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Idaira Pacheco-Fernández[1,2], Diego W. Allgaier-Díaz[1], Giulia Mastellone[1,3], Cecilia Cagliero[3], David Díaz Díaz[4,5,6], Verónica Pino[1,2,*]

[1]*Departamento de Química, Unidad Departamental de Química Analítica, Universidad de La Laguna (ULL), Tenerife, 38206, Spain*
[2]*Instituto Universitario de Enfermedades Tropicales y Salud Pública de Canarias, Universidad de La Laguna (ULL), Tenerife, 38206, Spain*
[3]*Dipartamento di Scienza e Tecnologia del Farmaco, Università degli Studi di Torino, Torino, 10125, Italy*
[4]*Departamento de Química Orgánica, Universidad de La Laguna (ULL), Tenerife, 38206, Spain*
[4]*Instituto Universitario de Bio-Orgánica Antonio González, Universidad de La Laguna (ULL), Tenerife, 38206, Spain*
[6]*Institut für Organische Chemie, Universität Regensburg, Regensburg, 93053, Germany*

Abstract

Since the introduction of the Green Chemistry guidelines within analytical method development, there has been an increasing concern on the sustainability of analytical sample preparation approaches, particularly if considering they constitute the most time-consuming step of the analytical method and the main source of wastes in the laboratory. Among the alternatives explored to overcome this issue, it is important to highlight the miniaturization of the extraction methods, which has been closely accompanied by the seek of greener solvents and sorbents. Biopolymers emerge as potential candidates to be used as sorbents in microextraction schemes taking advantage of their biodegradability, synthetic versatility, adaptation ability and easily functionalization. This review offers an overview on the use of biopolymers in sorbent-based microextraction approaches, paying attention to the preparation of the sorbent and the format in which biopolymers are incorporated into the sorbent/device, their role in the resulting sorbent material, and the reported analytical applications.

Keywords: biopolymer, microextraction, chitosan, cellulose, alginate, agarose, solid-phase extraction

*Corresponding author: Tel. +34 922318990. Email: veropino@ull.edu.es

I. Pacheco-Fernández	ipacheco@ull.edu.es
D.W. Allgaier-Díaz	diego.walter.allgaier.diaz.05@ull.edu.es
G. Mastellone	giulia.mastellone@edu.unito.it
C. Cagliero	cecilia.cagliero@unito.it
D. Díaz Díaz	David.Diaz@chemie.uni-regensburg.de

1. Introduction

The incorporation of the Green Chemistry principles in the analytical process has emerged as one of the most important research lines within the analytical chemistry community, leading to the development of the green analytical chemistry (GAC) [1]. Current efforts clearly shift to improve the sustainability of the analytical sample preparation stage since it involves numerous tedious steps, it is highly time-consuming, and entails the generation of large amounts of wastes [2]. Among the strategies, the minimization, replacement, or elimination of harmful organic solvents in the analytical sample preparation procedure [3], together with a simplification of the methodologies by using automated and microextraction approaches without sacrificing the analytical performance of the method [4,5], are the most productive approaches followed to comply with the GAC guidelines.

1.1. Overview of sorbent-based microextraction methods

Microextraction methods, in which low amounts of both extraction material and sample are used, have been introduced to overcome the sustainability drawbacks of conventional analytical sample preparation techniques [6]. In particular, sorbent-based microextraction approaches have attracted much attention due to the minimization and even elimination of organic solvents in the entire procedure, together with the possibility of taking advantage of material science technologies to prepare smart and task-specific solid materials [7,8]. Figure 1 includes a general scheme of different sorbent-based microextraction strategies, including several representations of most common devices.

Solid-phase extraction (SPE) is a widely used conventional extraction technique, that involves the use of a sorbent material packed in a small column device. A relatively high volume of sample (0.5 – 2 L) is passed through the column to ensure trapping of the

analytes by the sorbent, followed by a washing step to remove the interferences that may have been retained in the stationary phase. Finally, the target compounds are eluted using a low amount of solvent [9]. SPE constitutes the basis for the development of miniaturized and microextraction methods requiring a solid sorbent material.

The miniaturized sorbent-based method most similar to conventional SPE is termed miniaturized SPE (μ-SPE), in which lower amounts of sorbent (<500 mg) and liquid sample (<20 mL) are required. Indeed, different configurations apart from cartridges and microcolumns have been proposed with the aim of reducing the amount of sorbent, such as disks, membranes and pipette tips [10], thus implying a simultaneous decrease of the amount of sample to be loaded.

Despite the benefits of μ-SPE, it requires the activation of the packed sorbent, which involves the consumption of organic solvents, relatively long extraction times due to the slow flow rates required, possible cartridge blocking…. In this sense, dispersive μ-SPE (μ-dSPE) arises as an alternative to overcome these problems [11]. In this case, few mg (1 – 500 mg) of the solid sorbent is strongly dispersed in the liquid sample, thus improving the partitioning of the analytes to the sorbent. Then, the sorbent containing trapped analytes is separated and subjected to desorption using an adequate solvent. This strategy has also been applied for the analysis of solid samples, leading to matrix solid-phase dispersion (MSPD) method [12]. In this case, both solid sorbent and solid sample are strongly mixed during the microextraction stage, and then packed into a column to perform the desorption step.

However, μ-dSPE and MSPD exhibit some weaknesses, mainly associated to tedious and time-consuming filtration and centrifugation steps. The use of magnetic sorbents in the extraction procedure easily success in dealing with these limitations [13]. In the magnetic-assisted μ-dSPE approach (m-μ-dSPE), the magnetic sorbent is separated

from the initial sample or desorption solvent with the aid of an external magnet, thus facilitating and accelerating the entire operational procedure.

In 1990, Pawliszyn *et al*. introduced solid-phase microextraction (SPME) as a new non-exhaustive sampling, preconcentration and extraction technique [14]. The original SPME device consisted of a small amount of the active coating material immobilized on the surface of a small fiber, forming a coating of 1 cm with thicknesses up to 100 μm. In this technique, the fiber is exposed to the sample (or to the headspace) to perform the extraction of the analytes for a prefixed time. Then, the analytes are desorbed from the sorbent either by thermal desorption (in the inlet of a gas chromatograph (GC)) or by using a solvent. SPME offers simplicity, reusability, complete absence of organic solvent in the method if using thermal desorption, automation, and impressive enrichment capacity [5]. However, different SPME designs have been proposed over the years to improve the analytical performance of the original on-fiber configuration [15] and are schematically shown in Figure 1.

The in-tube SPME mode uses a small capillary as extraction device. It was introduced to improve the coupling of the SPME technique with liquid-chromatography (LC) systems [16]. In the most classic system, the inner walls of a capillary are coated with a thin layer of the sorbent material. Packed and monolith capillaries have also been proposed in recent studies [16]. The operating steps in this case resembles that of μ-SPE, following a flow-through procedure. Stir bar sorptive extraction (SBSE) is a technique that can be understood as a solution to the small amount of sorbent used in the previous configurations, which reduces the extraction capacity [17]. In this design, a magnetic stir bar is coated with a thicker layer of the sorbent material. This device can be used in both solvent and thermal desorption (with a suitable thermo-desorption unit) depending on the stability of the coating and on the nature of the target analytes. Besides an enhancement

in the extraction capacity, the use of higher amounts of sorbent in SBSE is also accompanied by long extraction times to reach the equilibrium. Thin-film microextraction (TFME) or sorptive tape extraction (STE), in which the sorbent coats a flat surface or consists of a free membrane with a reduced thickness, was proposed to address this issue [18,19]. While high amounts of sorbent are used, the thin film configuration allows the preparation of an extraction device with a high surface area. In this approach, the membrane is freely dispersed all over the sample or immersed in the sample with the aid of a wire. A variation of the TFME, named fabric-phase sorptive extraction (FPSE), was recently developed and involves the use of a thin film fabric substrate coated with a sorbent prepared using the sol-gel technique [20].

1.2. Novel materials in sorbent-based microextraction methods

These advances in sorbent-based microextraction methods have come together with the design and incorporation of new materials able to provide more efficient extractions, while compiling with the requirements of GAC [7,21]. It is important to highlight that methods incorporating these materials must be able to maintain adequate quality analytical performance despite the decrease in the amounts of sorbent and sample. Conventional sorbents in this microextraction strategies are commonly based on polymers, such as polydimethylsiloxane or divinylbenzene, which usually lack of selectivity, exhibit poor extraction capacity towards more polar compounds, and also show poor matrix-compatibility and low thermal stability. In this sense, trends within this research field have been focused on the use of tunable and highly porous materials to prepare smart, advanced and efficient sorbents.

Among the great diversity of sorbents explored, carbonaceous materials, including carbon nanotubes (CNTs), graphene and graphene oxide (GO) have been particularly

interesting for the extraction of a wide variety of compounds [7,22]. Magnetic nanoparticles (MNPs) have been fundamental for the development of m-μ-dSPE methods [7,13], while molecularly imprinted polymers (MIPs), aptamers and immunosorbents have been useful for target analysis [22,23]. Sorbent-based microextraction methods have also taken advantage of the synthetic versatility, environmental-sustainability and tunable properties of ionic liquids (ILs) and their derivatives [24]; as well as the high surface area and porosity of metal-organic frameworks (MOFs) [25,26] and covalent organic frameworks (COFs) [27]. Despite the success of all these new materials, there are several concerns regarding their toxicity and/or the harmful effect of the reagents required in their synthetic routes [3,28,29]. Therefore, it is imperative to search for truly environmental-friendly alternatives to prepare sorbent-based microextraction sorbents [30].

1.3. Biopolymers

Biopolymers are polymers obtained from natural sources [31] and constitute a renewable and biodegradable resource of materials that may meet both the requirements of GAC and microextraction methods. Indeed, they have been already explored in this field, being chitosan, cellulose, alginate, and agarose, the most common. Figure 2 includes a summary on the use of these biopolymers in sorbent-based microextraction methods in the last years, together with the formats/devices in which they are found in these applications. It is important to highlight that, despite their versatility, they have been mainly used in combination with other functional materials as shown in Figure 2. In fact, there are a reduced number of studies that report the use of the neat biopolymer in the microextraction procedure.

This review aims to provide an overview on the state of the art of the incorporation of biopolymers in sorbent-based microextraction approaches, reviewing the analytical

applications reported in the last five years (2014-2019). Considering the diversity of forms in which these materials has been used, together with the broad variety of composites or hybrid sorbents that have been synthesized, the applications for each biopolymer will be discussed according to the microextraction method developed.

2. Biopolymers in sorbent-based microextraction schemes

2.1. Chitosan

2.1.1. Chitosan nature and uses

Chitin is a natural polysaccharide with *N*-acetyl-D-glucosamine as monomeric unit, that occurs in many living organisms. Chitosan is the deacetylated derivative of chitin, which is obtained under alkaline conditions when the degree of deacetylation is 50% or higher, leading to the formation of a copolymer with *N*-acetyl-D-glucosamine and D-glucosamine units, as shown in Figure 3 [32]. Despite the high abundance of chitin in the nature, its negligible solubility in aqueous media and organic solvents limits its applicability. However, chitosan presents an interesting set of characteristics which makes this pseudo-natural polymer very useful in numerous applications [32,33]. It is soluble in acidic media, leading to the formation of a natural cationic polymer due to the protonation of the amino group, while it is water-insoluble at high pH values. Besides its non-toxicity and biodegradability, this biopolymer can be easily crosslinked using different reagents and the reactivity of the amino group allows the easy functionalization of its chemical structure. Given the physicochemical features of chitosan, it can be processed as powder, dissolved in solution, while being able to form gels, beads, films or foams.

189 Chitosan has been successfully exploited in cosmetic, pharmaceutical and
190 biomedical applications [33]. Due to its biocompatibility, it has been particularly useful
191 for drug delivery. In this sense, it is not surprising that it has also been explored in
192 analytical methods with extraction purposes. Indeed, it is the most used biopolymer in
193 sorbent-based microextraction schemes in the recent years (Figure 2).
194
195 ***2.1.2. Chitosan in sorbent-based microextraction methods***
196 The use of chitosan will be discussed in terms of its incorporation in the different
197 microextraction methods. In each type, its use as neat material or mainly incorporated in
198 sorbents together with other materials will be detailed, while paying attention to the
199 format of the device.
200 Several forms of chitosan have been used to prepare a number of packed devices
201 for μ-SPE. Zhu *et al.* [34] proposed commercial chitosan fibers hydrothermally treated
202 with different contents of acetic acid and then packed in glass pipettes. It is also
203 interesting to mention the microchip reported by Gan *et al*. [35]. The extraction device
204 consisted of a disk-shaped filter paper modified with chitosan by impregnation in a
205 solution of the biopolymer, which was then placed on a thermoplastic microchip, but the
206 extraction procedure involved the typical μ-SPE steps: loading of the sample, washing
207 and desorption.
208 Among hybrid chitosan-based sorbents for μ-SPE (meaning by hybrid the
209 incorporations of other materials than the biopolymer), carbonaceous materials are the
210 most common materials used to prepare the composites, including multi-walled carbon
211 nanotubes (MWCNTs) and GO. In the simplest strategy, both powdered materials are
212 blended [36] or dispersed in an aqueous solution [37], and then packed to prepare the
213 microextraction device. In any case, it results more common the addition of the carbon

material to an acidic solution of chitosan, followed by insolubilization and formation of beads by the increase of the pH [38], or by the addition of a crosslinking agent (glutaraldehyde as the most common agent to promote it) to the mixture [39]. A similar approach has been described for the preparation of devices containing chitosan and other sorbent materials, such as a cartridge packed with chitosan-metal oxide nanoparticles [40] and the fabrication of a monolith sorbent based on chitosan, GO, C_{18} and polypyrrole [41]. In several of the reported studies, chitosan was found to play an important role in the extraction efficiency of the developed device [36,39], while in other cases it simply acted as dispersive matrix to confine the main extraction sorbent [38,41].

Recently, Asiabi *et al.* described a composite material consisting of chitosan nanofibers and MOFs, prepared by electrospinning of an acidic solution containing chitosan and the MOF powder [42,43]. This procedure led to the preparation of spiderweb-like formed by electrospun nanofibers, presenting an enhanced surface area compared to the individual components. Both composites, with MOF MIL-68(Al) [42] and MIL-101(Fe) [43], were packed into filter disks to perform μ-SPE. Chitosan powder has also been impregnated with an IL solution and then lyophilized to prepare a more efficient sorbent for the fabrication of a μ-SPE cartridge [44].

Regarding μ-dSPE, the use of chitosan has also been quite useful due to the possibility of preparing chitosan-based sorbents with different forms that favors its dispersion. Neat chitosan powder has been used as sorbent in acidic aqueous extracts, taking advantage of its cationic structure to enhance the extraction of negatively charged analytes [45]. Beads or microspheres of chitosan have been prepared by adding dropwise the acidic solution of chitosan to a NaOH solution using a syringe, followed by its further crosslinking [46] or combination with GO [47]. Then, they were confined in a polypropylene envelope to perform the μ-dSPE method. Such envelope facilitates the

239 further separation of the sorbent during the extraction and desorption steps. Chitosan
240 beads have also been prepared using more sophisticated methods, such as sol-gel
241 transition by conventional emulsion using epichlorohydrin as crosslinker [48] or ionic
242 gelation using sodium tripolyphosphate [49]. In these cases, the beads are directly
243 dispersed in the sample solution and separated by centrifugation or filtration.

244 The combination of chitosan with other materials has led to the development of
245 interesting hybrid sorbents for μ-dSPE. Chitosan has been grafted with polyaniline to
246 obtain a composite with a rough surface, thus ensuring the presence of more pores to
247 improve the retention of target analytes [50]. In other study, the surface of MWCNTs was
248 modified with chitosan by dispersing the carbon material in an acidic solution of the
249 biopolymer [51]. In both cases, the powder of the composite was dispersed in the aqueous
250 sample to accomplish the μ-dSPE process. Li *et al.* proposed the use of porous
251 MOF/chitosan foams in μ-dSPE, which were easily dispersed in the sample during
252 extraction by ultrasounds, and then separated from the aqueous sample using tweezers to
253 subsequently perform the elution step [52]. For the preparation of the foam, the MOF
254 powder was dispersed in an acid solution containing chitosan, glutaraldehyde as
255 crosslinking agent, and a gelatin, and afterwards the mixture was placed in a mold and
256 freeze-dried to ensure formation the foam.

257 The miniaturized versions of MSPD methods have also benefited from the
258 incorporation of chitosan as as dispersant [53,54]. In these strategies, the chitosan powder
259 and the solid sample are mixed using a pestle to accomplish the extraction of the
260 compounds.

261 With respect to the use of chitosan in m-μ-dSPE, a high number of studies has
262 been reported in the recent years compared with the remaining sorbent-based
263 microextraction methods. All these applications involve the use of ferrite MNPs to obtain

magnetic chitosan-based sorbents. The preparation of these magnetic sorbents can follow one of this main routes: i) the coprecipitation method, which consists of adding dropwise a NaOH solution to an acidic solution containing Fe(II) and Fe(III) salts, and dissolved chitosan [55–69], or ii) the addition of the previously synthesized MNPs to an acidic solution of chitosan, followed by the crosslinking of the biopolymer using glutaraldehyde [70–81]. Other synthetic approaches include the chemical reduction of Fe(III) in presence of chitosan [82], the dispersion of modified-MNPs in an acidic solution of chitosan [83–85], or the use of (3-glycidyloxypropyl) trimethoxysilane [86] or sodium tripolyphosphate [69] as crosslinking agents. The functionalization of the MNPs with silica by the sol-gel method prior to the incorporation of chitosan has also been reported to improve the stability of the resulting composite [72,83]. Among other strategies that have been reported to prepare chitosan-based magnetic sorbents, it is interesting to mention the fabrication of stir beads composed of chitosan and polypyrrole in absence of any magnetic material [87]. In this case, the composite was prepared by crosslinking the chitosan with glutaraldehyde in presence of polypyrrole, while using a template to obtain the spherical shape. Then, a steel wire was inserted in the beads to obtain the magnetic sorbent, as shown in Figure 4 (A). In the study of Xiao *et al.* [88], the powder of chitosan was dispersed in the aqueous sample followed by the addition of the previously prepared MNPs instead of preparing the magnetic composite. Both materials interacted due to electrostatic interactions, and the chitosan could be captured by the MNPs to perform the m-μ-dSPE method.

The use of the neat chitosan-coated MNPs, in which the chitosan is the only material responsible for the extraction of the target analyte, has been scarcely reported [63,65,70–72,74,83,88]. In several of these studies, the chitosan was functionalized with

specific groups, such as dithizone [74] and diphenyl diselenide [65] to enhance the extraction capability of the sorbent.

In most applications, magnetic chitosan sorbents were combined with other materials to prepare hybrid composites, such as GO [73,75,77–79,81,84,89] MIPs [58,61,67,68,76,78,79,86,90]; other polymers including polyaniline [57,64,66], polypyrrole [55,59,87], and polythiophene [60,62]; and even ILs [75], deep eutectic solvents [67,80], surfactants [69], and antibodies [82]. When dealing with magnetic GO/chitosan sorbents, the GO is added to the reaction solution during the crosslinking of chitosan in presence of the MNPs. In the studies that incorporated imprinted or conventional polymers in the hybrid composite, the chitosan-modified MNPs prepared by any of the abovementioned methods are added to the polymerization solution. In the case of liquid additives, the magnetic chitosan is simply immersed in the liquid to ensure impregnation of its surface. Therefore, in most of these sorbents, the chitosan acts as protective layer to improve the stability of the MNPs while avoid their aggregation, or as matrix to homogenously disperse other materials in the resulting hybrid composite, rather than participating actively as main extraction agent in the microextraction process. Furthermore, all these preparation methods yield a heterogeneous composite, usually a polymeric matrix in which the MNPs are embedded. Main issue associated with heterogeneous composites link to inter-batch reproducibility issues. However, some authors have reported the formation of core-shell type particles, in which the MNP is perfectly coated with a layer of chitosan-based material [68,69,75,90].

Regarding SPME devices, chitosan-based coatings have been explored mainly in the TFME/STE configuration. This can be linked to the relatively easy fabrication of thin membranes composed of this biopolymer. In all reported studies, other materials besides chitosan were incorporated in the thin film to improve its mechanical stability and

sorption capacity, including MWCNTs [91,92], Ag nanoparticles [93,94], agarose [92,95], C_{18} [95], and halloysite nanotubes [96]. The most common method to prepare these devices consisted of blending a chitosan solution and a dispersion of the additional material, placing the mixture in a thin template, and then drying the mixture in an oven to evaporate the solvent. In the case of the chitosan/MWCNTs membrane prepared by Ge *et al.* [91], the surface of MWCNTs was modified by crosslinking the chitosan using glutaraldehyde, followed by immersion of a thin polypropylene membrane in a dispersion of such composite containing chitosan/MWCNTs. In all these studies, the membranes were freely dispersed all over the sample, or hold using a cotter pin, during the extraction step. Afterwards, membranes containing trapped analytes are removed using tweezers to accomplish the desorption step, being the exception the method reported by Wan Ibrahim *et al.* [92,95]. In this particular case, 4–5 pieces of the prepared thin films were pierced using a syringe needle, and silicon septa were placed between each film to avoid them to detach, as it can be observed in Figure 4 (B). This modified needle was immersed in the aqueous solution to perform the microextraction procedure, resembling the direct immersion mode of SPME (DI-SPME) using conventional fibers.

Composites containing chitosan have also been used in other SPME geometries. A SPME fiber was prepared using fused silica as support and a ZnO nanorods/chitosan composite as stationary phase [97]. The nanorods were *in situ* synthesized in a chitosan gel, where the fused silica fiber was immersed to form the coating. Then, the biopolymer immobilized on the fiber was crosslinked with glutaraldehyde to improve the stability of the coating, and used in DI-SPME followed by desorption using an organic solvent. Wu *et al*. reported the preparation of an in-tube SPME device taking advantage of the properties of chitosan [98]. In this study, the inner walls of polytetrafluoroethlyene tube were coated with polydopamine, followed by functionalization of this polymer with

dialdehyde starch and chitosan by filling the tube with an ethanolic solution of both materials, followed by heating at high temperatures.

2.1.3. Analytical applications with chitosan-based materials in sorbent-based microextraction

Chitosan-based sorbents have been applied for the extraction of a wide variety of analytes from samples of quite different nature. Table 1 includes some representative applications of these sorbents in the different sorbent-based microextraction methods [37,42,46,50,60,63,68,80,91,96,99–110]. Given the diversity of reported applications, general trends will be discussed in the following section considering the nature of the analyte and the application area. As a general comment, applicable to all reported applications, it is important to highlight the following characteristics: low amount of solid sorbents required, between 1 [47] and 500 mg [45]; and relatively low volumes of samples, with average values of 10 mL. In addition to this, it should also be noted that, despite the greenness properties of the biopolymer used and the environmental-friendliness associated to microextraction strategies, the reported applications still require the utilization of organic solvents (low amounts) to accomplish the desorption of the target analytes, while in most applications the biopolymers are commonly used with additional materials that are not always green.

The vast majority of the developed methods have been used for the extraction of organic compounds, covering from drugs and antibiotics [36,37,43,44,55,58,59,68,78,85,90,92], pesticides [40,41,60,62,69,70], other persistent and emerging endocrine disruptor contaminants, to natural bioactive compounds [39,51,53,54,67,84,88], and pigments [45,49]. Among the endocrine disruptor contaminants, polycyclic aromatic hydrocarbons (PAHs) [76,95], polychlorinated and

363 polybrominated biphenyls (PCBs and PBBs) [47,56,91], phthalate acid esters (PAEs)
364 [50,64,87], parabens [38,52], phenols [57,97], and other food contaminants [78,86], can
365 be cited. All of the above-mentioned organic compounds have been determined in water
366 samples coming from different sources [38,40,46,47,52,56,58,60,62,69,76,91,92,96,97],
367 or in aqueous extracts of food [36,37,44,45,50,70,82,86], diluted drinks and beverages
368 [41,51,57,67,84,95], plants [39,49,53,54], and dilutes or pre-treated biological samples,
369 such as urine, serum and blood [43,55,59,68,78,85,88,90].

370 Most of the proposed extraction procedures have been coupled with LC for the
371 determination of the target organic compounds, and using different detection systems
372 depending on the nature of the analytes [36–41,43–45,49–54,57–59,67–
373 69,82,85,87,88,90,92,95–97]. The high number of couplings with LC is due to the
374 compatibility of the solvent used in the desorption step with the chromatographic systems,
375 with methanol and acetonitrile the most common. Nevertheless, several of the analytical
376 applications have been performed in GC [46,47,56,60,62,64,70,76,91,84]. In these cases,
377 evaporation and reconstitution of the organic solvents used in the desorption step are
378 additional steps required, in order to obtain a final extract in a GC-compatible solvent.

379 Apart from the high number of applications devoted to organics, several of the
380 proposed methods have also been applied to the determination of metals in water samples
381 or in aqueous extracts, mainly using m-μ-dSPE [61,63,65,72–74,77,79,89], but also in μ-
382 SPE involving a MOF/chitosan composite [42] or in TFME/STE with a chitosan
383 membrane containing Ag nanoparticles [93]. It is worth mentioning that in this latter
384 TFME/STE application, the thin film with the extracted metal ions was dissolved in nitric
385 acid solution and analyzed by inductively coupled plasma mass spectrometry (ICP-MS),
386 instead of carrying out a desorption step, thus avoiding reusing of the device. In the
387 remaining methods, the metal ions were desorbed from the chitosan sorbent using acidic

388 solutions. Furthermore, several of these methods were applied to the analysis of certified
389 reference materials, thus demonstrating the applicability of the proposed methods with
390 adequate results in comparison with conventional approaches [72,74,93]

391 It is important to highlight the ability of chitosan-based sorbents to extract DNA
392 with high purity from complex matrixes, such as blood and saliva, using m-μ-dSPE
393 methods [66,80,83], as well as using the μ-SPE microchip prepared with a filter paper
394 modified with chitosan [35]. These methods were combined with UV spectroscopy
395 [80,83] or the polymerase chain reaction [35,76] for the quantification of the DNA. Other
396 interesting applications include the use of mesoporous crosslinked chitosan microspheres
397 in μ-dSPE followed by LC and tandem mass spectrometry (MS/MS) for the isolation of
398 *N*-glycopeptides from biological matrixes [48], while a reusable magnetic composite
399 composed of MNPs, chitosan and GO impregnated with an IL has been evaluated for the
400 extraction of different proteins [75]. Regarding other bioclinical applications, the
401 polydopamine in-tube SPME device modified with chitosan was successfully used in the
402 determination of aldehydes and ketones liver cancer biomarkers in human blood, using
403 LC and diode array detection (DAD) [98].

404 It is also interesting to mention that chitosan-based materials have been used not
405 only as extraction sorbent but for the removal of interferences in clean-up steps based on
406 μ-dSPE [111,112] and m-μ-dSPE [71,81] when analyzing food samples. It is worth
407 mentioning some specific applications, able to deal with complex samples, and
408 comprising challenging analytical problems in different industrial areas. In this sense,
409 magnetic chitosan-based sorbents have been used for the determination of PAEs in
410 samples such as diapers [64] and saliva in contact with baby teether [87], with the aim of
411 assessing the migration of these contaminants from the plastic products or containers.
412 Another complex application reported a μ-SPE device packed with neat chitosan fibers

for the extraction of petroleum acids from crude oils before their determination by two-dimensional gas chromatography (GC×GC) and mass spectrometry (MS) with satisfactory results [34]. In another study, authors used chitosan-coated MNPs functionalized with a specific antibody to develop a selective method for the determination of aflatoxins in foodstuffs [82].

2.2. Cellulose

2.2.1. Cellulose nature and uses

Cellulose is the most abundant biopolymer on earth [113], being a fundamental component not only in plants but also in a large number of living species. As shown in Figure 3, it is a linear polymer where 2 D-glucose units are linked by β-1-4 glycosidic bonds. Its structure contains many hydroxyl groups, resulting in a hydrophilic surface with numerous possibilities of chemical modifications. Besides its huge abundance, cellulose presents different interesting properties, including low cost, biodegradability, large surface area, and inertness. All these features have made this biopolymer very useful as drug carrier, flocculant or support in many different applications, such as in cosmetic, pharmaceutical and food areas [114].

2.2.2. Cellulose in sorbent-based microextraction methods

Recently, cellulose has received much attention in the extraction research field due to its high adsorptive capacity and biodegradability, and their use in this area has been recently reviewed [30,115]. Apart from the cellulose polymer, several of its derivatives have been particularly useful in this area. Cellulose acetate is the most studied cellulose derivative, in which the hydroxyl groups are replaced with acetate groups, leading to the preparation

438 of a versatile material that can be used as membrane, powder, fiber or hydrogel.
439 Nanocellulose is the term used to refer to nanometer-scale cellulose fibril, which exhibits
440 larger surface area and a higher number of hydroxyl groups. Microcrystalline cellulose,
441 prepared by the acid hydrolysis of cellulose, serves as an excellent support thanks to its
442 low density, insolubility in water and good mechanical properties [116].

443 Regarding μ-SPE devices, different forms of cellulose have been explored. Ruiz-
444 Palomero *et al*. functionalized nanocellulose with amino groups, which were used to
445 covalently bond β-cyclodextrins to the surface of the biopolymer [99]. This modification
446 of the nanocellulose provided nanocavities with selective recognition ability towards
447 danofloxacin antibiotic, and the sorbent could even be reused at least 40 times. In another
448 study, $CoFe_2O_4$ nanoparticles prepared by the co-precipitation method were coated with
449 commercial cotton cellulose [117]. In both cases, few mg of the sorbent were packed in
450 microcolumns and then used in an offline automated μ-SPE strategy. Aqda *et al*. proposed
451 a cellulose-based sorbent packed in a small cartridge for the development of an online μ-
452 SPE approach by replacing the loop of a LC valve by the μ-SPE device [118]. In this
453 case, cellulose triacetate fibers were synthesized by electrospinning, exhibiting different
454 morphology and porosity depending on the solvent used for their preparation. The fibers
455 prepared with acetone and dichloromethane showed higher surface area and led to better
456 extraction performance.

457 In μ-dSPE applications, microcrystalline cellulose has been used to prepare highly
458 efficient sorbents. In all cases, the sorbent has been used in combination with surfactants
459 to enhance the retention of the analytes. In the study reported by Cao *et al*. [119], a
460 micellar-IL extraction was carried out to extract the target compounds from propolis, and
461 then microcrystalline cellulose was added to trap and isolate the IL with the analytes.
462 Finally, the resulting mixture was filtered using a nylon filter and the analytes were

463 desorbed with an organic solvent. In a similar approach, sulfonated nanocellulose was
464 used to trap the surfactant previously added to the sample for the extraction of Ag
465 nanoparticles [120]. This sorbent was prepared by treating microcrystalline cellulose with
466 sulfuric acid. This functionalization provided a negatively charged surface that easily
467 interacts with the cationic surfactant. In the study reported by López-García *et al*.,
468 commercial microcrystalline cellulose was directly dispersed in the sample for the
469 selective determination of Cr [100]. Then, the surfactant Triton X-100 was added to the
470 sample to perform a cloud point extraction, thus facilitating the collection of the solid
471 phase. The use of low amounts (few mg) of neat microcrystalline cellulose has been
472 reported in the miniaturized version of MSPD to develop a greener and faster strategy
473 compared to conventional methods, for the extraction of natural compounds from plant
474 materials [121].

475 With regards to the preparation of magnetic sorbents for m-μ-dSPE, MNPs of
476 different nature have been combined with cellulose derivatives. $NiMn_2O_4$ MNPs were
477 synthesized by a hydrothermal method in presence of cellulose fibers obtained from
478 cotton wool. Finally, the sorbent is carbonized to obtain cellulose-based carbon fibers
479 [101]. Following this strategy, $NiMn_2O_4$ grown on the surface of the fibers, leading to the
480 preparation of a magnetic sorbent with a high surface area. Similarly, Abujaber *et al*.
481 fabricated magnetic cellulose nanoparticles by a solvothermal method using
482 microcrystalline cellulose swelled in solutions of Fe and Co salts [122]. These spheres
483 were then coated with a hydrophobic IL, which was the main responsible material of the
484 extraction of the target analytes. Ferrite MNPs have also been used in combination with
485 cellulose to prepare a magnetic sorbent [123]. In this case, carboxymethyl cellulose was
486 added to the reaction solution just after the synthesis of the MNPs by the co-precipitation
487 method. These cellulose MNPs were then coated with a molecularly imprinted polymer

488 to obtain a highly specific sorbent for the extraction of a plant hormone, with the cellulose
489 coating acting as protective layer of the MNP. In these applications, desorption,
490 evaporation and reconstitution steps were required for the determination of the analytes.

491 Certainly, cellulose have been more popular in TFME/STE, and particularly in
492 FSPE applications, for which the number of studies reported have increased in the recent
493 years (Figure 2). Different strategies have been followed to use cellulose to prepare thin
494 membranes for TFME/STE. Furthermore, in a number of applications, several films were
495 added to the sample to increase the amount of sorbent (without sacrifying the thickness
496 of the film) and improve the extraction efficiency [18,124,125]. Meng *et al*. employed
497 neat cellulose filter papers (3 films) for the easy and low-cost extraction of a biomarker,
498 taking advantage of their large surface area and the formation of hydrogen bonds with the
499 analyte [124]. As it has been pointed out in the application of cellulose in other sorbent-
500 phase microextraction methods, this biopolymer is very versatile and could be used in
501 combination with different types of materials to obtain efficient hybrids materials. In this
502 sense, cellulose filter papers have been easily modified with polydopamine by performing
503 the polymerization in the presence of the filter paper [102], and with ZrO_2 by depositing
504 Zr gel films on the surface using a layer-by-layer sol-gel methodology [126]. An
505 anticodeine aptamer has also been immobilized on aldehyde-modified cellulose filter
506 papers to obtain thin films [127]. In these studies, the main role of the cellulose was to
507 act as a support of the main extraction material. In a similar way, cellulose has been used
508 as polymeric matrix of the thin film to disperse the solid sorbent: MWCNTs together with
509 graphene [128] and C_{18} [125]. For the preparation of these films, briefly, the solid
510 materials were dispersed in a solution of cellulose acetate and placed on a flat surface,
511 and then the solvent was evaporated for the solidification of the polymeric membrane.

These tapes took advantage of the mechanical robustness of cellulose and the extraction capability of the solid materials.

Cellulose undoubtedly finds many applications in FPSE (Figure 2), a variant of TFME/STE, in which a sol-gel derived sorbent is dispersed in an ultra-thin film fabric substrate, as shown in Figure 5 (A) [20]. This new technique, developed by Kabir and Furton [129], benefits from the porosity, flexibility and permeability of the fabric support, together with the extraction capability of sorbent prepared by the sol-gel technique. This way, it is possible to perform simple, green, low cost, and fast analyses. FPSE is also a versatile technique since the choice of the fabric surface and the sorbent material directly influences the selectivity of the device. In this sense, polyester is used for the preparation of non-polar fabric phases, while cellulose substrate covers a wide range of polarity. It is important to highlight that in these applications the cellulose acts as support for the polymeric coating, thus it is not responsible of the extraction capability of the extraction device. Regarding the coating, polymers of different nature have been proposed, such as polydimethylsiloxane or C_{18} to fabricate non-polar media, and graphene or polyethylene glycol (PEG) to prepare more polar sorbents [20]. For the fabrication of the FSPE devices, the pretreated fabric substrate is immersed in a previously prepared sol solution and then dried to remove the solvent and to perform the condensation reaction that bonds the coating to the substrate. Among the possible coatings using fabric cellulose as substrate that can be prepared, PEG-based sorbents have been the most successful in FPSE applications for the extraction of highly polar compounds [103,130–133]. Carbowax 20 has also recently been used for the determination of polar compounds [104,134], while polytetrahydrofuran has been reported as a sorbent of medium polarity [135]. In most cases, these films can be reused at least 30 times, thus improving the greenness of the methodology [104,130,132,133]. In general, in the FPSE procedure, a single fabric film

537 is dispersed in the sample with the aid of a magnetic stir bar. However, different
538 approaches have been proposed to improve the extraction efficiency of the method.
539 Roldán-Pijuán *et al*. together with the original inventors, reported a stir FPSE unit in
540 which a magnetic stirring mechanism is integrated in the device using plastic cartridges
541 and an iron wire, resembling a stir-cake sorptive extraction device [131]. More recently,
542 a different configuration for FPSE was proposed by Pérez-Mayán *et al*. and the original
543 authors [134]. In this case, three discs of the coated fabric substrate (4 mm in diameter)
544 were vertically immersed in the sample using a stainless steel pin, in a way similar to DI-
545 SPME.

546 SBSE has also benefited from the incorporation of cellulose to prepare reusable
547 extraction devices. Abujaber *et al*. used in a SBSE application [136] the same type of
548 cellulose MNPs material that was prepared for a previous m-μ-dSPE study [122]. In this
549 case, instead of employing a direct dispersion of the magnetic material in the sample
550 solution, the cellulose containing MNPs material was used to coat a stir bar, which could
551 be reused for 5 consecutive extractions. During the stirring step, the MNPs were dispersed
552 in the sample. Once the stirring was stopped, the MNPs rapidly returned to the stir bar,
553 which facilitated their collection for the desorption step. In a totally different approach, a
554 sol-gel coated cellulose fiber (using different polymers) was introduced in a
555 polypropylene membrane [137]. This capsule was joined to another polypropylene
556 membrane containing a magnet, as shown in Figure 5 (B). This microextraction capsule
557 device was stirred in the sample thanks to the magnetic component, under the typical
558 extraction procedure for SBSE applications. The use of this sorbent allowed the direct
559 and fast analysis of complex matrixes due to the polypropylene protective membrane and
560 the autonomous-stirring features of the device, which could be reused up to 10 times.
561

2.2.3. Analytical applications with cellulose-based materials in sorbent-based microextraction

As shown in Table 1, cellulose-based sorbents are very versatile and have been employed in different analytical applications, without following a general trend depending on the microextraction approach. As a common feature for all these applications, low amounts (few mg) of the sorbent or a small piece of cellulose material were employed, together with low amounts of initial sample, thus improving the preconcentration of the method. As for chitosan-based sorbent-based extraction methods, the use of cellulose-based sorbents in microextraction required the desorption of the analytes (and cleaning before reusability) using an organic solvent or a buffer solution. Given the low thermal stability of this biopolymer, thermal desorption could not be used in these applications.

Most methods using cellulose-based sorbents were intended for the determination of organic compounds, including pharmaceuticals and antibiotics [99,102,103,118,122,127,130,132,137], pesticides [104,131,133,134], plasticizers [101,125,136], and hormones [135]. The extraction of natural or bioactive compounds from plant-derived materials has also been reported in several studies [117,119,121,123]; being also useful in bioclinical analysis for the extraction of nucleosides [126] and biomarkers [124]. The determination of metal species using cellulose-based sorbents has been barely described [100,120] while this biopolymer has been found.

The methods have been mainly applied for the analysis of environmental waters [100,101,122,125,128,131,133,135], body fluids, including urine and blood plasma [118,124,126,127,130], and beverages [99,103,132–134,136,137]. In the case of the analysis of solid samples, such as food and plants, the application of the sorbent-based microextraction method usually required a previous extraction step of the sample using an organic solvent, which may reduce the sustainability of the process [119,120,123].

However, it is interesting to mention the suitability of FPSE for the extraction of target analytes from complex matrixes without requiring an exhaustive pretreatment of the sample, such as milk [103,132], juices [133], vegetables [104], and wine [134].

In the majority of the cases due to composition of the solvent used in the desorption step, the desorption solvent after applying the microextraction method is injected in a LC system coupled with UV-Visible, MS or fluorescence detection depending on the nature of the analytes [99,101–103,117–119,121–125,127,128,130–132,134,135,137]. Only a few studies reported the use of GC in combination with different detectors for the determination of the target compounds [104,133,136]. Others determination instruments have been used considering the nature of the extracted analytes, such as electrothermal AAS for Cr determination [100], capillary electrophoresis for Ag nanoparticles [120], fluorimetric determination of danofloxacin [99], or direct nanoelectrospray ionization-tandem mass spectrometry for nucleosides detection [126].

2.3. Alginate

2.3.1. Alginate nature and uses

Alginate is a biopolymer extracted from the cell walls of a large number of algae species, normally as sodium salt. This anionic polymer consists of linked residues of D-mannuronic acid (M-block) and L-guluronic acid (G-block), as it can be observed in Figure 3. The physical properties of alginate depend on the distribution of M- and G-block units along the chain, which is strongly related to the natural source from which it is obtained. One of the most attractive features of alginate is its ability to form viscous and biocompatible hydrogels when it is crosslinked with different agents, with divalent

612 cations the most common [138]. However, these ionically crosslinked materials suffer
613 from certain stability issues in complex media, while hydrogels with a wide range of
614 mechanical properties are obtained using covalent crosslinkers. Furthermore, grafting
615 alginate hydrogels with other polymers or the functionalization of its structure with
616 specific groups lead to the formation of stimuli-responsive materials, including pH and
617 thermo-sensitive hydrogels [139]. Given all these characteristics, hydrogels prepared
618 from alginate have been particularly useful in biomedical applications [138].
619
620 ***2.3.2. Alginate in sorbent-based microextraction methods including analytical features***
621 ***and their applications***
622 More recently, several studies have reported the incorporation of this biopolymer in
623 sorbent-based microextraction methods (Figure 2) [140]. All reported applications of
624 alginate in microextraction strategies used $CaCl_2$ as crosslinker agent to prepare the
625 alginate hydrogel. Furthermore, the alginate always serves as a matrix to disperse an
626 additional solid material and to increase the surface area, this way improving the
627 interaction of the target compounds with the sorbent. Table 1 includes representative
628 examples. The preparation of the sorbent containing alginate is different depending on
629 the sorbent-based approach, and also depending on the additional materials included in
630 the sorbent.
631 Wang *et al*. [105] prepared an alginate monolithic sorbent containing layered
632 double hydroxides nanosheets to develop a μ-SPE device for the selective extraction and
633 determination of Pb (II) in beverages using flame atomic absorption (FAAS). In this case,
634 the nanosheets were hydrothermally prepared and dispersed in an aqueous solution of
635 alginate. This mixture was added to a $CaCl_2$ solution placed in an empty cartridge to
636 prepare the monolithic column.

637 The incorporation of alginate in μ-dSPE methods has been accomplished in
638 different ways, as a function of the format in which the biopolymer was used. Thus, beads
639 or spherical particles of alginate containing GO [141] or MWCNTs [106] have been
640 prepared and directly used for the extraction of non-steroidal anti-inflammatory drugs and
641 PAHs, respectively. The fabrication of the sorbent consists on mixing a dispersion of the
642 carbonaceous material with a sodium alginate solution, followed by the dropwise addition
643 of the previous mixture to a $CaCl_2$ solution. The obtained beads are then cured in the
644 metal solution, and washed with water to remove the excess of reagents. Depending on
645 the characteristics of the needle and the distance needle-solution used during the dropwise
646 addition step, beads of different sizes were obtained. In the microextraction procedure,
647 around 100 mg of the beads were dispersed in the sample to retain the analytes.
648 Afterwards, analytes are desorbed from the beads using an adequate organic solvent and
649 determined by LC [141] or GC [106].
650 Zare *et al*. reported the use of alginate fibers containing Zr nanoparticles in a μ-
651 dSPE approach for the extraction of pesticides from water and juice samples [142]. The
652 preparation of the sorbent resembles that of the alginate-based beads with slight
653 modifications. In this case, the dispersion of Zr nanoparticles in the sodium alginate
654 solution was rapidly injected into the $CaCl_2$ solution to obtain a tangled fiber as shown in
655 Figure 6 (A). 100 mg of swelled fiber were added to the sample and dispersed with the
656 aid of a magnetic stir bar. The sorbent was then easily separated from the sample using
657 tweezers, and the desorption of the analytes was carried out by immersing the fiber in a
658 small volume of organic solvent. The configuration of this sorbent provided enhanced
659 surface area, which led to high recoveries of the analytes in real samples in a short time
660 compared with other methods reported in the literature.

Most applications of alginate in m-μ-dSPE methods have been reported by Bunkoed *et al*. [107,143,144]. For the preparation of the magnetic sorbents, MNPs were firstly prepared by the coprecipitation method, and then dispersed in a sodium alginate solution. Afterwards, the mixture is dropwise added to the metal stock solution to obtain the magnetic beads. In the first study, MWCNTs were also included in the initial dispersion to prepare a composite with improved extraction ability towards PAHs [107]. In the following applications, the Fe_3O_4/alginate beads were coated with a layer of polypyrrole [143] or polyaniline [144], by dispersing the magnetic beads in the monomer solution before the polymerization reaction. In all cases, low amounts (few mg) of the magnetic sorbent were dispersed in the water samples to isolate the PAHs [107,144] or endocrine-disrupting compounds [143]. Desorption of trapped analytes by the magnetic material is normally accomplished with acetonitrile, followed by evaporation and reconstitution prior to the LC-fluorescence detection analysis. It is interesting to mention that, besides the advantages of the paramagnetic features of the sorbent, these beads could be reused from 6 [144] to 16 times [143], after proper washing with acetonitrile.

Recently, Tan *et al*. reported the use of a magnetic composite that included alginate beads and an amino-functionalized MOF MIL-101(Cr) [145]. Both the MNPs and the MOF were synthesized by the solvothermal method, dispersed in a sodium alginate solution, and added dropwise to a $CaCl_2$ solution to obtain the composite beads with a diameter around 2.5 mm, as shown in Figure 6 (B). Authors demonstrated that the MOF was the main responsible in the extraction of polar herbicides from water samples, showing better performance compared to other conventional sorbents. This sorbent could be also reused in 10 consecutive extractions without any loss in its extraction capability.

Alginate hydrogels have also been used for the preparation of a SPME fiber that could be reused for at least 5 consecutive extractions in DI-SPME mode, followed by

desorption in methanol [146]. The preparation of the fiber consisted of immersing a polypropylene hollow fiber in an aqueous solution containing sodium alginate and zein, a corn protein. After heating for a few hours, a stainless-steel wire was inserted in the lumen of the hollow fiber as fiber support, and the device was then immersed in a $CaCl_2$ solution to accomplish the crosslinking of the alginate on the hollow fiber pores. The proposed device exhibited better results for the extraction of polar organic compounds, with the alginate hydrogel being the main component, thus playing an important role in the extraction capacity of the sorption phase rather than acting as a mere support.

2.4. Agarose

2.4.1. Agarose nature and uses

Agarose is a natural biopolymer extracted from seaweed. As shown in Figure 3, this polysaccharide presents alternating D-galactose and 3,6-anhydro-L-galactose units in its structure, with a hydroxyl groups-rich surface, which leads to its characteristic inertness. For this reason, agarose usually requires functionalization in order to improve its reactivity. It also presents stability in a wide range of pH and temperature, hydrophily, flexibility and mechanical strength [147].

One of the most interesting properties of agarose is its gelling capacity, that facilitates the fabrication of agarose films. Agarose gels are suitable for diffusion and electrokinetic migration of compounds and can be easily modified to tune their physicochemical properties. Moreover, it is possible to incorporate other components in its structure during the gelation process, leading to the preparation of interesting hybrid materials [148]. Due to this set of features, agarose (mainly in its gel form) has been widely used in many research fields, such as biomedicine, food industry, immunology

711 and separation science, including electrophoresis techniques and extraction methods
712 [140,149].
713
714 ***2.4.2. Agarose in sorbent-based microextraction methods including analytical features***
715 ***and their applications***
716 Regarding the use of this biopolymer in extraction techniques, agarose particularly finds
717 numerous applications in electromembrane extraction (EME), acting as a support of the
718 extraction solvent or as an interface between the donor and acceptor phases [150]. These
719 applications will not be covered in the present review since EME is classified as a liquid-
720 phase extraction technique, considering the liquid nature of the extracting phase. With
721 regards to sorbent-based microextraction methods, agarose has been scarcely used in the
722 recent years compared with the previously discussed biopolymers (Figure 2). In the
723 reported applications, the main role of agarose gels is to act as support or as dispersion
724 media of other solid materials to increase the surface area of the resulting sorbent, as
725 shown in Table 1.
726 Sanagi *et al*. have reported the use of agarose to prepare sorbents for μ-dSPE
727 applications [108,151]. In one of the proposed methods, the biopolymer was grafted with
728 poly(methyl methacrylate) following a microwave-assisted free radical copolymerization
729 approach, in which agarose was mixed with the starting reagents required for the
730 preparation of the polymer [151]. The resulting material was ground, and 80 mg were
731 used in the μ-dSPE method for the extraction of Cd, Ni, Cu and Zn present in waters and
732 digested vegetables samples, followed by determination using ICP-MS. In a different
733 strategy, authors incorporated MWCNTs into the agarose gel [108]. In this case,
734 MWCNTs and agarose were mixed in different proportions under stirring, and then
735 allowed to form the gel. The resulting material was cut in cubic pieces of 3 × 3 × 3 mm

736 as shown in Figure 7 (A), to obtain a sorbent that could be easily dispersed and
737 manipulated during the μ-dSPE procedure. The presence of MWCNTs increased the
738 number of interaction sites, and therefore the amount added in the gel was significant for
739 the efficient extraction of herbicides from waters. In the desorption step, tetrahydrofuran
740 was used as desorption solvent and then injected in the GC-MS system for the
741 determination of the analytes.

742 In m-μ-dSPE applications, agarose is combined with ferrite-based MNPs to
743 synthesize the magnetic sorbent [109,152,153]. In the method reported by Poursheikhi *et*
744 *al*., the MNPs were prepared by the coprecipitation method in presence of agarose to
745 obtain the agarose gel matrix containing MNPs [109]. In the remaining methods, the
746 dispersion of the MNPs in the agarose gel was accomplished by a water-oil emulsion
747 technique using Span-80 [153] or Span-85 [152] as the oil phase, and the aqueous agarose
748 solution as the water phase. This procedure was carried out either simultaneously during
749 the synthesis of the MNPs by the coprecipitation method [152], or by adding the prepared
750 core-shell MNPs@SiO_2 particles to the water-oil mixture [153]. In all cases, the sorbent
751 particles were subjected to an epoxy activation step, followed by their functionalization
752 with the aim of improving the selectivity for the target compounds. The reported surface
753 modifications included phenylephrine for the extraction of Mo from beans [109], a Schiff
754 base ligand for the formation of complexes and extraction of UO_2(II) from waters [152],
755 and an aptamer to selectively extract aflatoxins from maize samples [153]. Trapped
756 analytes are desorbed from the magnetic materials using organic solvents, and
757 subsequently determined by spectrophotometric techniques [109,152] or LC-
758 fluorescence detection [153], depending on the nature of the analytes. It is interesting to
759 mention the magnetic field agitation device reported by Hashemi *et al*. [109,152], which

760 could be programmed to change the magnetic field around the sample cell in order to
761 control the dispersion of the magnetic sorbent through the sample.
762 TFME/STE methods have also taken advantage of the gelation ability of agarose to
763 form thin films. Molecularly imprinted silica gel [110] and C_{18} [154] have been dispersed
764 in warm agarose aqueous solutions and placed on a flat surface, followed by the
765 evaporation of the sorbent to allow solidification of the gel, thus forming the films. Figure
766 7 (B) shows the surface morphology of the agarose and molecularly imprinted silica gel-
767 agarose thin films, which were used for the selective extraction of sulphonamides in
768 waters due to the imprinting properties of the membranes [110]. In the case of the agarose
769 films containing C_{18}, the incorporation of the additional solid material to the agarose
770 matrix led to the enhanced extraction of PAHs from coffee beverages [154]. The use of
771 agarose as polymeric matrix is important since it ensures the preparation of an
772 environmentally friendly film with a high mechanical stability. In both applications, the
773 films were directly introduced in the sample to perform the extraction with the aid of a
774 magnetic stir bar [110] or ultrasounds [154]. For the desorption step prior to the injection
775 in the LC system, the films were immersed in a low volume of desorption solvent.
776
777 **3. Concluding remarks**
778 The current sorbent-based microextraction approaches that have been designed with
779 the aim of enhancing the operational characteristics, environmentally friendliness and
780 extraction performance of the analytical procedure have also taken advantage of the
781 biodegradability and biocompatibility of biopolymers. Chitosan, cellulose, alginate and
782 agarose are the most explored options among the existing biopolymers, with an increasing
783 number of studies reported in the last 5 years. Their success mainly lies in the versatility
784 of their physicochemical properties, and their flexibility of design and adaptation, which

allow their use un numerous formats and configurations suitable for the different microextraction approaches, such as spherical particles, membranes, fibers, gels, and foams.

However, there is a still a need for a better understanding of the inherent physicochemical properties of these biomaterials to provide reliable and founded guidelines that allow the adequate selection of the most suitable biopolymer according to specific requirements. In general, the incorporation of these biopolymers in microextraction is based on their use as polymeric matrix with other solid materials (CNTs, GO, MNPs, MIPs, MOFs, etc.), with the purpose of improving the overall extraction capacity of the sorbent. Therefore, their main role in these applications is to serve as support or protection for other materials that are responsible of the extraction of the target compounds. In this sense, biopolymers seem to find a promising application in TFME/STE as flexible membranes, and clearly the use of cellulose as fabric substrate in FPSE is quite successful nowadays. In the same way, chitosan is the most adequate option in m-μ-dSPE in combination with MNPs due to its crosslinking ability, that allows the preparation of stable magnetic sorbents.

In comparison with other methods reported in the literature, the use of these biopolymers to obtain extraction materials with enhanced surface area provides faster sample preparation strategies. In addition, the protection role of biopolymers in most of the extraction devices allows the analysis of complex matrices with satisfactory relative recovery values.

Considering the scope of the present review, future advances may be mainly focused on exploiting the gelling properties of these materials to prepare new microextraction devices with increasing surface area. The chemical functionalization of their surface still requires to be addressed to avoid the use of additional solid materials

that may reduce the greenness of the sorbent. In this sense, it would be interesting the incorporation of thorough studies trying to elucidate the possible interactions between the analytes and the biopolymers to understand the mechanism behind the extraction process, which undoubtedly will help in the design of more useful biomaterials.

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List of abbreviations

µ-dSPE	Dispersive miniaturized dolid-phase extraction
µ-SPE	Miniaturized solid-phase extraction
AAS	Atomic absorption spectroscopy
BPs	Bisphenols
CNTs	Carbon nanotubes
COFs	Covalent organic frameworks
DES	Deep eutectic solvent
DAD	Diode-array detection
DI-SPME	Direct immersion solid phase microextraction
EME	Electromembrane extraction
FAAS	Flame atomic absorption spectroscopy
FD	Fluorescence detection
FID	Flame ionization detection
FPSE	Fabric-phase sorptive extraction
GAC	Green analytical chemistry
GC	Gas chromatography
GFAAS	Graphite furnace atomic absorption spectroscopy
GO	graphene oxide
ICP	Inductively coupled plasma
IL	Ionic liquid
LC	Liquid-chromatography
m-µ-dSPE	Magnetic-assisted dispersive miniaturized solid-phase extraction
MIPs	Molecularly imprinted polymers
MNPs	Magnetic nanoparticles
MOFs	Metal-organic frameworks
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
MSPD	Matrix solid-phase dispersion
MWCNTs	Multi-walled carbon nanotubes
OES	Optical emission spectrometry
PAEs	Phthalate acid esters
PAHs	Polycyclic aromatic hydrocarbons
PBBs	Polybrominated biphenyls
PCBs	Polychlorinated biphenyls
PEG	Polyethylene glycol
SBSE	Stir bar sorptive extraction
SPE	Solid-phase extraction
SPME	Solid-phase microextraction
STE	Sorptive tape extraction
TFME	Thin-film microextraction

Figure Captions

Figure 1 Summary of different solid-based microextraction methods: μ-SPE for miniaturized solid-phase extraction, μ-dSPE for miniaturized dispersive solid-phase extraction, FPSE for fabric-phase sorptive extraction, m-μ-dSPE for magnetic-assisted dispersive solid-phase extraction, MSPD for matrix solid-phase dispersion, SBSE for stir bar sorptive extraction, SPME for solid-phase microextraction, STE for sorptive tape extraction, and TFME for thin-film microextraction

Figure 2 Summary of the number of publications that use biopolymers (chitosan, agarose, alginate and cellulose) in different sorbent-based microextraction methods in the period 2014-2019, together with the main formats/devices of the sorbents, and main materials used in combination with biopolymers in the sorbents.

Figure 3 Structures of the biopolymers most frequently used in solid-based microextraction methods.

Figure 4 Examples of novel microextraction devices based on chitosan: A) Polypyrrole-chitosan cryogel beads for m-μ-dSPE, adapted from [87], with permission from Elsevier, 2017; and B) Agarose-chitosan-MWCNTs films for TFME/STE, adapted from [92], with permission from Wiley, 2018.

Figure 5 Examples of novel microextraction devices based on cellulose: A) Scanning electron microscopy images of a FPSE device using PEG-coated cellulose fabrics, adapted from [103], with permission from Elsevier, 2015; and B) Encapsulated sol-gel coated cellulose fibers for SBSE, adapted from [137], with permission from Wiley, 2019.

Figure 6 Examples of novel microextraction devices based on alginate: A) alginate fibers containing Zr nanoparticles for μ-dSPE, adapted from [142], with permission from Elsevier, 2016; and B) magnetic Fe_3O_4/alginate/MIL-101(Cr) beads for m-μ-dSPE, adapted from [145], with permission from Springer Nature, 2019.

Figure 7 Examples of novel microextraction devices based on agarose: A) MWCNTs-agarose cubes for μ-dSPE, adapted from [108], with permission from Royal Society of Chemistry, 2015; and B) neat agarose and molecularly imprinted silica gel-agarose membranes for TFME/STE, adapted from [110], with permission from Elsevier, 2019.

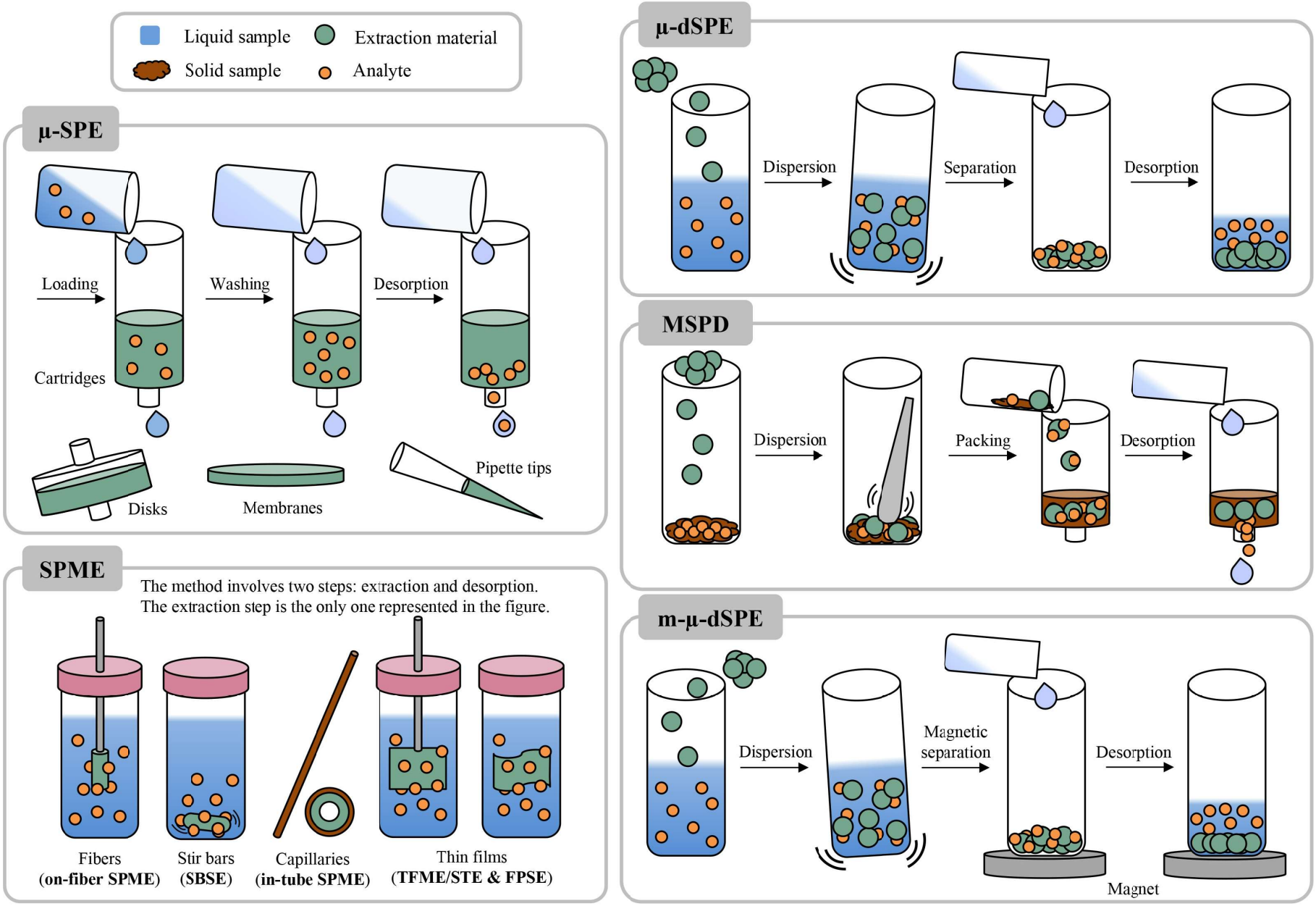
Table 1. Main characteristics of representative analytical applications of biopolymers in sorbent-based microextraction methods.

Method*	Additional material in the composite*	Configuration	Amount of sorbent	Analytes* (number)	Sample	Analytical technique*	LOD	Ref.
Chitosan-based sorbents								
µ-SPE	GO	packed pipette tip	4 mg	sulfonamides (5)	eggs & honey	LC-UV	0.7 – 1 $ng \cdot g^{-1}$	[37]
µ-SPE	MIL-68(Al)	packed filter disk	6 mg	metals (2)	molluks	ICP-OES	0.16 $\mu g \cdot L^{-1}$	[42]
µ-dSPE	–	beads enclosed in an envelope	20 mg	btex (5)	waters	GC-MS	10 – 40 $ng \cdot L^{-1}$	[46]
µ-dSPE	polyaniline	composite powder	20 mg	PAEs (3)	milk	LC-UV	0.4 – 0.5 $\mu g \cdot L^{-1}$	[50]
m-µ-dSPE	Fe_3O_4 MNPs	magnetic composite gel	25 mg	Cd	plants	FAAS	0.2 $\mu g \cdot L^{-1}$	[63]
m-µ-dSPE	Fe_3O_4 MNPs, MWCNTs & DES	magnetic composite powder	8 mg	DNA	blood	UV-Vis	–	[80]
m-µ-dSPE	MNPs & MIP	magnetic composite powder	25 mg	drug (1)	serum & urine	LC-DAD	1 – 9.6 $\mu g \cdot L^{-1}$	[68]
m-µ-dSPE	Fe_3O_4 MNP & polythiophene	magnetic composite powder	40 mg	herbicides (3)	waters	GC-MS	25 – 40 $ng \cdot L^{-1}$	[60]
TFME/STE	MWCNTs	film (1 cm × 0.4 cm × –)	1 film	PBBs & PCBs	waters	GC-MS	0.12 – 0.6 $ng \cdot L^{-1}$	[91]
TFME/STE	halloysite nanotubes	film (1 cm × 2 cm × ~15 µm)	1 film	hormones (1)	waters	LC-FD	0.4 $\mu g \cdot L^{-1}$	[96]
Cellulose-based sorbents								

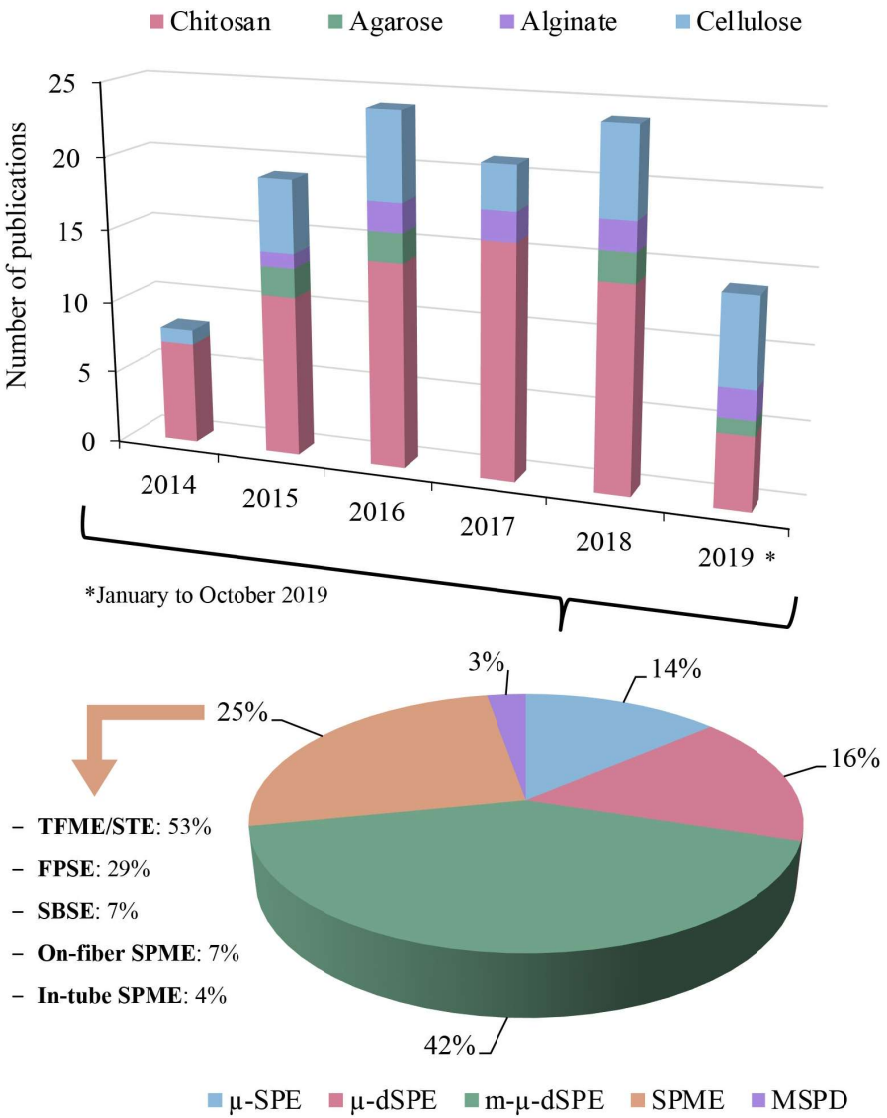
µ-SPE	β-cyclodextrin	packed microcolumn	20 mg	danofloxacin	milk	FD	2.5 $\mu g \cdot L^{-1}$	[99]
µ-dSPE	Triton X-100	microcrystalline cellulose powder	5 mg	Cr	waters	AAS	6 $\mu g \cdot L^{-1}$	[100]
m-µ-dSPE	$NiMn_2O_4$ MNPs	magnetic composite powder	30 mg	BPs (6)	waters & plastic food container	LC-UV	0.56 – 0.83 $\mu g \cdot L^{-1}$	[101]
TFME/STE	polydopamine	film (1 cm × 2 cm × –)	1 film	phenols (2)	vegetable oils	LC-UV	1.54 – 2.16 $ng \cdot L^{-1}$	[102]
FPSE	PEG	film (2.5 cm × 2 cm × –)	1 film	amphenicols (3)	milk	LC-UV	55.9 – 58.9 $\mu g \cdot g^{-1}$	[103]
FPSE	Carbowax 20 M	film (– cm × – cm × –)	1 film	pesticides (4)	vegetables	GC-MS	0.033-0.136 $ng \cdot g^{-1}$	[104]
Alginate-based sorbents								
µ-SPE	metal hydroxides	monolithic cartridge	–	Pb (II)	beverages	FAAS	0.39 $\mu g \cdot L^{-1}$	[105]
µ-dSPE	MWCNTs	beads	100 mg	PAHs (3)	waters	GC-FID	0.22 – 0.42 $\mu g \cdot L^{-1}$	[106]
m-µ-dSPE	MNPs & polypyrrole	magnetic beads	300 mg	endocrine-disrupting compounds (3)	waters	LC-FD	0.5 $\mu g \cdot L^{-1}$	[107]
Agarose-based sorbents								
µ-dSPE	MWCNTs	composite gel cubes (3 cm × 3 cm × 3 cm	–	herbicides (2)	water	GC-MS	0.319– 0.340 $\mu g \cdot L^{-1}$	[108]

m-µ-dSPE	Fe_3O_4 MNPs	magnetic composite suspension	200 µL (20%, w/v)	Mo	beans	GFAAS	49 ng·L^{-1}	[109]
TFME/STE	molecularly imprinted silica gel	film (1 cm × 1 cm × 1 mm)	1 film	sulfonamides (3)	waters	LC-UV	0.60-0.17 µg·L^{-1}	[110]

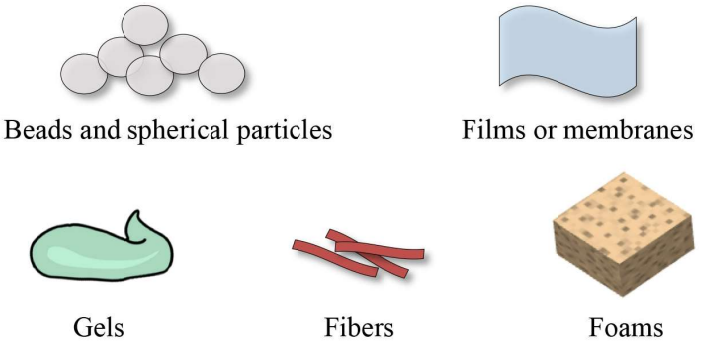
* for the definition of the abbreviations, refer to the list of abbreviations.


Liquid sample
Extraction material
Solid sample
Analyte
µ-SPE
Loading
Washing
Desorption
Cartridges
Disks
Membranes
Pipette tips
µ-dSPE
Dispersion
Separation
Desorption
MSPD
Dispersion
Packing
Desorption
m-µ-dSPE
Dispersion
Magnetic separation
Desorption
Magnet
SPME
The method involves two steps: extraction and desorption.
The extraction step is the only one represented in the figure.
Fibers (on-fiber SPME)
Stir bars (SBSE)
Capillaries (in-tube SPME)
Thin films (TFME/STE & FPSE)

Biopolymers in microextraction strategies



Formats/Devices for biopolymers in microextraction



Materials used with biopolymers in microextraction