Trends in Analytical Chemistry 162 (2023) 117048

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

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

Electromembrane extraction based on biodegradable materials: Biopolymers as sustainable alternatives to plastics

Cristina Román-Hidalgo [a, b, *], Luisa Barreiros [a], Mercedes Villar-Navarro [b], Germán López-Pérez [c], María Jesús Martín-Valero [b], Marcela A. Segundo [a, **]

[a] LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-213, Porto, Portugal
[b] Department of Analytical Chemistry, Faculty of Chemistry, Universidad de Sevilla, C/Prof. García González, s/n, 41012, Seville, Spain
[c] Department of Physical Chemistry, Faculty of Chemistry, Universidad de Sevilla, C/Prof. García González, s/n, 41012, Seville, Spain

ARTICLE INFO

Article history:
Received 13 February 2023
Received in revised form
20 March 2023
Accepted 29 March 2023
Available online 30 March 2023

ABSTRACT

Green and environmentally friendly approaches are increasingly necessary when developing new analytical methodologies. Electromembrane extraction (EME) has contributed to this by offering new alternatives to the traditional and widely used plastic materials. Specially, those derived from biopolymers (such as agarose or chitosan) have recently gained a great importance in EME as they are biodegradable and sustainable, which constitutes a major advantage in the environmental impact of these processes. This review is intended to cover the recent advances made on EME procedures based on the use of sustainable biopolymer-based materials by addressing the properties and synthesis of these materials as well as their analytical application. Extraction devices and EME methods will be extensively discussed, highlighting their strengths and weaknesses, aiming at improving analytical methodologies for sample processing, while contributing to their sustainability.

1. Introduction

The development of green and environmentally friendly analytical approaches is almost mandatory when implementing a new methodology. In this respect, the pre-treatment stage required in the analysis of complex samples (such as biological or environmental) is frequently a great challenge. Thus, in addition to making the sample suitable for subsequent determination by means of analytical instrumentation (clean-up and preconcentration mainly), it also aims to comply with the principles of so-called Green Chemistry. Therefore, sample preparation techniques have focused on miniaturization and automation in order to reduce the amount of sample and potentially hazardous reagents, as well as to accelerate the measurement process and increase sensitivity and selectivity, respectively.

In 2006, Pedersen-Bjergaard and Rasmussen introduced electromembrane extraction (EME) as a LPME modality to reduce extraction times by applying a potential difference across the liquid membrane generated by two electrodes immersed in both donor and acceptor solutions [1]. Briefly, under the action of the electric field, the ionized analytes migrate firstly towards an organic phase impregnating a porous support (supported liquid membrane, SLM) and then towards the oppositely charged electrode located in the acceptor phase (AP), where they finally remain. Due to the presence of the electric field, mass transfer is faster in EME compared to LPME. In addition, high selectivity can be achieved and controlled by the direction and magnitude of the applied voltage. Thus, negatively charged acidic analytes are extracted from the sample solution by immersing the positive electrode in the AP, while the polarity of the electrodes is reversed for the extraction of basic compounds [2].

Due to its numerous advantages, EME is one of the most widely used sample preparation techniques, with diverse applications in the analysis of biological, environmental and food samples, as demonstrated by more than 600 published papers in this research field. Various groups of analytes (acidic and basic compounds, polar and non-polar, ions or drugs, among others) have been determined in a multitude of formats and extraction devices (such as hollow fibers, flat membranes, microfluidic devices, or free liquid

* Corresponding author. LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, 4050-213, Porto, Portugal.
** Corresponding author.
E-mail addresses: croman2@us.es (C. Román-Hidalgo), msegundo@ff.up.pt (M.A. Segundo).

https://doi.org/10.1016/j.trac.2023.117048

membranes) by using different types of supporting materials. In this respect, polypropylene (PP) has been the material of choice in most EME procedures, both as a hollow fiber and as a flat sheet membrane. Polyvinylidene difluoride (PVDF) or polyacrylonitrile (PAN) have also been used, although to a lesser extent [3].

However, these materials have some limitations, such as low conductivity, which limits the number of possible organic solvents as a liquid membrane. Furthermore, they usually act exclusively from a physical point of view, i.e., only as a porous support for the organic solvent, therefore, their participation in the extraction process is purely passive. Moreover, all of them are plastic and single-use, having a potential environmental impact after disposal. Consequently, numerous efforts have been made to develop alternative materials to overcome these drawbacks. In this regard, latest trends and advances have been mainly focused on the modification of the liquid membrane or commercial supports. In the first case, the chemical composition of the SLM has been modified by incorporating some additives, such as carrier agents, nanoparticles (NPs), and molecularly imprinted polymers (MIPs). Moreover, the use of ionic liquids (ILs) as solvents in EME instead of the classical organic solvents have been also reported [4–6]. Similarly, some approaches have focused on modifying, both physically and chemically, the nature of commercial supports with the addition of functional materials [7]. On the other hand, EME procedures based on the use of fabricated membranes have been also reported, such as polymer inclusion membranes (PIMs) [8] or nanostructured tissues (Tiss®-OH) [9].

Currently, the development of more eco-friendly EME procedures based on the use of alternative materials is increasing. Specially, those derived from biopolymers (such as agarose or chitosan) have recently experienced a great importance in EME as they are biodegradable and sustainable materials. This fact constitutes a major advantage in the environmental impact of these processes, both in terms of the type and quantity of waste generated. Moreover, as the materials are obtained from natural sources, the costs are reduced, which is always desirable from an economic point of view. In addition, most of these materials can be synthesized according to analytical requirements, which results in a high selectivity of the proposed procedures. Although new materials in sample preparation techniques have been widely reported, most reviews are focused mainly on SPE, SPME or LPME procedures [10–12], with only a few references to the use of biopolymers in EME [7,13–15]. This review is intended to cover the recent advances made on EME procedures involving the use of biopolymers, mainly agarose-based materials (both films and gels formats) and chitosan-based membranes, although additional types will be introduced, by addressing aspects such as biopolymer properties, membrane preparation strategies, EME device formats and procedures, target analytes, and matrix of application.

2. Natural materials: biopolymers

Biopolymers can be defined as polymers obtained from living matter with carbon, nitrogen, and oxygen atoms in their structure, thus most of them can be considered as biologically degradable [16]. Natural biopolymers have gained a great importance in recent years due to their abundance and availability from natural sources with minimal environmental impact and low cost. According to the monomer unit of their structure, natural biopolymers can be mainly classified into polysaccharides, polynucleotides and polypeptides or proteins. Their natural sources are wide and diverse and include plants, animals, and microorganisms, such as bacteria and fungi [17].

Besides their biodegradability, non-toxicity, and renewability, they present a number of highly advantageous and versatile properties, such as high thermal, chemical and structural stability, controllable porosity, high chemical diversity, ability to produce molecular recognition and biocompatibility. Furthermore, due to their chemical diversity with numerous available reactive sites, they offer the possibility of being structurally modified by functionalization, which makes them eligible for a multitude of environmental, biomedical, pharmaceutical, food, textile, agricultural, or cosmetics applications [18,19]. The following sections present the biopolymer-based materials used to date in EME analytical procedures in decreasing order of importance or reported applications. They comprise mostly polysaccharide-derived biopolymers, whose main characteristics are summarised in Table 1. As can be seen, these biopolymers are characterised by the presence of hydroxyl and amino groups in their structure, which makes them potentially functionalizable and, consequently, highly reactive and versatile.

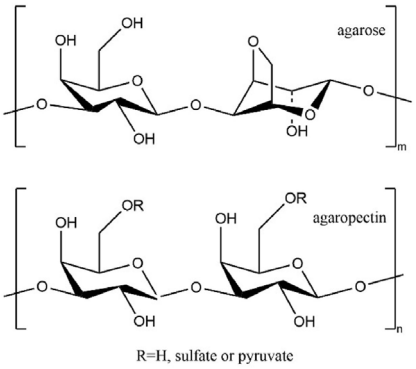
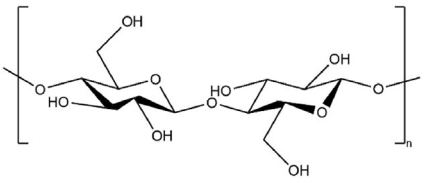
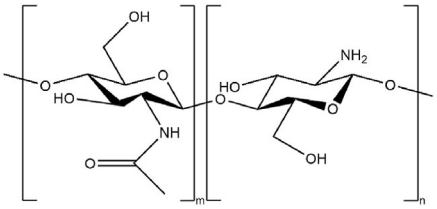
3. Agar or agarose-based materials in EME

Agar is a neutral polysaccharide of marine origin obtained from the cell wall of several species of red algae. Chemically, it is a heterogeneous mixture of two polysaccharides: agarose (gelling fraction) and agaropectin (non-gelling fraction). Due to its gelling capacity, agarose is more interesting than agaropectin in many applications, thus agaropectin is usually removed at the processing stage of agar [20]. Most of its applications are related to its behaviour in aqueous solution, as it is soluble in water (above 85-90 °C), but forms gels (cooled to 30-40 °C) in variable shapes (membranes, fibres, or beads), allowing the preparation of films of different thickness. It is also stable in a wide range of pH and organic solvents. Furthermore, the presence of polar groups in its chemical structure provides it with a certain functionality, which can be chemically modified to enhance both reactivity and applicability. All these characteristics make agar a polysaccharide with numerous advantages widely used in diverse fields, such as in microbiology, food industry, gel electrophoresis, or drug delivery, as well as serving as a membrane in EME. EME procedures based on the application of agar and agarose as biomaterial are summarised in Table 2.

The first use of agar as material in EME was reported in 2015 [21]. In this work, agar films containing silver nanoparticles were developed dissolving a certain amount of agar powder in ultrapure water under boiling and continuous stirring, followed by in-situ generation of AgNPs by reduction of $AgNO_3$ with PVP. The composition of the membrane was controlled by the addition of different amounts of the silver salt, while membrane with variable thicknesses were obtained by modifying the volume of solution poured into a Petri dish. Both the presence and nature of AgNPs were found to be decisive in the extraction process since films without AgNPs conducted to much lower efficiency. This was attributed to a stabilization of the electric field by the AgNPs, decreasing the electrical current generated and, consequently, increasing the extraction efficiency. Moreover, films containing smaller and spherical NPs (Fig. 1a) provided the best results in terms of enrichment factor (EF). Compared to PP membranes, this material demonstrated up to 10- and 70-times higher extraction efficiency, as well as reusability, thus it could be considered as a good alternative support.

Later, Hanapi et al. introduced agarose films similarly prepared by replacing NPs with the addition of IL to enhance their mechanical properties and thermal stability [22]. The incorporation of IL improved the diffusion of analytes through the membrane due to the formation of pores in its chemical structure (Fig. 1b). This structure was stabilized by hydrogen bonds between the negative charges of the hydroxyl groups of the agarose and the positive

Table 1
Characteristics of the main polysaccharide-derived biopolymers.

Biopolymer	Type	Main natural source	Monomeric unit
Agar	Neutral	Red algae	
Cellulose	Neutral	Green plants, algae, bacteria	
Chitosan	Cationic	Crustacean skeletons	

charges of the IL, which are much stronger than the agarose-water interactions. For this IL-AF-μ-EME procedure, a two-phase configuration provided with 3 platinum electrodes was employed, two of them were used for applying the potential difference and a third one for electric current monitoring (Fig. 2a). Therefore, the greenness of the proposed method is also achieved by replacing the usual organic solvents with ILs.

In addition to the films, the use of agarose in EME is mainly represented by gel membranes (G-EME), which were introduced for the first time in 2017 by Tabani et al. [23]. These agarose gels are prepared, essentially, by dissolving the agarose in deionized water, heating in a microwave oven and then, allowing the solution to solidify by cooling in an Eppendorf tube (Fig. 2b). With this approach, agarose gel membranes allowed the extraction to be carried out in the absence of organic solvent, which is a great advantage for the development of green processes. However, parameters such as gel composition and thickness must be carefully controlled as they have a considerable influence on the EME procedure. In fact, low agarose concentrations lead to higher pore size, which translates into so-called electroosmotic flow (EOF), causing gel destruction. In contrast, high concentrations make the gel difficult to handle. Similarly, EOF raises by decreasing the gel thickness, whereas thicker membranes lead to lower EME yields and longer extraction times are required.

Since their introduction, agarose gel membranes with different composition and thickness have been widely used in EME procedures. Thus, by changing the chemical and physical properties of the gel, numerous applications can be achieved, which is an advantage of these tailor-made materials over those supplied commercially. Thereby, by acidifying the solution of the gel, the EME of two zwitterionic compounds was enhanced, preventing them from being trapped in the membrane due to the presence of both positive and negative charges occurring at higher pH values [24].

More recently, agarose gel membranes were used in the G-EME of polar and non-polar drugs from human urine samples [25]. In comparison to the use of deep eutectic solvents supported on PVDF filters, when using agarose, half of the applied potential and lower stirring speed were required to obtain similar recoveries. Polar compounds, which are often a challenge in EME, were successfully extracted in the absence of ion-pairing reagents due to the hydroxyl groups present in the gel structure, which gives it a certain hydrophilicity, thus demonstrating the active participation of biopolymer in the extraction process. Similarly, the EME of hypothalamic-related peptides was also achieved, providing better results than those obtained with PP membrane, with the additional advantage that no organic solvent or ionic carrier is required, since ionization of target analytes is assumed to be controlled by the aqueous gel [26].

In another approach, a RE-G-EME consisting of two platinum electrodes with ring-shape termination was proposed to overcome the remaining double layer at the membrane-AP interface and, therefore, to enhance the mass transfer of the analytes across the gel [27]. The electrode located inside the AP was additionally connected to the shaft of an electric motor to promote its rotation (Fig. 2c). Therefore, under continuous stirring of the donor and acceptor solutions, extraction efficiency increased by 19.5–23.5% compared to conventional G-EME, where only the donor phase (DP) is agitated.

Moreover, two agarose gel membranes containing different colorimetric reagents were proposed for their use in the EME of

Table 2
EME procedures based on agar and agarose as a biomaterial.

Format	Preparation method	Characteristics (thickness, composition, pH)	EME conditions	Target analytes	Matrix	Determination	Extraction efficiency		LOD (μg L^{-1})	Ref.
							EF	ER (%)		
Agar film	Dissolving in water – heating – in situ AgNPs generation – reflux – dryness in darkness	20 μm, 107.9 mg Ag/g agar, AgNPs 20–30 nm diameter	SLM: DHE 50V, 40min	NSAIDs: SAC, KTP, NAX, DIC, IBU	–	HPLC-UV	2.5–15.3	–	–	[21]
Agarose film	Dissolving in water – heating – IL addition – dryness – heating in oven	Not provided	IL-AF-μ-EME SLM: [C6MIM] [PF6] 10V, 8min	Antidepressant drugs: IMI, AMT, CHLO	River and tap water	HPLC-UV	110–150	–	0.1–0.4	[22]
Gel membrane	Dissolving in water – heating – cooling	5 mm, 3%(w/v)	G-EME SLM-free 25V, 25min (0.9 mA)	Basic drugs: RIV, VER, AML, MOR	Wastewater	HPLC-UV	–	38.2–73.6	1.5–1.8	[23]
Gel membrane	Dissolving in water – heating – cooling	7 mm, 3% (w/v), pH 1.5	G-EME SLM-free 40V, 15min	Amino acids: TYR, PHE	Watermelon and grapefruit juices Human plasma	HPLC-UV	33.9–51.0	56.6–85.0	7.5	[24]
Gel membrane	Dissolving in water – heating – cooling	2.5% (w/v), pH 5	G-EME SLM-free 30V, 15min	Polar drugs: ATN, EPHD, MTP Non-polar drugs: RIV, FXT, AMT	Human urine	HPLC-UV	110.3–148.7	51–88	5–10	[25]
Gel membrane	Dissolving in water – heating – cooling	8 mm, 3% (w/v), pH 4	G-EME SLM-free 30V, 15min	Peptides: OCT, GOS, TRP, CTX, SST	Human plasma	HPLC-UV	31.1–38.8	62.3–77.6	4.5–6.0	[26]
Gel membrane	Dissolving in water – heating – cooling	5 mm, 3% (w/v), pH 5	RE-G-EME SLM-free 25V, 25 min (0.6 mA) AP speed: 125 rpm	Basic drugs: NLX, NTX, NLB	Human urine	HPLC-UV	26.0–30.4	74.3–87.0	0.3–1.5	[27]
Gel membrane	Dissolving in water – heating – cooling	11 mm 4% (w/v) agarose, 5% (v/v) H_2O_2, 1% (w/v) starch in 2 mM HCl for I^-; 2% (w/v) agarose, 1% (w/v) DPC in 0.5 mM HNO_3 for Cr (VI)	EC-GSA SLM-free 50V, 15min (100 μA)	Iodide (I^-) Cr(VI)	Iodide food supplement Drinking water	Colorimetry	38–69	76–80	5–18	[28]
Gel membrane	Dissolving in water – heating – cooling	5 mm, 3% (w/v)	G-EME SLM-free 65V, 23min	Cr(III), Cr(VI)	Drinking, mineral and tap water	Colorimetry (μPADs)	40–47	58.8–83.3	2.0–3.0	[29]
Gel membrane	Dissolving in water – heating – cooling	15 mm, 1% (w/v), pH 3	IG-EME SLM-free 25V, 30min (0.6 mA)	Basic drugs: MOR, COD	Human plasma and urine	HPLC-UV	–	67.7–73.8	1.5	[30]
Gel membrane	Dissolving in water – heating – cooling – solvent impregnation	2 mm, 0.8% (w/v), 200 nm pore size	EMM SLM: 1-octanol 25V, 20min	Phenols: 4CP, 2NP, 2,4DCP	River and lake water	μHPLC-UV	–	–	0.03–0.1	[31]
Gel membrane	Dissolving in water – heating – cooling	2.5 mm, 3% (w/v) agar	IT-G-EME SLM-free 38V, 19min, 200 rpm (0.15 mA)	Cr(III), Cr(VI)	Drinking and mineral water	Colorimetry (μPADs)	36–42	72–84	7.0	[32]

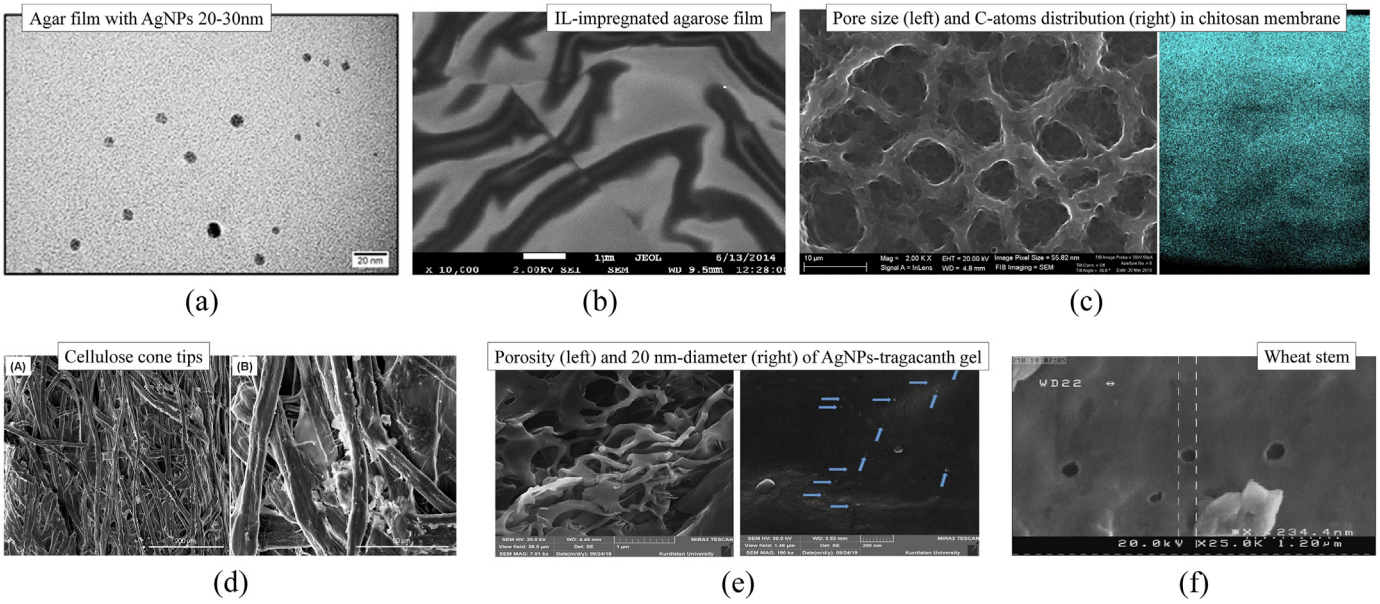


Fig. 1. Microscopic characterization of biopolymer-based materials. a) TEM image of synthesized AgNPs in the agar film with 107.9 mgAg g^{-1} agar (Reprinted from Ref. [21] with permission from Springer Nature); b) FESEM image of IL-impregnated agarose film (Reprinted from Ref. [22], Copyright (2017), with permission from Elsevier); c) SEM images of chitosan membrane and homogeneous distribution of C atoms (Reprinted from Ref. [35], Copyright (2019), with permission from Elsevier); d) SEM images of cellulose cone tips (Reprinted from Ref. [42], Copyright (2020), with permission from Elsevier); e) FESEM images of the porosity of the AgNPs-tragacanth gel and AgNPs embedded in tragacanth (Reprinted with permission from Ref. [44]); f) SEM image of wheat stem (Reprinted from Ref. [45], Copyright (2015), with permission from Elsevier).

ions [28], serving as both the extracting AP and the in situ colorimetric detector, resulting in an electro colorimetric-gel sensing approach (EC-GSA). In this way, target analytes present in the sample migrate into the gel (which is also acting as AP), where they react with the colorimetric reagents and form the corresponding-coloured complex, visible to the naked eye by a change of the agarose gel colour. This is an interesting approach where, in addition to the use of biodegradable material as membrane, analysis time is reduced by combining extraction, preconcentration and determination in a single step.

Additionally, two agarose gel membranes were simultaneously used using both cathodic and anodic gels that differed only in their acidity (Fig. 2d) [29]. Despite no organic solvent is required, in this dual-EME system the volumes of cathode and anode solutions increased and decreased respectively due to the existence of EOF. This phenomenon constitutes one of the main drawbacks of agarose gels, which is caused by the presence of anionic groups (sulphates) in the gel structure. Agarose gels have a low electrical resistance and therefore a high conductivity, which favours the EOF. This fact makes the system unstable producing changes on the volumes of the donor and acceptor phases, which reduces the extraction yield. Thus, gels with low EOF but sufficient electrical conductivity are desirable. In addition, this effect is raised when decreasing the thickness of the gel. However, thicker gels membranes increase the electrical resistance since analytes must pass through a larger pathway. As a result, most of them are trapped in the membrane, requiring excessively long times for their complete removal. For this reason, these gel membranes are single use, as their reusability in not possible due to memory effects. On the other hand, the composition of the gel also plays a key role in the existence of EOF. Thus, gels with a higher agarose concentration have a smaller pore size, reducing the EOF.

In order to overcome the EOF, an aqueous AP was placed inside the agarose gel by decreasing the agarose gel composition to 1% (w/v) (Fig. 2e) [30]. However, it also required a larger thickness of the membrane, being even more decisive in this case because it limits the volume of AP. With this new concept, the agarose gel acts as an extraction/separation membrane and, at the same time, as a support for the aqueous AP, eliminating the problems of changes in the volume of the AP associated with EOF. For this purpose, one of the platinum electrodes was placed inside the gel, where the aqueous AP is retained. After the extraction, the agarose gel containing the AP enriched with the target analytes was centrifuged to separate the two phases, releasing the aqueous extract for subsequent determination. With this IG-EME procedure, the volume of the AP increased by only 2%, whereas the increment was around 25–50% with conventional G-EME, thus decreasing the effect of EOF.

Additionally, agarose gel membranes have also been used in a different format (Fig. 2f). Chong et al. proposed the use of agarose gel membrane discs in EME by inserting one of the electrodes inside the gel, so that the disc would be held in place [31]. Once the extraction is completed, the disc was removed from the sample and the organic solvent (which also acts as an AP) was released by centrifugation. An unusual observation from this system was that the extraction efficiency increased in the absence of agitation. Additionally, the simplicity of the extraction format makes it suitable for use as a portable device.

More recently, Tabani et al. introduced the so-called in-tube gel electro-membrane microextraction (IT-G-EME), where a few μL of agarose solution is placed at the end of a narrow, transparent tube and cooled to serve simultaneously as an extraction device and AP compartment [32]. The sample solution is placed in a homemade circular vial equipped with holes at the ends to insert two micro-extraction devices, each containing the cathodic and anodic acceptor solutions, as well as the negatively and positively charged electrodes, respectively (Fig. 2g). Finally, both APs were collected for subsequent analysis by colorimetric reaction using μPADs. With this approach, monitoring the extraction process is achieved through the colorimetric reaction, enhancing the preconcentration step by increasing the volume of the DP, which is not possible in previous similar devices (e.g., free-liquid-membranes) due to the dimensions required for the liquid solutions. In addition, the size of

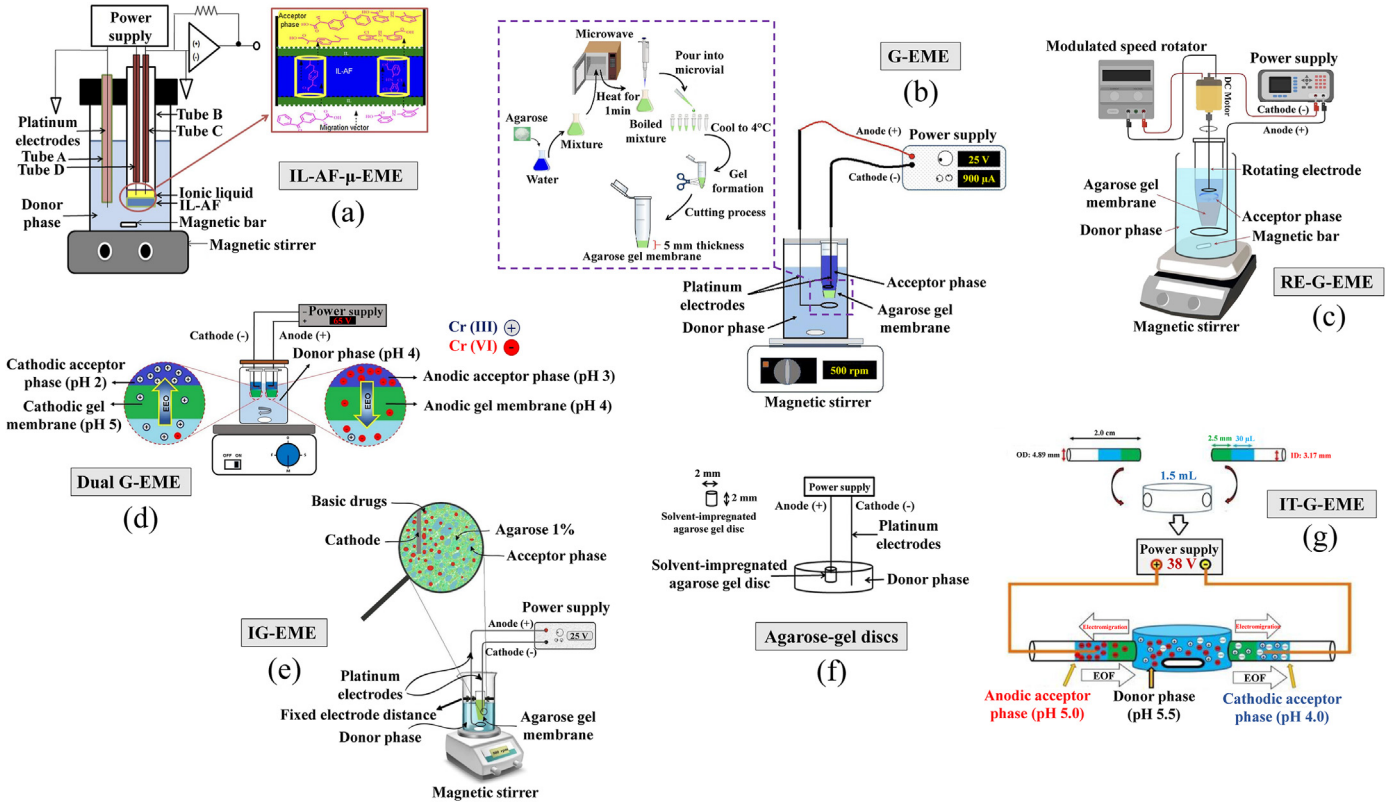


Fig. 2. Selection of different devices and EME formats used with agarose-based materials. a) IL-AF-μ-EME device (Reprinted from Ref. [22], Copyright (2017), with permission from Elsevier); b) Synthesis of agarose gel membrane and EME device (Reprinted from Ref. [23], Copyright (2017), with permission from Elsevier); c) Extraction setup for RE-G-EME procedure device (Reprinted from Ref. [27], Copyright (2020), with permission from Elsevier); d) Dual G-EME setup (Reprinted from Ref. [29] with permission from Springer Nature); e) IG-EME device (Reprinted from Ref. [30], Copyright (2020), with permission from Elsevier); f) EME setup (Reprinted from Ref. [31], Copyright (2018), with permission from Elsevier); g) IT-G-EME device (Reprinted from Ref. [32], Copyright (2022), with permission from Elsevier).

the fabricated circular compartment allows the sample solution to be stirred during extraction, facilitating a faster analyte migration. Despite its advantages, one of the main drawbacks of this IT-G-EME procedure is still the EOF, which results in changes in AP/DP volume of approximately 15%.

4. Chitosan-based materials in EME

Chitosan is the most widely used biopolymer in EME systems after agarose, being the second most abundant in nature. It is a cationic polysaccharide derived from chitin which can be obtained from aquatic organisms with hard skeletons such as crabs, shrimps, or lobsters [33], from bone plates of cuttlefish and squid, as well as from fungi and insects [20]. Moreover, it can be easily obtained by a deacetylation process from chitin, as the chemical difference between both structures lies in their glucose units. The deacetylation process can be carried out enzymatically or chemically by means of alkyne reactions, so that different types of chitosan with varying molecular weight (10–1000 kDa) and degree of deacetylation (70–95%) are obtained commercially. The latter determines the physical and chemical properties of chitosan, as well as its biological activity. It is soluble in acidic aqueous solutions, being positively charged by protonation of the amino group (pKa ≈6.5), but insoluble in water and alkaline media. Due to the amino and hydroxyl groups, it has a high reactivity and can easily form hydrogen bonds. As a result, it can be chemically modified by alkylation, acetylation, sulphonation, phosphorylation, or copolymerisation reactions, among others, yielding a large number of structural derivatives for targeted applications. In addition to the general characteristics of natural biopolymers, chitosan has many other advantages, such as mechanical properties, antimicrobial activity, chelation, and the ability to form gels, allowing different shape formats, such as powder, gels, films, membranes, beads, pills, microspheres, or foams [34]. All these properties make it an excellent and versatile candidate to participate as a natural substrate in the development of composite biomaterials. The main characteristics of EME procedures with chitosan membranes are shown in Table 3.

Chitosan-based flat membrane was introduced for the first time to be used in EME in 2019, which were prepared by dissolving chitosan in slightly acidic media, followed by pH 5 adjustment and the addition of Aliquat®336 [35]. To accelerate the evaporation of the solvent, the Petri dish with the solution was placed into a vacuum oven until it was completely dried. The use of high molecular weight chitosan (310–375 kDa) provided more homogeneous membranes and better reproducibility, while Aliquat®336 acted only as a plasticizer and not as a carrier, varying the flexibility of the membrane but not the extraction efficiency (Fig. 1c). A homemade EME device, similar to the one described in Ref. [21] was used (Fig. 3a), where L-shaped DP-electrode was employed to favour the electric field around the membrane, providing much higher preconcentration and performance compared to other previously described EME materials (such as PP).

In a subsequent work, chitosan membranes were used in the selective EME of FQs [36], demonstrating to play an active role in the extraction of three FQs in the presence of other ones. The interaction mechanisms between the biomembrane and the target analytes was studied for the first time in EME by QTAIM in order to assess the active participation of the chitosan membrane. The

Table 3
EME procedures based on other natural biopolymeric materials.

Format	Preparation method	Characteristics (thickness, composition, pH)	EME conditions	Target analytes	Matrix	Determination	Extraction efficiency		LOD (μg L^{-1})	Ref.
							EF	ER (%)		
Chitosan film	Dissolving in water – vacuum drying – cleaning – vacuum drying	30–35 μm, 60% (w/w) chitosan, 40% (w/w) Aliquat®336, pH 5	SLM: 1-octanol 100V, 10min (0.095–0.45 mA)	Acidic drugs: AMX, ANT, HIP, IBU, KTP, NAX, NIC, SAC	Human urine	HPLC-UV	20 –118	10–59	1.0–7.0	[35]
Chitosan film	Dissolving in water – vacuum drying – cleaning – vacuum drying	30–35 μm, 60% (w/w) chitosan, 40% (w/w) Aliquat®336, pH 5	SLM: 1-octanol 80V, 20min (0.2–0.3 mA)	FQs: ENR, MRB, FLM	Dog urine	HPLC-UV	58–83	–	1.3–1.7	[36]
Chitosan film	Dissolving in water – vacuum drying – cleaning – vacuum drying	10–11 μm, 60% (w/w) chitosan, 40% (w/w) Aliquat®336, pH 5	SLM-free 100V, 15min (0.15–0.4 mA)	Polyphenolic compounds: BPZ, BZA, CAF, CIN, CLO, FER, GAL, HBA	Food	HPLC-UV	63 –131	31.5 –65.5	15.9–37.1	[37]
Chitosan film	Dissolving in water – vacuum drying – cleaning – vacuum drying	30–35 μm, 60% (w/w) chitosan, 40% (w/w) Aliquat®336, pH 5	SLM-free 80V, 15min (0.1–0.4 mA)	Parabens (MeP, EtP, PrP, iPrP, BuP, iBuP, BzP) and FQs (ENR, MRB, FLM)	Water	HPLC-UV	28 –195	–	0.2–1.1	[38]
Cellulose cone tip	Commercialized – soaked with Acetic Acid	Manila paper, 28 mm length, 0.8 mm vertex diameter containing silicate and gum tragacanth	MPEF SLE: Acetic acid Filter: 1-octanol 300V, 3 min	Antibiotic dyes: CV, LCV	Fish muscle extracts (obtained previously by SLE)	DIA	–	~80	1.37	[41]
Cellulose cone tip	Commercialized – soaked with Acetic Acid	Composition: C, O and traces of Ca, Si, S. 4 –20 μm i.d., spherical surface particles 2.5 –20 μm diameter	MPEF SLE: Acetic acid Filter: 1-octanol 300V, 35 min (5 μA)	COC	Human saliva	UHPLC-MS/MS	–	56–70	0.3	[42]
AgNPs-tragacanth gel	Dispersion in AgNPs aqueous solution – heating – cooling	4 mm, 2.5% (w/v)	SLM-free 50V, 20min (1.1 mA)	Basic drug: CAP	Human plasma	HPLC-UV	79	79	0.84	[43]
AgNPs-tragacanth gel	Dispersion in AgNPs aqueous solution – heating – cooling	4 mm, 2.5% (w/v)	SLM-free 30V, 15min	Polar acidic antiviral drug: TDF	Human plasma	HPLC-UV	85	85	5.55	[44]
Hollow cylindrical wheat stem	Commercialized – treatment in HCl:MeOH – cutting – direct use	160 μm, 1.5 mm i.d., 234 nm pore size	Culm-EME-UV–Vis SLM: 5% (v/v) DEHP in 1-octanol 90V, 30min	Thorium (Th)	Water	UV–Vis spectrophotometry	50	91.8 –93.1	0.29	[45]

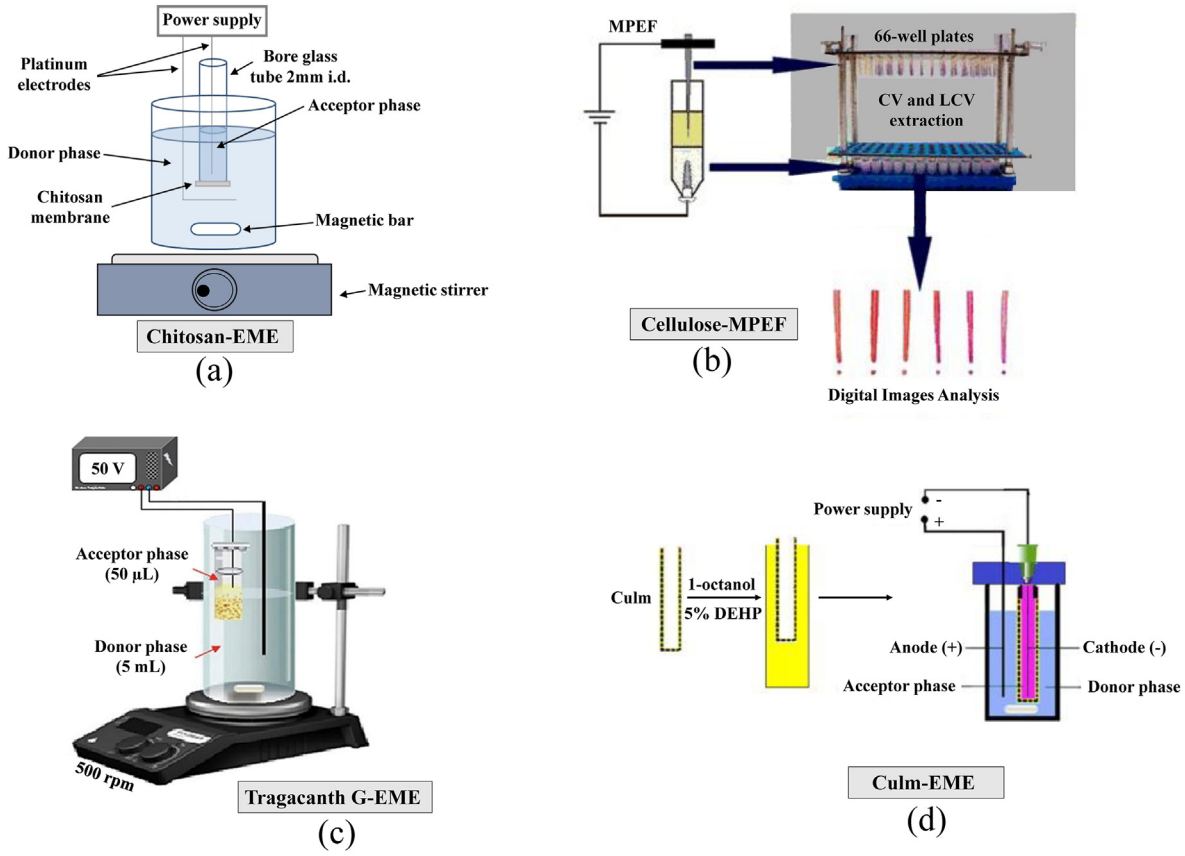


Fig. 3. EME setups used with other biomaterials. a) EME device based on chitosan membrane (Reprinted from Ref. [35], Copyright (2019), with permission from Elsevier); b) Setup for the multiphase-EME procedure (Reprinted (adapted) with permission from Ref. [41]. Copyright 2019 American Chemical Society); c) EME device for AgNPs-tragacanth gel (Reproduced (or adapted) from Ref. [43] with permission from Wiley-VCH); d) EME device based on wheat stem as hollow fiber (Reprinted from Ref. [45], Copyright (2015), with permission from Elsevier).

geometry involving direct approximation of the carboxyl and keto groups of the FQs with both the amine and hydroxyl groups of the glucosamine units was found to be the most favourable, which is stabilized by H—N and H—O hydrogen bonds, respectively. Thus, the selective extraction of three FQs over the others could be explained by the coexistence of mixed occupational interactions on the chitosan membrane, with the extracted analytes corresponding to stronger and more favourable interactions. Therefore, by modifying the media and polarity of the membrane, the extraction of other compounds could be selectively enhanced.

Later, chitosan-based membranes were used in a greener EME procedure for the determination of polyphenolic compounds [37]. In this case, the use of organic solvent was completely removed as the active participation of chitosan in the extraction process was previously demonstrated, which is an important and remarkable advantage. Greenness of this EME approach was additionally assessed by performing, for the first time, the analytical greenness metric for sample preparation (AGREEprep). Accordingly, the proposed method was settled as the most environmentally friendly in comparison with other microextraction techniques for that group of target analytes.

Furthermore, as mentioned above, this biopolymeric support has been shown to present a high selectivity in the extraction of target analytes. In this regard, very recently, it has been used in the selective EME of pollutants belonging to different families of compounds [38]. Thus, parabens and fluoroquinolones were simultaneous extracted from environmental water samples without the interference from other contaminants, such as NSAIDs. The active role of the chitosan film allowed the extraction to be carried out in the absence of organic SLM, demonstrating the environmentally friendly nature of this procedure, further confirmed by the application of analytical tools for ecological assessment. This fact, together with its biodegradability, makes chitosan membranes an efficient and green alternative to traditional plastic supports with unique selective properties. This selectivity could be even improved by functionalization, thus expanding the number of future applications.

5. Other biopolymers-based materials in EME

In addition to those described above, there are also some contributions reporting the use of other types of natural biopolymers in EME (Table 3). In this respect, cellulose is the most abundant natural polymer in nature. It is a non-ionisable or neutral polysaccharide that acts as a structural component of plant, cells and tissues, such as green plants and algae. Alternatively, it can also be produced by bacteria, in this case providing pure cellulose, without the presence of other components such as pectin, lignin or hemicellulose, so the physical properties are different. A linear or fibrous structure is achieved by formation of hydrogen bonding between the hydroxyl groups of the chains, so it has high mechanical strength and favourable thermal properties [39,40]. Cellulose derivatives (carboxymethyl- and methyl-cellulose or cellulose triacetate) can be easily obtained due to the reactivity of the hydroxyl groups, having a wide variety of applications in different fields such as biomedical, pharmaceutical, food or textile. Additionally, it is a

polymer insoluble in water and some organic solvents, with piezoelectric properties and high deformation capacity, making it suitable as a physical supporting material.

In this regard, commercial cellulose cone tips were used as sorbent supporting an aqueous electrolyte acceptor solution in multiphase extraction assisted by electric fields (MPEF) [41]. The composition of the cellulose (manila paper) cone tips was reported to contain sodium silicate and gum tragacanth, a polysaccharide. For this purpose, a lab-made 66-well plate was used for simultaneous extractions. EME devices were developed from PP Eppendorf tubes by inserting stainless steel screws into the bottom of the tubes (sealing with glue), which act as DP electrodes. EME procedure was carried out by using a multiphase approach: i) a DP containing the sample (aqueous solution); ii) a double AP consisting of the cellulose cone tip (sorbent) supporting an electrolyte solution and immersed in iii) an organic phase acting as a filter between donor and acceptor solutions. Finally, cellulose cone tips were attached to a stainless-steel plate that served as an electrode for the AP (Fig. 3b). This technique proved to overcome the instability problems associated to single drop extraction and the material showed an adequate porosity to act as a sorbent (Fig. 1d), as well as enough hydrophilicity to be impregnated with the electrolyte solution, thus allowing the passage of electric current [42].

Furthermore, natural polysaccharide gums, such as tragacanth, have been also described in EME. Thus, AgNPs-tragacanth conjugated gel [43] was developed and prepared by dissolving tragacanth in a solution of AgNPs, thus the AgNPs were immobilized on the surface of the gel (Fig. 3c). Results revealed that the presence of AgNPs increased the extraction efficiency by 15% compared to pure tragacanth gel. These findings are related to the stabilization and homogeneity of the electric field by the presence of AgNPs. In the same way, a larger contact surface favours the mass transfer of the analytes, improving the extraction yield. These results agree with previously reported by Román et al. [21] when using agar films containing AgNPs. However, high electrical current was achieved during the extraction process compared to those recorded with other similar materials, such as agarose gels, although without a significant effect on the extraction performance. Additionally, the same EME device was then applied to the EME of polar acidic drug [44]. Here, FESEM was also used to characterize the gel, revealing the presence of spherical silver nanoparticles homogeneously arranged on the surface of the gel (Fig. 1e). In this case, the extraction efficiency was increased by 20% when tragacanth gel with AgNPs was used, compared to the use of the pure gel.

On the other hand, Khajeh et al. introduced the use of a wheat stem as a hollow fiber (Figs. 1f and 3d) [45]. It was cut into 3 cm pieces, previously treated with HCl and MeOH and closed at one end by a knot. The results were compared to those obtained by using PP-hollow fibers, providing comparable extraction recovery (ER) and enrichment factor (EF).

Accordingly, the use of biopolymers in EME systems is a real and sustainable alternative to plastic supports, the main advantages of which are summarised in Table 4. Compared to plastic-based materials, they can be tailored-made according to requirements, thus allowing their production in different compositions, thicknesses, and formats. On the contrary, physicochemical properties of synthetic materials are limited by commercial suppliers, i. e. fixed thickness and composition. In addition, the EME performance using biopolymeric materials provides numerous advantages. Thus, they are mostly solvent-free whereas plastic supports usually requires the use of organic SLM and could be functionalized to enhance the extraction of target analytes due to their active participation trough specific interactions. Therefore, the extraction efficiency can be further improved by modifying the properties of the material in addition to the EME parameters, thus allowing the extraction of a large number of varied compounds. On the other hand, plastic supports have a passive role in the extraction, since they act just as a physical barrier to keep AP/DP separated. As a result, the extraction can be only controlled by modifying the EME parameters, which limits their applicability.

6. Conclusions and future perspectives

As described in this review, the use of biopolymers as suitable extraction materials for greener and sustainable EME procedures have been demonstrated through reported literature. However, most of the published works are limited to the use of agarose-based materials, mainly gel membranes and, therefore, the development of new alternative biodegradable materials for those purposes is still lacking. In this sense, natural polysaccharides constitute a broad group of biopolymers with varied structures and very attractive properties that make them excellent candidates to replace the undesirable plastic materials in an increasingly environmentally conscious society. They offer numerous advantages, such as biodegradability, renewability, biocompatibility, availability, non-toxicity, and versatility, as well as each of them can provide additional benefits due to their own unique and individual characteristics. Accordingly, some approaches still need to be addressed: i) take advantage of the variety of biopolymers derived from polysaccharides in terms of functional groups and charges for the extraction of compounds of diverse nature, such as polar, acidic or basic analytes; ii) extend the functionality and selectivity of these biopolymers by chemical modification of their structures through reactions with their main functional groups, such as hydroxyl, amino, or carboxyl, providing a wide diversity of derived materials; iii) conduct theorical studies and calculations for a better understanding of the interaction mechanisms between target analytes and different biopolymers during their active participation

Table 4
Evaluation of biopolymers versus plastics as supports/barriers in EME systems.

	Plastic-based materials	Biopolymer-based materials
Common materials in EME	PP	Agar or agarose
	PVDF	Chitosan
	PAN	Tragacanth gum
		Cellulose
General properties	Synthetic	Natural source
	Non-biodegradable	Biodegradability
	Limited physical and chemical properties	Tailored-made
Performance in EME	SLM requirement	Solvent-free
	Non-functionalizable	Functionalizable
	Passive role	Active role
	Limited selectivity	High selectivity
	Limited applicability	High versatility

in the extraction procedure in order to design materials for specific applications; iv) enhance the properties of individual components through the development of biocomposite materials consisting on a combination of two or more biopolymers. These biopolymeric supports constitute, therefore, a great advance in EME systems, having an impact on emerging applications towards addressing societal challenges, such as reducing the environmental burdens.

Declaration of competing interest

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

Data availability

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

Acknowledgments

This work was supported by the coordinated project PID2021-123073NB-C22 from the Spanish Ministry of Science and innovation (MCIN) (Generación del Conocimiento. MCIN/AEI/10.13039/501100011033/FEDER "Una manera de hacer Europa"). Authors are grateful to Servicio General de Investigación de Microscopía, CENTRO DE INVESTIGACIÓN TECNOLÓGICA E INNOVACIÓN (CITIUS), Universidad de Sevilla, for the use of the microscopic equipment. This work was supported by PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020 and UIDP/50006/2020. Cristina Román-Hidalgo thanks FCT for funding through the Scientific Employment Stimulus - Individual Call (Ref. 2021.03610. CEECIND/CP1662/CT0002). L. Barreiros acknowledges funding from FCT through program DL 57/2016 - Norma transitória.

References

[1] S. Pedersen-Bjergaard, K.E. Rasmussen, Electrokinetic migration across artificial liquid membranes. New concept for rapid sample preparation of biological fluids, J. Chromatogr. A 1109 (2006) 183–190. https://doi.org/10.1016/j.chroma.2006.01.025.

[2] C. Huang, Z. Chen, A. Gjelstad, S. Pedersen-Bjergaard, X. Shen, Electromembrane extraction, TrAC, Trends Anal. Chem. 95 (2017) 47–56. https://doi.org/10.1016/j.trac.2017.07.027.

[3] N. Drouin, P. Kuban, S. Rudaz, S. Pedersen-Bjergaard, J. Schappler, Electromembrane extraction: overview of the last decade, TrAC, Trends Anal. Chem. 113 (2019) 357–363. https://doi.org/10.1016/j.trac.2018.10.024.

[4] S. Pedersen-Bjergaard, C. Huang, A. Gjelstad, Electromembrane extraction – recent trends and where to go, J. Pharm. Anal. 7 (2017) 141–147. https://doi.org/10.1016/j.jpha.2017.04.002.

[5] A. Gutiérrez-Serpa, R. González-Martín, M. Sajid, V. Pino, Greenness of magnetic nanomaterials in miniaturized extraction techniques: a review, Talanta 225 (2021), 122053. https://doi.org/10.1016/j.talanta.2020.122053.

[6] E.V. Soares-Maciel, A.L. Toffoli, E.S. Neto, C.E. Domingues-Nazario, F.M. Lanças, New materials in sample preparation: recent advances and future trends, TrAC, Trends Anal. Chem. 119 (2019), 115633. https://doi.org/10.1016/j.trac.2019.115633.

[7] J. Li, R. Zhu, X. Shen, C. Huang, Functional materials and chemicals in electromembrane extraction, TrAC, Trends Anal. Chem. 150 (2022), 116574. https://doi.org/10.1016/j.trac.2022.116574.

[8] K. Maiphetlho, L. Chimuka, H. Tutu, H. Richards, Technical design and optimisation of polymer inclusion membranes (PIMs) for sample pre-treatment and passive sampling – a review, Sci. Total Environ. 799 (2021), 149483. https://doi.org/10.1016/j.scitotenv.2021.149483.

[9] C. Román-Hidalgo, M.J. Martín-Valero, R. Fernández-Torres, M. Callejón-Mochón, M.A. Bello-López, New nanostructured support for carrier-mediated electromembrane extraction of high polar compounds, Talanta 162 (2017) 32–37. https://doi.org/10.1016/j.talanta.2016.10.022.

[10] S. Abbasi, S.A. Haeri, Biodegradable materials, and their applications in sample preparation techniques–A review, Microchem. J. 171 (2021), 106831. https://doi.org/10.1016/j.microc.2021.106831.

[11] N.H. Godage, E. Gionfriddo, Use of natural sorbents as alternative and green extractive materials: a critical review, Anal. Chim. Acta 1125 (2020) 187–200. https://doi.org/10.1016/j.aca.2020.05.045.

[12] I. Pacheco-Fernández, D.W. Allgaier-Díaz, G. Mastellone, C. Cagliero, D. Díaz-Díaz, V. Pino, Biopolymers in sorbent-based microextraction methods, TrAC, Trends Anal. Chem. 125 (2020), 115839. https://doi.org/10.1016/j.trac.2020.115839.

[13] H. Tabani, M. Alexovic, J. Sabo, M. Ramos-Payán, An overview on the recent applications of agarose as a green biopolymer in micro-extraction-based sample preparation techniques, Talanta 224 (2021), 121892. https://doi.org/10.1016/j.talanta.2020.121892.

[14] H. Tabani, F. Dorabadizare, S. Pedersen-Bjergaard, Gel electro-membrane extraction: an overview on recent strategies for extraction efficiency enhancement, TrAC, Trends Anal. Chem. 160 (2023), 116990. https://doi.org/10.1016/j.trac.2023.116990.

[15] R. Oliveira-Martins, G.L. de Araújo, R. Costa-Simas, A. Rodrigues-Chaves, Electromembrane extraction (EME): fundamentals and applications, Talanta Open 7 (2023), 100200. https://doi.org/10.1016/j.talo.2023.100200.

[16] A. George, M.R. Sanjay, R. Srisuk, J. Parameswaranpillai, S. Siengchin, A comprehensive review on chemical properties and applications of biopolymers and their composites, Int. J. Biol. Macromol. 154 (2020) 329–338. https://doi.org/10.1016/j.ijbiomac.2020.03.120.

[17] M.C. Biswas, B. Jony, P.K. Nandy, R.A. Chowdhury, S. Halder, D. Kumar, S. Ramakrishna, M. Hassan, M.A. Ahsan, M.E. Hoque, M.A. Imam, Recent advancement of biopolymers and their potential biomedical applications, J. Polym. Environ. 30 (2022) 51–74. https://doi.org/10.1007/s10924-021-02199-y.

[18] A. Vinod, M.R. Sanjay, S. Suchart, P. Jyotishkumar, Renewable and sustainable biobased materials: an assessment on biofibers, biofilms, biopolymers and biocomposites, J. Clean. Prod. 258 (2020), 120978. https://doi.org/10.1016/j.jclepro.2020.120978.

[19] E. Jamróz, P. Kulawik, P. Kopel, The effect of nnanofillers on the functional properties of biopolymer-based films: a review, Polymers 11 (2019) 675. https://doi.org/10.3390/polym11040675.

[20] R. Gheorghita, L. Anchidin-Norocel, R. Filip, M. Dimian, M. Covasa, Applications of biopolymers for drugs and probiotics delivery, Polymers 13 (2021) 2729. https://doi.org/10.3390/polym13162729.

[21] C. Román-Hidalgo, M. Ramos-Payán, J.A. Ocaña-González, M.J. Martín-Valero, M.Á. Bello-López, Agar films containing silver nanoparticles as new supports for electromembrane extraction, Anal. Bioanal. Chem. 407 (2015) 1519–1525. https://doi.org/10.1007/s00216-014-8375-6.

[22] N.S.M. Hanapi, M.M. Sanagi, A. Ismail, W.A.W. Ibrahima, N. Saimc, W.N.W. Ibrahim, Ionic liquid-impregnated agarose film two-phase micro-electrodriven membrane extraction (IL-AF-μ-EME) for the analysis of antidepressants in water samples, J. Chromatogr. B 1046 (2017) 73–80. https://doi.org/10.1016/j.jchromb.2017.01.028.

[23] H. Tabani, S. Asadi, S. Nojavan, M. Parsa, Introduction of agarose gel as a green membrane in electromembrane extraction: an efficient procedure for the extraction of basic drugs with a wide range of polarities, J. Chromatogr. A 1497 (2017) 47–55. https://doi.org/10.1016/j.chroma.2017.03.075.

[24] S. Sedehi, H. Tabani, S. Nojavan, Electro-driven extraction of polar compounds using agarose gel as a new membrane: determination of amino acids in fruit juice and human plasma samples, Talanta 179 (2018) 318–325. https://doi.org/10.1016/j.talanta.2017.11.009.

[25] H. Abbasi, S. Abbasi, S.A. Haeri, S. Rezayati, F. Kalantari, M.R.P. Heravi, Electromembrane extraction using biodegradable deep eutectic solvents and agarose gel as green and organic solvent-free strategies for the determination of polar and non-polar bases drugs from biological samples: a comparative study, Anal. Chim. Acta 1222 (2022), 339986. https://doi.org/10.1016/j.aca.2022.339986.

[26] A. Pourahadi, S. Nojavan, S.S.H. Davarani, Gel-electromembrane extraction of peptides: determination of five hypothalamic agents in human plasma samples, Talanta 217 (2020), 121025. https://doi.org/10.1016/j.talanta.2020.121025.

[27] M. Behpour, H. Tabani, S. Nojavan, Gel electromembrane extraction using rotating electrode: a new strategy for mass transfer enhancement of basic drugs from real human urine samples, J. Chromatogr. B 1152 (2020), 122258. https://doi.org/10.1016/j.jchromb.2020.122258.

[28] A. Sahragard, W. Alahmad, P. Varanusupakul, Electrocolorimetric gel-based sensing approach for simultaneous extraction, preconcentration, and detection of iodide and chromium (VI) ions, Talanta 235 (2021), 122715. https://doi.org/10.1016/j.talanta.2021.122715.

[29] H. Tabani, F.D. Zare, W. Alahmad, P. Varanusupakul, Determination of Cr(III) and Cr(VI) in water by dual-gel electromembrane extraction and a microfuidic paper-based device, Environ. Chem. Lett. 18 (2020) 187–196. https://doi.org/10.1007/s10311-019-00921-w.

[30] A. Rahimi, S. Nojavan, H. Tabani, Inside gel electromembrane extraction: a novel green methodology for the extraction of morphine and codeine from human biological fluids, J. Pharm. Biomed. Anal. 184 (2020), 113175. https://doi.org/10.1016/j.jpba.2020.113175.

[31] Y.T. Chong, M.M. Ariffin, N.M. Tahir, S.H. Loh, A green solvent holder in electro-mediated microextraction for the extraction of phenols in water, Talanta 176 (2018) 558–564. https://doi.org/10.1016/j.talanta.2017.08.068.

[32] H. Tabani, T. Samkumpim, W. Alahmad, F.D. Zare, P. Varanusupakul, In-tube gel electro-membrane combined with microfluidic paper-based device: a green and miniaturized extraction mode for the chromium speciation, Adv.

Sample Prep. 3 (2022), 100036. https://doi.org/10.1016/j.sampre.2022.100036.
[33] S. Ahmed, S. Ikram (Editors), Chitosan. Derivatives, Composites and Applications, John Wiley & Sons, Dehli, India, 2017.
[34] P.S. Bakshi, D. Selvakumar, K. Kadirvelu, N.S. Kumar, Chitosan as an environment friendly biomaterial—a review on recent modifications and applications, Int. J. Biol. Macromol. 150 (2020) 1072–1083. https://doi.org/10.1016/j.ijbiomac.2019.10.113.
[35] C. Román-Hidalgo, G. López-Pérez, M.J. Martín-Valero, M.Á. Bello-López, Chitosan tailor-made membranes as biopolymeric support for electromembrane extraction, Talanta 199 (2019) 290–295. https://doi.org/10.1016/j.talanta.2019.02.079.
[36] C. Román-Hidalgo, N. Aranda-Merino, G. López-Pérez, A. Sánchez-Coronilla, M. Villar-Navarro, M.J. Martín-Valero, Chitosan biofilms: insights for the selective electromembrane extraction of fluoroquinolones from biological samples, Anal. Chim. Acta 1179 (2021), 338832. https://doi.org/10.1016/j.aca.2021.338832.
[37] C. Román-Hidalgo, G. López-Pérez, M. Villar-Navarro, M.J. Martín-Valero, Green electromembrane extraction procedure based on biodegradable chitosan films for determination of polyphenolic compounds in food samples: greenness assessment of the sample preparation approach, Talanta 253 (2023), 124034. https://doi.org/10.1016/j.talanta.2022.124034.
[38] C. Román-Hidalgo, M.J. Martín-Valero, G. López-Pérez, M. Villar-Navarro, Green method for the selective electromembrane extraction of parabens and fluoroquinolones in the presence of NSAIDs by using biopolymeric chitosan films, Membranes 13 (3) (2023) 326. https://doi.org/10.3390/membranes13030326.
[39] A. Etale, A.J. Onyianta, S.R. Turner, S.J. Eichhorn, Cellulose: a review of water interactions, applications in composites, and water treatment, Chem. Rev. 123 (5) (2023) 2016–2048. https://doi.org/10.1021/acs.chemrev.2c00477.
[40] F. Jabbari, V. Babaeipour, Bacterial cellulose as a potential biopolymer for wound care. A review, Int. J. Polym. Mater. Polym. Biomater. (2023). https://doi.org/10.1080/00914037.2023.2167080.
[41] R.M. Orlando, C.C. Nascentes, B.G. Botelho, J.S. Moreira, K.A. Costa, V.H.M. Boratto, Development and evaluation of a 66-well plate using a porous sorbent in a four-phase extraction assisted by electric field approach, Anal. Chem. 91 (2019) 6471–6478. https://doi.org/10.1021/acs.analchem.8b04943.
[42] D.V.M. Sousa, F.V. Pereira, C.C. Nascentes, J.S. Moreira, V.H.M. Boratto, R.M. Orlando, Cellulose cone tip as a sorbent material for multiphase electrical field-assisted extraction of cocaine from saliva and determination by LC-MS/MS, Talanta 208 (2020), 120353. https://doi.org/10.1016/j.talanta.2019.120353.
[43] S. Hajizadeh, K. Farhadi, R. Molaei, M. Forough, Silver nanoparticles-tragacanth gel as a green membrane for effective extraction and determination of capecitabine, J. Separ. Sci. 43 (2020) 2666–2674. https://doi.org/10.1002/jssc.202000251.
[44] S. Hajizadeh, K. Farhadi, Development of AgNPs-tragacanth conjugated gel as a novel green membrane in electro-membrane extraction: tenofovir disoproxil fumarate assay in human plasma samples, Anal. Bioanal. Chem. Res. 7 (2020) 415–429. https://doi.org/10.22036/ABCR.2020.210593.1439.
[45] M. Khajeh, S. Pedersen-Bjergaard, A. Barkhordar, M. Bohlooli, Application of hollow cylindrical wheat stem for electromembrane extraction of thorium in water samples, Spectrochim. Acta, Part A 137 (2015) 328–332. https://doi.org/10.1016/j.saa.2014.08.103.