co-ZIF-67-CS (nanofiber)	PT-SPE	5 mg sorbent, 6 mL sample, adsorption with H_2O for 3 cycles, desorption with 300 µL PrOH	Juice, milk, vegetables and honey	Pesticides	GC-FID	88–95	0.5–1.0 ng mL^{-1}	[129]
Apt-CS (nanofibers)	DSPE	5 mg sorbent, 5 mL sample, adsorption with Tris-HCl buffer, desorption in 300 µL ACN	Corn, wheat, and beer	Zearalenone	LC-FLD	101–108	18.0 ng L^{-1}	[133]
PIL-CS (particles)	DSPE	20 mg sorbent, 10 mL sample, adsorption for 15 min at 35 °C, desorption with 1 mL NH_3 (5 %, v/v) in MeOH/H_2O (1:1 v/v) for 10 min	Milk and egg	Sulfonamide antibiotics	LC-UV	77–100	0.93–1.21 µg L^{-1}	[131]
Fe/Ni-MIL-53-MCS (nanospheres)	DSPE	30 mg sorbent, 20 mL sample, adsorption with 5 % NaCl at pH 7.5 for 7.68 min, desorption with 175 µL ACN for 8.36 min	Black tea and corn	Aflatoxins	LC-FLD	88–98	0.02 mg mL^{-1}	[130]
PVA-citric acid–CS–AV (nanofiber)	TFME	20 mL sample, adsorption with 20 % NaCl (w/v) for 10 min, desorption with 500 µL 1-butanol for 4 min	Fruit juice and vegetables	Pesticides	LC-UV	86–97	0.2–0.5 ng mL^{-1}	[132]
Biowaste								
MIP-rice husk (particles)	SPE	80 mg sorbent, adsorption with MeOH, desorption with 2 mL MeOH/H_2O (8:2, v/v)	Maize	Zearalenone	LC-FLD	92–98	1.5 µg kg^{-1}	[49]
Peanut shells biochar	PT-SPE	4 mg sorbent, 3 mL sample, adsorption for 1.5 min, desorption with 200 µL MeOH for 0.3 min	Bottled water, milk, and tea	Endocrine-disrupting phenols	LC-UV	84–117	0.25–2.5 µg/L,	[134]
CS-*Zizyphus jujuba* seeds derived biochar (particles)	PT-SPE	3 mL sample, adsorption with H_2O:ACN (9:1, v/v), desorption with 900 µL MeOH/ACN (1:1, v:v)	Rice	Triazine herbicides	LC-UV	96–116	1.41–3.35 ng g^{-1}	[135]
Moringa oleifera seed	µSPE	100 mg sorbent, 10 mL sample, extraction 30 s, 2 min desorption with 200 µL ACN for 3 min	Honey and fruit juice	Triazole fungicides	LC-UV	70–112	30–50 µg L^{-1}	[105]
Basil seeds	DSPE	20 mg sorbent, 0.5 mL sample, adsorption with H_2O at 50 °C for 6 min, 3 min elution with 100 µL 5 % TFA in ACN	Milk	Tetracyclines	LC-UV	83–110	5–7 µg L^{-1}	[136]
Nectarine core-derived biochar	US-MSPE	10 mg sorbent, 10 mL sample, adsorption with 9 % NaCl for 25 min, desorption with 200 µL CH_2Cl_2	Tomato paste	PAHs	GC-MS	88–98	0.028–0.053 ng g^{-1}	[137]
Pomegranate peels@starch@Fe_3O_4	MSPE	15 mg sorbent, adsorption for 15 min,	Fruit juice	Ascorbic acid	LC-UV	92–104	0.004 µg mL^{-1}	[138]

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Table 2 (*continued*)

Material (configuration)	Extraction technique	Extraction conditions	Sample	Analytes	Instrumental technique	Recovery (%)	Limits of detection	Ref.
Natural sorbents								
		desorption with 5 mL MeOH for 6 min						
Materials prepared using sustainable approaches								
SiO_2@PVA/HA	SPE	120 mg sorbent, 10 mL sample, adsorption with PBS, desorption with 1 mL $NH_3·H_2O$:MeOH	Honey, eggs and milk	Antibiotics	LC-MS/MS	80–118	0.003–0.150 μg kg^{-1}	[55]
E. Coli@γFe_2O_3 (NPs)	MDμ-SPE	30 mg sorbent, adsorption at 38 °C for 25 min, desorption with 1 mL HCl 1 M for 5 min	Honey	Thymol	Spectrofluorometry	>93	9 ng mL^{-1}	[139]
Vitamin B_3-based MOF	DSPE	30 mg sorbent, 10 mL sample, adsorption for 3 min at 500 rpm, desorption with 200 μL MeOH for 3 min	Soy milk	Aflatoxins	LC-MS/MS	64–75	11.3–48.2 ng L^{-1}	[140]
Vitamin B_3-based MOF	DSPE	15 mg sorbent, 5 mL sample, adsorption for 2.5 min, desorption with 140 μL ChCl:EG DES for 2.5 min	Fruit juice	Patulin and OTA	LC-MS/MS	75 (Patulin) 87 (OTA),	24.8 ng L^{-1}	[141]
Succinimide diacid-MOF(Cu)	SPE	5 mg sorbent, 10 mL sample, adsorption with 2 % NaCl at pH 6.0 for 7 min at 4000 rpm	Pistachio	Aflatoxins	LC-FLD	95	–	[142]
Fe_3O_4-UiO-66-NH_2-[BMIM][Br]-CS (beads)	MSPE	40 mg sorbent, 20 mL sample, adsorption with ACN:H_2O (84/16, v/v) for 2 min, desorption with 1 mL 0.1 % HCl/ACN (1:9, v/v)	Cereals	Aflatoxins	LC-UV	77–119	0.08–0.56 μg kg^{-1}	[123]
MCS@DES-MIP (particles)	MSPE	100 mg sorbent, 1 mL sample, adsorption with MeOH/H_2O (1:1, *v/v)* at 25 °C for 30 min, desorption with 1 mL MeOH/AcOH (9:1, v/v) for 30 min	Black tea	Polyphenols	LC-UV	88–98	0.15–0.5 μg L^{-1}	[128]
HMICS with DES.	SPME	20 mg sorbent, 1 mL sample, adsorption with MeOH/water (80:20, v/v) for 4 h, desorption with 1.6 mL acetone/AcOH (85:15, v/v)	Red ginseng tea	Gallic acid	LC-UV	90–103	0.4 μg mL^{-1}	[83]
DES/Zn-MOF nanocomposite	MSPE	10 mg sorbent, 35 mL sample, adsorption at pH 6.0 for 2.5 min, desorption with 1 mL EtOH/0.5 M HNO_3 for 2 min	Fruit juice	Carmoisine dye	UV/VIS	92–100	2.4 μg L^{-1}	[144]
Fe_3O_4-CA-DES (beads)	μSPE	10 mg sorbent, 5 mL sample, adsorption with 1 % NaCl (w/v) for 10 min, desorption with 300 μL MeOH for 5 min	Milk	Melamine	LC-UV	77–105	0.5 μg L^{-1}	[72]
CA-DES (beads)	μSPE	20 mg sorbent, 5 mL sample, adsorption with 1 % NaCl (w/v) for 5 min, desorption with 150 μL EtOH for 1 min	Nonalcoholic malt beverages	Pesticides	GC-MS	68–116	0.003–0.069 μg L^{-1}	[72]

ACN: acetonitrile; **AcOH:** acètic acid; **AG:** agarose**; Apt:** aptamer; **AV:** aloe vera; **BDC:** terephthalic acid; **BMIM**: 1-butyl-trimethylimidazole bromide; **CA:** calcium alginate; **CMC:** carboxymethylcellulose**; CPME:** capsule phase microextraction; **CS:** chitosan; **CW20 M:** carbowax 20 M; **DES:** deep eutectic solvent; **DI:** direct infusion; **DSPE:** dispersive solid-phase extraction; **ESI:** electrospray; **EtOH:** ethanol; **FLD:** fluorescence detector; **FPSE**: fabric phase sorptive extraction; **GO**: graphene oxide; **HA:** humic acid; **HFCS:** high fructose corn syrup; **HFor:** formic acid; **HMICS:** hydrophilic molecularly imprinted chitosan; **IT-SPE**: in-tube solid phase extraction; **MCS:** magnetic chitosan; **MEPS**: microextraction by packed sorbent; **MGO**: magnetic graphene oxide; **MIP**: molecularly imprinted polymer; **MOF**: metal organic framework**; MS**: mass spectrometry; **MSPE**: magnetic solid-phase extraction; **NPs**: nanoparticles; **PAHs:** polycyclic aromatic hydrocarbons; **PBS:** phosphate buffered saline**; PEG**: poly(ethylene glycol); **PIL:** polymeric ionic liquid; **PPG**: poly(propylene glycol); **PPY**: polypyrrole; **PrOH:** propanol; **p(ST-Co-AC):** styrene acrylonitrile copolymer; **PT-SPE**: pipette tip solid phase extraction; **PVA**: poly(vinyl alcohol; **RSDE**: rotating-disk sorptive extraction; **SBSDME:** stir bar-sorptive dispersive microextraction**; SPME:** solid-phase microextraction; **TFME:** thin film microextraction; **US:** ultrasound-assisted.

and reusable SiGO@CS biosorbent (>15 reuses), reduced extract volumes (500 μL), and shorter preparation times. Compared with conventional microextraction protocols, these features demonstrate clear improvements in material efficiency and waste minimization. Overall, while the AGREE evaluation underscores areas requiring further greening, such as solvent substitution or step simplification, the method remains a competitive and environmentally favourable approach for routine monitoring of food contaminants.

Moreover, chitosan has been also modified with several polymers to synthesize MIPs [128], with MOFs [129,130], with polymeric ionic liquids [131] or with other molecules to be used as substrates to fabricate nanofibers for TFME [46,132]. Additionally, the functionalization of chitosan with high affinity ligands, such as aptamers (Apts), has been described in a very interesting study reported by Liu et al. [133]. In detail, chitosan nanofibers modified with an Apt were used to extract zearalenone from different food samples by DSPE, and Fig. 3 illustrates the preparation of nanofibers and the DSPE process. The Apt immobilization on the nanofibers surface was performed using the EDC/NHS coupling chemistry giving place to Apt-chitosan nanofibers that showed high stability and repeatability jointly with a large specific surface area. Also, the resulting Apt-chitosan sorbent demonstrated excellent specificity toward zearalenone, and under optimal extraction conditions a LOD of 18.0 ng L^{-1} and recoveries comprised between 101 and 108 % with RSD below 4.7 % were achieved. Also, the reusability of the sorbent was demonstrated after 5 times with no significant change in the extraction efficiency. Finally, the applicability of the method was successfully demonstrated by quantifying residual zearalenone at trace levels in different food samples (corn, wheat, and beer), highlighting its effectiveness for food safety monitoring.

3.2.1.5. Materials based on biowaste. As commented above, the use of biowaste residues as sorbents for sample preparation has attracted much interest in the scientific community due to their well-known properties. Rice husk, peanut shells, or seeds from different botanical species, among others have demonstrated to be potential sorbents of a wide range of compounds, including mycotoxins, endocrine disrupting pesticides (EDPs), herbicides, or fungicides. In some cases, the raw biowaste residues have been used as sorbents in SPE [49,134,135] or DSPE configurations [136], while other authors incorporated MNPs to the biowaste residues to perform MSPE [137,138]. For example, in an interesting study nectarine core-derived magnetite biochar was employed for PAHs extraction from tomato paste [137]. The innovative use of this agricultural by-product as sorbent highlights the dual benefits of sustainability and efficiency. The findings demonstrate excellent adsorption capacity and recovery rates (>88 %), reinforcing the potential of biochar-based sorbents in food applications. However, further investigation into long-term reusability and large-scale implementation would strengthen the practical impact of this research.

3.2.2. Materials prepared using sustainable approaches

Among this category, a bio-based organic-inorganic hybrid material has been carried out by simply integrating polyvinyl alcohol (PVA) and humic acid (HA) onto a silica substrate (SiO$_2$@PVA/HA) for cost-effective and sustainable monitoring of antibiotic residues in different foods [55]. The results demonstrate low LODs (<0.15 μg kg^{-1}), high recovery rates (above 80 %), good reproducibility (RSD<15 %), good stability, and eco-friendliness, aligning with green chemistry principles. This innovative approach not only addresses environmental concerns but also offers a practical solution for antibiotic residue detection in food.

In addition, magnetic bio-adsorbents, which enables the immobilization of organisms onto the surface of the materials, allow the extraction of a wide range of compounds. For example, *E.Coli* has been used as biosorbent biomass for the successful isolation of thymol from honey samples using magnetic dispersive micro-solid phase extraction (MDμ-SPE) [139]. The prepared sorbent was able to extract the analyte with recoveries above 93 % and with a LOD of 9 ng mL^{-1} in 30 min for the entire extraction process. This work reinforces the viability of biosorbents as sustainable alternatives, contributing to the development of eco-friendly and cost-effective extraction methods.

Another class of materials based on green MOFs synthesized using bio-linkers, such as vitamin B$_3$ and succinimide diacid, has been reported as effective biosorbents for DSPE of aflatoxins and mycotoxins from food matrices [140–142]. For instance, a vitamin B3-based MOF sorbent was successfully used to isolate patulin and ochratoxin A (OTA) from fruit juices prior to their analysis by LC-MS/MS [141]. The extraction recoveries were acceptable, reaching 75 % for patulin and 87 % for OTA, with LODs above 24.8 ng L^{-1}. These findings demonstrated the strong performance and potential of this type of biosorbent.

Finally, the use of DESs has been also explored in the synthesis of sustainable materials [72,83,128,143,144]. In a study developed by Karami et al. [72], a copolymerized DES encapsulated in calcium alginate (CA) hydrogel beads was successfully applied for the analysis of pesticides in non-alcoholic malt beverages. For this purpose, a polymeric

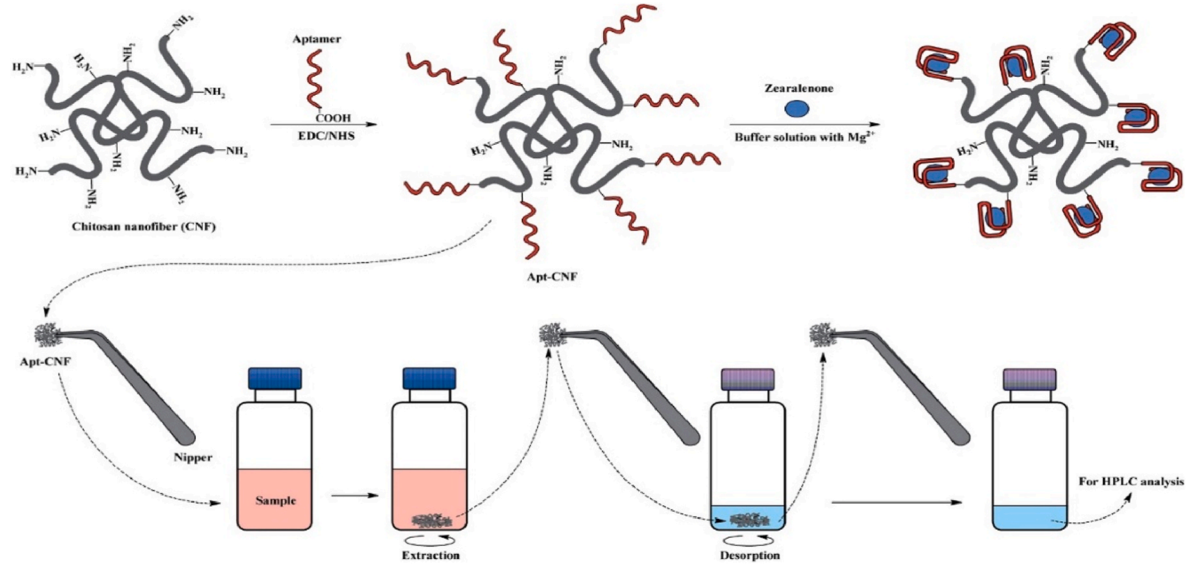

Fig. 3. Schematic illustration of the Apt-chitosan nanofibers preparation and process of the developed DSPE [133] with permission of RSC Publishing.

DES was synthetised by copolymerizing methacrylic acid (MAA) with thymol (Thy) using ethylene glycol dimethacrylate/EGDMA) as a crosslinker, resulting in [poly(MAA-co-EGDMA)]:[Thy] DES. The developed sorbent exhibited a 1.5–3.4-fold improvement in extraction efficiency compared to unmodified CA beads. The method, validated by GC-MS, achieved low LODs (0.003−0.069 μg L^{-1}), satisfactory recoveries (68−116 %) with RSD values below 10.2 %. Moreover, the sorbent maintained its performance for up to four reuse cycles without significant loss in extraction efficiency. The environmental sustainability of the procedure was evaluated using the Complex Green Analytical Procedure Index and Analytical Eco-Scale protocols, yielding a score of 72/100, confirming its suitability as a green analytical approach.

3.3. Biological samples

The analysis of biological samples using sustainable materials has been also explored, although the number of publications in this area remains lower compared to other type of matrices. Table 3 provides a summary of applications involving the use of sustainable materials in sorptive extraction methods for the analysis of biological samples.

3.3.1. Natural materials

3.3.1.1. Cellulose-based materials. Cellulose filter paper and cotton have been applied to the analysis of biological samples [145]. The use of unmodified cellulose filter paper as sorbent to extract pesticides in blood can be found in literature [146]. In this study, pieces of cellulose were employed in a simple in-tip paper device for the extraction of pesticides taking profit of the hydrogen bonding interactions between the pesticides and the hydroxyl groups on the cellulose surface. After several cycles of adsorption and desorption, the adsorbed pesticides were eluted and transferred to the GC-MS system. The developed method provided acceptable recoveries (above 60 %, with RSDs <10 %) and LODs between 0.003 and 0.010 μg mL^{-1}. The proposed method achieved an AGREE score of 0.68, indicating a high level of greenness compared to conventional techniques such as LLE or SPE. This favourable score is mainly attributed to the use of a minimal volume of solvent (only 0.5 mL of acetone), the avoidance of energy-intensive equipment, the employment of biodegradable cellulose paper as the sorbent, and the overall simplification of the sample preparation process.

On the other hand, cotton fibers have been functionalized with β-cyclodextrin (β-CD) for the D-μSPE of drugs of abuse in saliva [28]. The functionalized fibers were placed inside a syringe to perform the extraction, being the eluates directly injected into the MS system. The results confirmed that the hybrid nanocomposite was able to efficiently extract hydrophobic compounds due to the presence of βCD, obtaining good recoveries (ca. 115 %), jointly with low LODs (0.6–0.8 μg L^{-1}) and RSD values below 15.8 %.

3.3.1.2. Wood. In a study conducted by Millán-Santiago et al. [36], the effectiveness of a Nylon 6 wood tip as a sorbent for drugs from oral fluids was demonstrated. This device enabled the multiple analysis of some samples using direct infusion mass spectrometry (DI-MS), resulting in a high sample throughput. The method achieved a LOD of 1.5 μg L^{-1}, with recoveries exceeding 86 % and good reproducibility (RSD<9.1 %). These results highlight the potential of sustainable sorbents in analytical applications, offering a sustainable and efficient alternative for oral fluid sampling.

3.3.1.3. Natural fibers. Cellulose acetate fibers were incorporated to μ-SPE devices for the on-line preconcentration of NSAIDs from urine and plasma [147]. Specifically, the sorptive material was placed inside a μ-SPE cartridge located in the six-port valve of the LC system. The developed cartridge showed high efficiency, recoveries compressed between 85 % and 105 %, LODs of 1.0–2.4 μg L^{-1}, RSD values below 7.8 % and an outstanding reusability of 100 cycles without any loss in efficiency. In another interesting study [148], cellulose paper was coated with sol-gel phases to be used for the simultaneous FSPE and analysis of antidepressants in urine. After testing different sorptive phases, sol-gel graphene coating was the most efficient, providing high selectivity and recovery. The optimized protocol required only 15 min of extraction, achieving recoveries above 90 %, and demonstrating a good sensitivity (with a LOD of 0.15 ng/μL) and precision (RSD below 13.9 %). The results demonstrated that compared to traditional techniques, FPSE offers significant advantages, including faster sample preparation, lower solvent consumption, and improved sensitivity, making it a promising tool for drug monitoring in biological fluids.

3.3.1.4. Biopolymers. Fashi et al. [149] reported a green sorbent based on agarose gel modified with glucose-fructose syrup (AG/HFCS) for the determination of the biological marker malondialdehyde (MDA) in urine samples using rotating-disk sorptive extraction (RDSE) (see Fig. 4). The developed method allows the direct detection of the extracted analyte without desorption, using solid-phase spectrophotometry and smartphone-based RGB analysis. The AG/HFCS sorbent exhibited excellent hydrophilicity, high specific surface area, and stability, enhancing the extraction efficiency, with extraction recoveries above 88 % (with RSD values less than 3.5 %). The developed sample preparation method was assessed for its environmental impact using the analytical Eco-Scale tool. Thanks to its green attributes, such as avoiding toxic organic solvents, requiring low energy for instrumental analysis, and generating negligible waste, the method achieved an Eco-Scale score of 79/100, classifying it as an “excellent green analysis”. When compared with other reported microextraction techniques for MDA determination, the proposed procedure demonstrated superior sustainability, making it suitable for trace analysis in laboratories with minimal risk to human health and the environment.

3.3.1.5. Materials based on biowaste. Magnetic activated carbon (MAC) derived from coffee waste was used as sorbent for the isolation of parabens from urine, which were eluted using a DES of DL-menthol and acetic acid [150]. The MSPE-DES/HPLC-UV developed method demonstrated excellent sensitivity (LODs of 0.1–0.3 ng mL^{-1}), good precision (RSD<9.15 %) and achieved high recoveries (82.60–118.20 %) urine samples. These results confirm the method’s reliability and potential for real-world analytical applications.

3.3.2. Materials prepared using sustainable approaches

The use of other materials synthesized following green approaches, such as nanocrystalline cellulose [151] or MOFs [152], have been also investigated for the extraction of different compounds from biological samples. For example, covalent organic polymer (COP) functionalized NCC films were prepared for the TFME of imipramine, as a model compound, from urine and plasma samples [151]. In this case, the high amount of aromatic and polar functional groups (N–H and O–H) present in the developed nanocomposite framework allowed a satisfactory efficiency with recoveries above 78 %, good repeatability and reproducibility (RSDs <10 %) and an acceptable reusability (10 times).

Table 3
Application of sustainable materials for biological sample analysis.

Material	Extraction technique	Extraction conditions	Sample	Analytes	Instrumental technique	Recovery (%)	LoD	Reference
Natural materials								
Cellulose paper and cotton								
Cellulose	PT-SPE	Paper piece (1 × 3 cm), 5 mL sample, adsorption at pH 7.0 for 60 cycles, desorption with 0.5 mL acetone for 40 cycles	Blood	Pesticides	GC-MS	60–90	0.003–0.010 μg mL^{-1}	[146]
PIL-cellulose	TFME	Pieces (3 × 0.75 cm) 1.5 mL sample, adsorption with H_2O at pH 8.0 for 30 min, desorption with 250 μL MeOH	Urine	NSAIDs	LC-MS/MS	72–95	3.8–15.7 μg L^{-1}	[154]
Gelatin-cellulose	Filter paper	Paper piece (ID 3 cm), 20 mL sample, adsorption with H_2O for 2 h, desorption with 0.5 mL acetone for 15 min	Urine	Steroid hormones	LC-MS/MS	76–100	0.04–5 μg L^{-1}	[145]
Octanol-cellulose	RDSE	20 % NaCl, pH 11.0, 30 min, elution with MeOH, 10 min	Urine and blood	Drugs	GC-MS	50–98	0.017–0.029 μg mL^{-1}	[155]
βCD-cotton	Dμ-SPE	5 mg sorbent, 2 mL sample, adsorption with H_2O at pH 10.0 for 1 min, desorption with 500 μL ACN	Saliva	Cocaine and methamphetamine	DI-MS	111–115	0.6–0.8 μg L^{-1}	[28]
Wood								
Nylon 6-wood tip	SPME	1.5 mL sample, adsorption with H_2O at pH 10.0 for 45 min, desorption with 150 μL MeOH for 30 min	Saliva	Methadone, cocaine and methamphetamine	DI-MS	86–103	1.5 μg L^{-1}	[36]
Natural fibers								
Cellulose acetate	μ-SPE	6 mg sorbent, 10 mL sample, adsorption with H_2O at pH 3.0 for 20 min, desorption with CH_2Cl_2:acetone for 5 min	Urine and plasma	NSAIDs	LC-UV	85–105	1.0–2.4 μg L^{-1}	[147]
PVA-PAA-CNT-NCC	PT-SPE	5 mg sorbent, 1 mL sample, adsorption with H_2O at pH 8.0 for 3 cycles, desorption with 200 μL ACN/2-PrOH (1:1) for 2 cycles	Plasma	Opioid analgesics	LC-UV	87–98	0.15–0.50 ng mL^{-1}	[156]
Graphene-cellulose	FSPE	Fabric piece (2.5 cm × 2.0 cm), 0.5 mL sample, adsorption in MeOH for 15 min, desorption in 0.5 mL ACN/MeOH (1:1) for 15 min	Urine	Antidepressants	LC-UV	25–67	150 ng mL^{-1}	[148]
Biopolymers								
AG-HFCS	RDSE	5 mL sample, adsorption with 2 % NaCl at pH 2.5 for 5 min	Urine	Malondialdehyde	Solid-phase spectrophotometry	88–100	1.6 ng g^{-1}	[149]
Biowaste								
MAC	MSPE	10 mg sorbent, 3 mL sample, adsorption for 8 min, desorption with 200 μL of DES (DL-menthol and AcOH)	Urine	Parabens	LC-UV	83–114	0.1–0.3 ng mL-1	[150]
Materials prepared using sustainable approaches								
COPs-NCC	TFME	Pieces (10 × 5 mm), 10 mL sample, adsorption with H2O for 45 min, desorption with 500 μL MeOH for 50 min	Urine and plasma	Imipramine	GC-FID	78–93	0.5 ng mL-1	[151]
TiO_2-NCC	TFME	10 mL sample, adsorption with 16.7 % Na_2SO_4 at pH 3.5 for 30 min, desorption with 400 μL MeOH for 1 min	Urine	NSAIDs	LC-UV	73–85	0.2–0.5 μg L^{-1}	[157]
MIP-MCS	MSPE	4 mg sorbent, adsorption with H_2O at pH 9.0 for 30 °C, desorption with 0.5 mL EtOH: AcOH (8:2)	Urine and plasma	Carbamazepine	LC-UV	88–101	1.0–9.6 μg L^{-1}	[158]
CS@MOF-199	MEPS	7 mg sorbent, 2 mL sample, adsorption at 166 μL min^{-1}, desorption with 350 μL MeOH at 83 μL min^{-1}	Plasma, saliva, and urine	β-blocker drugs	LC-UV	77–112	1.5–4.5 μg L-1	[152]

ACN: acetonitrile; **AcOH:** acetic acid; **AG:** agarose**; βCD:** β-cyclodextrins; **CNT:** carbon nanotube; **COP**: covalent organic polymer; **DES:** deep eutectic solvent; **DI:** direct infusion; **Dμ-SPE:** dispersive micro-solid phase extraction**; EtOH:** ethanol; **FSPE:** fabric solid-phase extraction; **HFCS:** high fructose corn syrup; **MAC:** magnetic-activated carbon; **MCS:** magnetic chitosan; **MEPS:** microextraction by packed sorbent; **MIP**: molecularly imprinted polymer; **MS:** mass spectrometry**; MSPE**: magnetic solid-phase extraction; **NCC**: nanocrystalline cellulose; **NSAIDs:** non-steroidal anti-inflammatory drugs; **PAA**: poly(acrylic acid); **PIL**: polymeric ionic liquid**; PrOH:** propanol; **PT-SPE:** pipette tip solid-phase extraction; **PVA: poly(vinyl alcohol); RDSE**: rotating disk sorptive extraction; **SPME:** solid-phase microextraction; **TFME**: thin film microextraction.

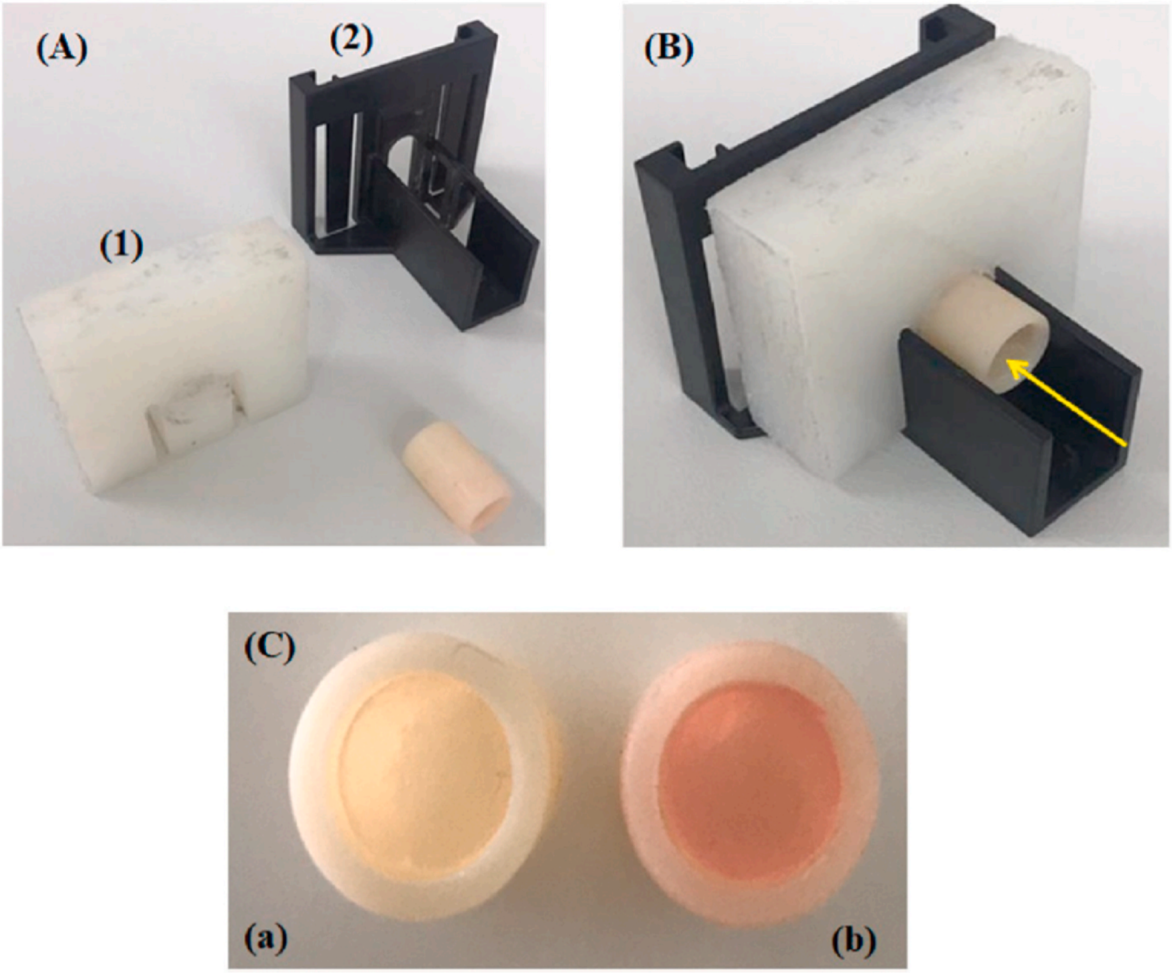

Fig. 4. Components of the designed spectrophotometric method for the analysis of MDA using agarose gel impregnated with high fructose corn syrup (AG/HFCS) as extraction phase in rotating-disk sorptive extraction (RDSE) (A), detection holder (B), and AG/HFCS disk without (left) and with MDA (right) [149] with permission of Elsevier.

4. Conclusions and future trends

The incorporation of sustainable materials into sample preparation has undoubtedly enhanced the sustainability of this step, thereby contributing to the overall greenness of the entire analytical process. In this context, different strategies and materials has been adopted over the last years offering a broad range of options for a variety of extraction techniques to be applied to sorted type of environmental, food, biological and other type of samples.

The performance and efficiency of these sustainable materials (whether derived from natural sources or synthesized through sustainable approaches) are comparable to those prepared using conventional methods. However, aspects such as preparation costs, reusability, and material robustness are seldom addressed in the literature. In addition, none of commercially available sorbents is sustainable or obtained using sustainable approaches. Thus, researchers working in this area still have significant progress to make in the development of sustainable materials that are even more appealing to both scientists and commercial stakeholders. Advancing in this direction is essential to ensure that such materials become widely available to the broader scientific community.

Research should also prioritize the integration of natural materials into miniaturized and portable analytical devices, such as paper-based microfluidics and lab-on-a-chip platforms, to enhance their applicability in on-site and rapid testing. Moreover, the development of automated and high-throughput extraction systems based on natural sorbents is expected to become a major direction, further improving their practicality, efficiency, and sustainability in analytical sciences.

CRediT authorship contribution statement

N. Fontanals: Writing – review & editing, Writing – original draft, Investigation, Conceptualization. **M. Vergara:** Writing – original draft, Investigation, Conceptualization. **S. Cárdenas:** Writing – original draft, Investigation, Funding acquisition, Conceptualization. **M. Llompart:** Writing – original draft, Investigation, Funding acquisition, Conceptualization. **T. Dagnac:** Writing – original draft, Investigation, Funding acquisition, Conceptualization. **R.M. Marcé:** Writing – review & editing, Writing – original draft, Investigation, Funding acquisition, Conceptualization.

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.

Acknowledgments

The authors acknowledge financial support from the Spanish State Research Agency (AEI//10.13039/501100011033/), the Spanish

Ministry of Science, Innovation and Universities (MICIU) and the European Union (NextGeneration EU/PRTR) through projects PID2021-125459OB-I00, PID2023-146313OB-I00, PID2023-148939NB-I00. This article is based upon work from the National Network for Sustainable Sample Preparation (RED2022-134079-T funded by MICIU/AEI/10.13039/501100011033). Also, MVB acknowledges the projects CIGE/2023/69 and CIAICO/2022/183 funded by Generalitat Valenciana. This article is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society.

Data availability

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

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