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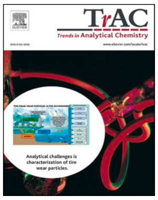

Natural/bio-based sorbents as greener extractive materials for endocrine disrupting compounds in samples of different matrix composition

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ABSTRACT

Endocrine-disrupting compounds (EDCs) are a group of chemicals that interfere with the endocrine system, leading to adverse effects on human health and the environment. Increasing concerns over the EDCs presence in various environmental compartments has driven the search for greener extraction materials. Recently, the use of polymers of natural origin (biopolymers) has been demonstrated to be an effective and promising research direction due to their undeniable advantages over synthetic polymers. In this review, strategies for cellulose, chitin, and chitosan functionalization and their applicability for numerous microextraction techniques have been widely discussed. Following the trend related to the reuse of waste, various agricultural wastes that were employed for the isolation and enrichment of EDCs are described. The benefits and limitations of using natural sorbents have been highlighted.

1. Introduction

The term endocrine-disrupting chemicals (EDCs) encompasses a group of chemicals able to interfere with the endocrine system by modifying: (i) hormones synthesis pathways; (ii) hormones excretion mechanisms; (iii) cell/tissue transport of hormones in the organism; (iv) hormones degradation pathways; (v) mimicking the endogenous hormones' functioning; (vi) antagonism with the synthesis of natural hormones or their metabolism; (vi) changes of level or activity of the hormonal receptors [1]. Therefore, EDCs could cause a wide range of health problems to humans and wildlife, such as reproductive, developmental, metabolic, immune, or neurological diseases, and even hormone-related cancers [2,3]. So far, hundreds of chemicals considered to be endocrine disruptors have been identified in nearly every environmental compartment, as well as in consumer goods, personal care and medical products, and building materials. Among them, compounds such as bisphenols (BPs), phthalates (PAEs), parabens, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), perfluorinated compounds (PFCs), brominated flame-retardants (BFRs), dioxins and pesticides are the most prominent ones [4]. Because of their widespread distribution and possible health risks, it is becoming more important to monitor their concentrations. However, EDCs are mostly present at trace or ultra-trace concentration levels in samples of complex matrix composition and obtaining reliable information of pollution levels is a very challenging task. To overcome these difficulties, it is necessary to use an appropriate sample preparation strategy before instrumental analysis. Among the most frequently used methods for preconcentration and clean-up of EDCs are those relying on solid sorbents. So far, various materials including commercially available ones, such as polydimethylsiloxane (PDMS), divinylbenzene (DVB), carboxen (CAR) and those classified as modern sorbents like molecularly imprinted polymers (MIPs), ion-imprinted polymers (IIPs), nanostructured materials, metal-organic frameworks (MOFs) and others have been synthesized and successfully employed [5–7]. Despite their

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advantages, it should be kept in mind that their use (even in small quantities) may contribute to environmental pollution, both via the disposal of used materials and the use of hazardous substances during their production. Therefore, to reduce the environmental impact of sample preparation methods, the research activities are focused on finding greener sample preparation strategies, which fits into the concept of Green Analytical Chemistry (GAC) [8]. Recently, the use of polymers of natural origin (biopolymers) has been demonstrated to be an effective and promising research direction due to their undeniable advantages over synthetic polymers, such as biodegradability, low cost, low toxicity, and abundant availability [9]. Therefore, by applying these natural polymers, it is possible to meet points such as: (i) elimination of hazardous substances which are created during the production of conventional sorbents (GAC principle number 11), (ii) less energy consumption (GAC principle number 9), (iii) possibility to use renewable materials (GAC principle number 10), (iv) use of biodegradable materials to reduce wastes amount (GAC principle number 7 and 10). According to the monomer unit of their structure, natural polymers can be categorized into three classes such polysaccharides, polynucleotides, and polypeptides or proteins [10]. Fig. 1 shows a schematic classification of biopolymers.

The natural sources of biopolymers are numerous and include microorganisms such as bacteria and fungi, plants, and animals. In addition, they might be present in some agricultural and industrial wastes [11,12]. In addition to biodegradability and renewability, biopolymers have a number of extremely desirable features, including high thermal, chemical, and structural stability and controllable porosity. Furthermore, due to the presence of numerous functional groups, they are capable of binding with various compounds, and more importantly, the adsorption performance may be easily increased by further functionalization [9]. According to the literature, polysaccharides and especially cellulose, chitosan and chitin are the most frequently used as extraction phases. Basic information on cellulose, chitin, and chitosan is summarized in Table 1 [13–16], while extended information and their applications are presented in the following sections.

Therefore, since the early 2000s, there has been a steady increase in the number of published articles related to the use of biopolymers as the extraction phase (Fig. 2).

In recent years, several review articles have also been published on the application of diverse biopolymers [9,17–19] in sample preparation methods; however, none of them strictly focuses on the analysis of endocrine-active compounds. In this context, we present a comprehensive overview of recent applications of biopolymers as greener extractive materials for the determination of EDCs, targeting on pesticides, parabens, hormones, PAEs, phenolic compounds and metal ions in environmental, food, and biological samples. In this review, strategies for cellulose, chitin, and chitosan functionalization and their applicability for numerous microextraction techniques have been widely discussed. Additionally, following the trend related to the reuse of waste, we described various agricultural wastes that were used for the isolation and enrichment of EDCs. The benefits and limitations of using natural sorbents have been highlighted.

2. Cellulose-based sorbents

Cellulose is one of the structural elements of plants and other living species such as bacteria [20], which makes it an easily available substrate. Cellulose found application not only as sorbent for removal EDCs

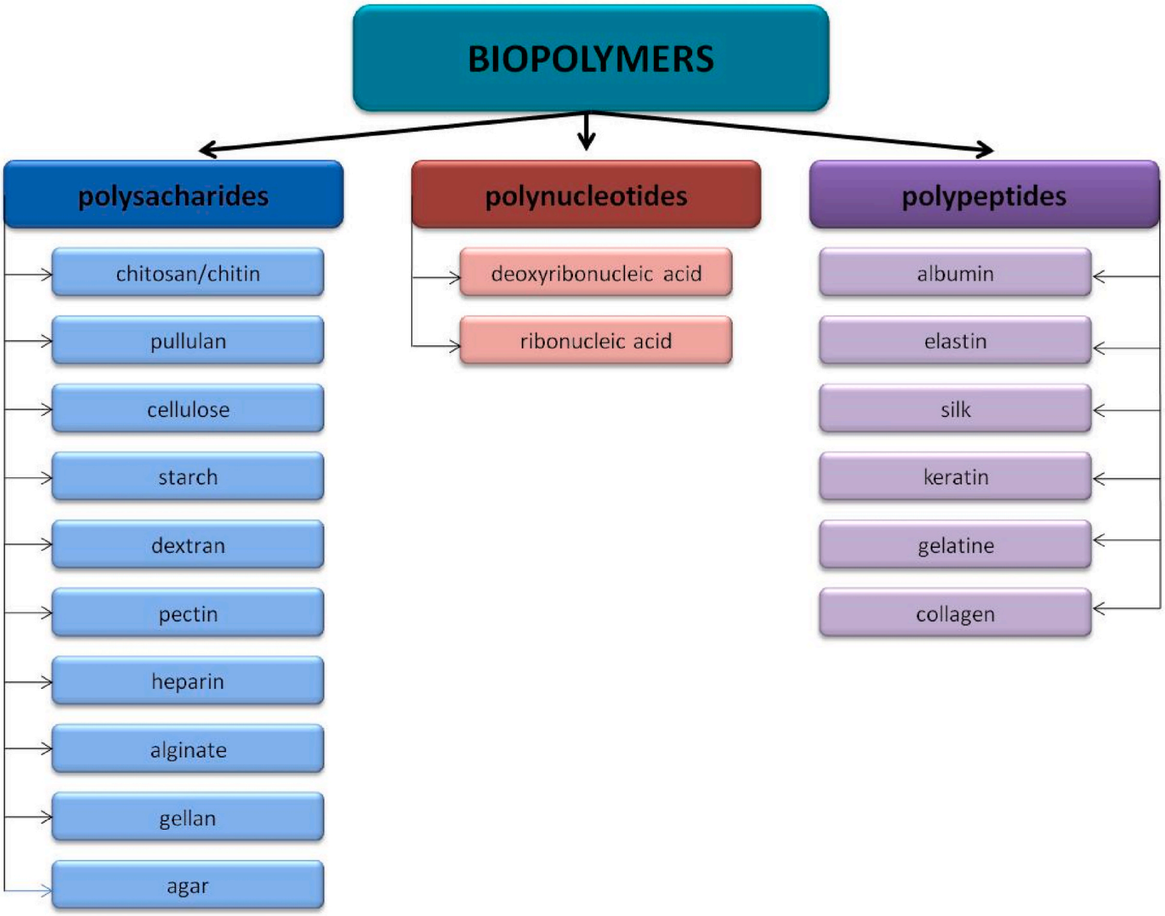
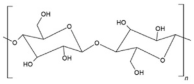
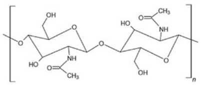
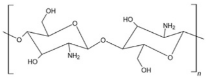


Fig. 1. Schematic classification of biopolymers.

Table 1
Basic information on cellulose, chitin, and chitosan.

Biopolymer	Cellulose	Chitin	Chitosan
Sources	- Plant sources (wood, bamboo, sugarbeet, banana rachis, cotton, fique, kapok, agave, jute, kenaf, flax, hemp, vine, sisal, coconut) - Other living species (algae, fungi, bacteria, and some sea animals such as tunicates) - Agricultural wastes (sugarcane bagasse and rice husk)	- Aquatic organisms (corals, horseshoe worms, lamp shells, sponges, squid, cuttle fish, shrimps, lobster, krill, prawns, crabs), - Terrestrial organisms (insects, spider, scorpion, grasshopper, ladybug, beetle) - microorganisms (yeasts, fungi, algae)	crustacea, insects and fungi (*Mucoraceae*)
Chemical stucture			
Structure type	Linear	Linear	Linear
Function	structural support in plant cell walls; component in some bacterial extracellular matrix	structural support in insects and crustaceans exoskeleton	constituent of fungi cell walls

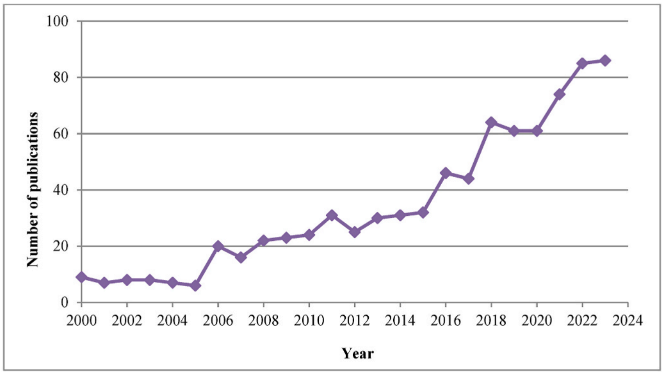


Fig. 2. Evolution in the number of publications devoted to the topic published during 2000–2023 (based on Scopus database, accessed on February 2024, keywords: biosorbent; biopolymer; solid-phase extraction; sample preparation).

from aqueous solution [21], but also in development of novel equipment, such as highly selective and sensitive microfluidic paper-based colorimetric sensor for the detection of bisphenol A [22]. Nowadays it is rising in popularity even in extraction of EDCs such as pesticides [23–28], UV-filters [29–31], BPs [32,33], parabens [31,32,34], PAHs [35,36], metal ions [37], and many more [38–42] as a greener alternative to commercially available sorbents.

2.1. Solid phase extraction

In solid phase extraction (SPE) analytes are adsorbed onto the surface of solid sorbent utilizing their affinity. This technique is widely used due to its potential of automation, the possibility to reduce solvent volumes and the large variety of available sorbents which may selectively extract analytes. SPE is widely applied for cleaning, extraction and concentration of analytes present in sample solution. In most cases, it has replaced liquid-liquid extraction (LLE) because of its time saving approach and employing smaller amounts of organic solvent. Moreover, due to diversity of commonly applied sorbents, it enables extraction of not only non-polar substances but also the polar ones [43]. It is possible to eliminate or minimize solvent volume to a micro-scale leading to solid phase microextraction (SPME) [44]. SPME as well as micro-solid-phase extraction (μ-SPE) meet the GAC principles also with regard to minimization of sorbent amount. The possibility to replace conventional sorbent with cellulose-based one led to the development of a low-cost funnel-shaped partially carbonized cellulose filter paper for pesticides extraction from fruit juices [27]. This method was cheap, simple and provided low limits of detection (LODs), good precision and wide linear range. Moreover, the developed sorbent was reused for several times, which minimized the waste amount. Another application of cellulose as SPE sorbent was presented by A. Mehdinia for the extraction of organochloride pesticides (OCPs) from seawater samples [45]. In this case, Polyaniline/Polypyrrole-Cellulose nanocomposite was applied for up to 50 extractions without significant compromise in extraction efficiency. Nowadays, the application of commercial equipment for development of new extraction strategies is also getting famous. A. Voulgari et al. introduced solid ink-printed filter paper as a green sorbent material for SPE of UV filters. The solid ink office printer was used for coating with melted ink the filter paper without using difficult chemical synthesis or modification procedures. This approach adopts the Principles of GAC [8] and reduces environmental foot print of extraction sorbent production. However, some drawbacks should be underlined, like the fact that filter paper and wax specifications are not fully known.

Not only modified materials can be used as sorbents, since F. Deki et al. presented an unmodified naturally available Luffa cylindrica sponge gourd, which is lignocellulosic material, as a SPE sorbent for the extraction of estrone, 17-β-estradiol, and testosterone in aquaculture water [39]. The sorbent was reused for 22 times without decrease in extraction efficiency. Another approach with application of cellulose-based materials was introduced in rotating-disk sorptive extraction (RDSE), where the sorbent was produced from cork stoppers. Firstly, the stoppers were conditioned, cleaned and dried at 110 °C for 12 h, then conditioned again and sliced to 2 mm thick circular-shaped pieces, with a diameter equal 10 mm. After cleaning, they were placed into the disk cavity and used for the extraction of 20 multiclass organic micro-pollutants from aqueous samples followed by GC-MS analysis. The laminar cork as an extraction sorbent, proposed by C. M. S. Vieria et al. was renewable, simple to use and with low-cost [28]. However, the drawbacks related to utilization of organic solvents during cleaning steps and high energy consumption should be addressed.

For the extraction of parabens in river water samples, cork pellet was applied in bar adsorptive microextraction (BAμE) [34]. The substrate was recycled from used wine stoppers, so the cleaning step was an indispensable task of cork pellet preparation. The advantages of this method included reduced amount of organic solvent in desorption step, minituarized extraction equipment and low-cost, and ubiquitous substrate. Moreover, each cork pellet was reused up to 5 times without reduction in the extraction efficiency.

The cork pellet in BAμE was also used for the extraction of aldrin, chlordane, dieldrin, endrin, lindane, 4,4- DDD, 4,4-DDE, 4,4-DDT, α-endosulfan and β-endosulfan in water samples (drinking water, stream water and river water) [24].The desorption solvent volume was also minimized to 120 μL indicating less negative environmental impact. A. N. Diaset al. also presented preparation of bars for BAμE for benzophenone, triclocarban, parabens [31], when A.L. Oenning et al. developed a method for hexanal and heptanal isolation [38]. The extraction bars were prepared of polypropylene hollow cylindrical tubes coated with adhesive films and then cork powder. Although the proposed sorbents were sustainable and effective for chosen analytes, the analysis time was long and organic solvent was required for desorption.

Bracts also can be applied in the SPME approach. For example, SPME fiber was created by immobilizing the bract powder on the nitinol wire by using an epoxy glue [23,29]. After heating and thermal conditioning the prepared SPME device was used in direct immersion (DI) mode. The biosorbent-based material showed satisfactory analytical performance. Moreover, the procedure of SPME device preparation was easy, cheap, simple and showed some merits over commercially available sorbents. In addition, the biosorbent-based SPME device was compared with DVB/Car/PDMS coating and similar extraction performance was observed [23]. In case of comparison among cork fiber with PDMS/DVB and PDMS fiber in UV filters extraction, cork fiber provided better results [29]. The main advantage of working with SPME is eliminating the use of organic solvents in desorption step, as analytes were released directly into GC system by the thermal desorption. Another solution with the application of a cellulose-based sorbent was proposed [32], where a 96-well plate system with a cork coating for thin-film solid phase microextraction (TF-SPME) was reported. Due to the possibility to carry out 96 experiments simultaneously, this approach offered 2 min of extraction/desorption time per experiment, which makes this method excellent for the preparation of a high quantity of samples at the same time.

2.2. Dispersive solid phase extraction

Dispersive solid phase extraction (d-SPE) is relatively fast and requires lower amounts of solvent compared to traditional SPE. In this technique, a solid sorbent is dispersed directly into the sample solution, increasing the contact area of analytes and sorbent. Once equilibrium is achieved, the sorbent is isolated by centrifugation or filtration. After that, it is possible to easily eluate the analytes from the sorbent using different solvents. It is needed to apply mechanically stable and functional sorbent of high surface area in d-SPE.

A novel approach was utilized for the extraction of PAHs, in which MOF (metal organic framework) was coupled with cellulose microspheres obtained from natural sources, resulting in creation high-surface area, stable and efficient sorbent for the d-SPE. Although the proposed method used ubiquitous cellulose as a sorbent base and reduced cost of sorbent preparation, 8 mL of organic solvent (acetonitrile) was necessary for the desorption step. Nevertheless, this method had better analytical performance than commercially available MOF-5 [35]. Modified cellulose nanoparticles were also employed for preconcentration of heavy metal ions from biological and aqueous samples [46]. Not only high preconcentration factor (200 times) was achieved, but also high recoveries and low LODs. In addition, sorbent was reused at least 5 times without any decrease of its adsorption capacity. Another MOF modification was used for the ultrasound-assisted dispersive SPME (UA-DSPME) for trace level analysis of fungicides in water, fruits and vegetable samples [41], which cause potential developmental toxicity [47]. The modification of carboxymethylcellulose biopolymer with zinc-based MOF and graphene oxide resulted in high preconcentration factors (419–426) and good analytical performance.

Carbonized cellulose nanoparticles were used for the vortex-assisted DSPE (VA-DSPE) of pesticides from vegetable and fruit juices [42]. As a result, low LODs (0.31–0.53 μg L^{-1}), high enrichment factor (257) and low relative standard recoveries (RSDs) for intra- and inter-day precision were achieved. Another approach utilized microcrystalline cellulose (MCC) in DSPME for the determination of chromium in water. Although MCC is cheap and can be used separately for extraction, it was coupled with Triton X-100 and heating procedure to increase surface availability by achieving cloud point extraction. Also, carbon fiber sorbent was used for the extraction of PAHs from tea infusions [36], however, in this case the enrichment factor compared to the above mentioned techniques, was low.

2.3. Magnetic solid-phase extraction

Magnetic SPE (MSPE) works almost on a similar concept to DSPE except the application of magnetic sorbent, which can be easily retrieved using an external magnet. Thus, the sorbents are usually comprised of composites of magnetic and other materials. For example, cellulose-based carbon fiber produced from recyclable cotton wool were modified with hollow porous $NiMn_2O_4$ nanospheres, creating together excellent extraction material with magnetic properties and utilized for BPs separation from environmental samples [33]. This material achieved low LODs (0.56–0.83 ng mL^{-1}) and good recoveries (84.3–103.5 %). In addition, after 7 cycles of extraction/desorption, no significant loss of extraction efficiency was observed. Another carbonized cellulose–ferromagnetic nanocomposite was developed for PAEs extraction from fruit juices, mineral water, injection solution, cola, and yoghourt drink packed in plastic containers [40]. Synthesis of this nanocomposite was simple and analytical performance under optimized conditions enabled achieving recoveries in a range of 57–80 % while LODs ranged between 0.15 and 0.50 μg L^{-1} and high enrichment factors from 286 to 403.

Magnetic-carboxymethyl cellulose nanofiber (Fe_3O_4-cmCNF) was employed for extraction of organophosphorus pesticides(OPPs) [25]. Although this sorbent meets the criteria for sustainable product, the issue lies in using large amounts of chemicals during carboxymethylation and sol-gel technique. Additionally, no data about reusability of Fe_3O_4-cmCNF was shown. Magnetic carbonized cellulose-MIL101(Fe) composite was also used for extraction of OPPs [26]. It presented satisfactory analytical performance and it was reusable up to 11 extraction cycles.

To sum up, cellulose-based extraction materials in comparison to commercially available sorbents do not show a decrease in efficiency. In addition, the majority of the above-mentioned sorbents may be reused, reducing by this way the cost of the extraction material. Moreover, they are biodegradable, which minimizes production of wastes. Although the production of bio-based sorbents requires application of chemicals while cleaning and manufacturing, they seem to be better solution for systematic analytical performances. Information of application of cellulose-based sorbents to EDCs extraction is presented in Table 2.

3. Chitin and alginate polymer-based sorbents

This section focuses on the use of chitin and alginate polymer-based sorbents as natural and bio-based materials for the extraction of EDCs from samples with diverse matrix compositions. Chitin and alginate, which are abundant biopolymers derived from natural sources, have a potential as sorbents because of their unique physicochemical properties [48–51]. Chitin and alginate are commonly used in various fields, including biomedical and environmental applications. When it comes to extracting environmentally friendly or biocompatible materials, chitin and alginate can be utilized to obtain a range of encapsulated delivery systems (EDSs) [49]. There are a few examples of EDCs that can be extracted using chitin and alginate.

Chitin, a natural polysaccharide found in various organisms, is composed of N-acetyl-D-glucosamine units.

Chitin has been used in cosmetics, pharmaceuticals, and biomedicine, particularly in drug delivery. The use of chitin as a biopolymer for the adsorption of EDCs has been widely studied, making it the most frequently employed biopolymer in microextraction techniques that utilize sorbents [52]. Because of its biocompatibility, it is particularly useful for drug delivery. Therefore, it is not surprising that it has also been explored in analytical methods for extraction purposes. Indeed, it has been the most commonly used biopolymer in sorbent-based microextraction schemes in recent years.

Alginate is an anionic biopolymer extracted from the cell walls of various algae species, typically in the form of sodium salt. It consists of linked residues of D-mannuronic acid (M-block) and L-guluronic acid (G-

Table 2
Cellulose-based sorbents applied to EDCs extraction.

Target analytes	Sample	Sample preparation technique	Sorbent	Determination technique	LOD	Recovery [%]	Reusability (cycles)	Reference
Pesticides	fruit juices	SPE	partially carbonized cellulose filter paper	GC-FID	0.30–0.61 μg L^{-1}	85–101	YES	[27]
OCPs	seawater	SPE	PANI/PPY/cellulose nanocomposite	GC-EDC	0.28–0.51 μg L^{-1}	77.4–102.7	YES (50)	[45]
UV filters	water	SPE	filter paper coated with a synthetic wax-like coating	LC-UV	3.4–18.1 μg L^{-1}	74.5–111.0	ND	[30]
Chloramphenicol (CAP) and Bisphenol-A	water	SPE	crosslinking cellulose with 4,4–methylenebisphenyldiisocyanate (CMDI-1)	LC-UV	10–71.9 ng L^{-1}	86.8–96.2	ND	[39]
Pesticides, PAHs and UV filters	aqueous	RDSE	laminar cork	GC-MS	0.08–1.5 μg L^{-1}	80–119	YES	[28]
Parabens	river water	BAμE	cork pellet	LC-DAD	0.3–3 μg L^{-1}	53–124	YES (5)	[34]
OCPs	water	BAμE	cork pellet	GC-ECD	3–15 ng L^{-1}	40.2–138.2	YES	[24]
Benzophenone, triclocarban and parabens	aqueous	BAμE	cork	LC-DAD	0.2–2.5 μg L^{-1}	65–123	YES (50)	[31]
Aldehydes	human urine	BAμE	cork	LC-DAD	1.00–0.73 μmol L^{-1}	88–111	YES (50)	[38]
OCPs	water	SPME	lignocellulosic material (bract powder), supported on a nitinol wire	GC-ECD	0.19–0.71 ng L^{-1}	60–113	YES (50)	[23]
UV filters	river water	SPME	cork	GC-MS	0,004–0,03 μg L^{-1}	67–117	YES (50)	[29]
3-(4-methylbenzylidene) camphor, ethylparaben, triclocarban, and bisphenol A	water	TF-SPME	96-well plate system with a cork coating	LC-DAD	0.3–5.5 μg L^{-1}	72–125	ND	[32]
PAHs	water	d-SPE	cellulose/zeolitic imidazolate frameworks-8 composite microspheres (ZIF-8@CM)	LC–FLD	0.1–1.0 ng L^{-1}	66.7–121.2	ND	[35]
Metal ions	water	d-SPE	cellulose nanoparticles modified with folic acid (Cell-FoNPs)	FAAS	0.11–3.9 μg L^{-1}	95.2–99.2	YES	[46]
Triazole fungicides	water, fruits, and vegetables	UA-d-SPME	carboxymethylcellulose/Zn-based metal–organic framework/graphene oxide (CMC/Zn(BDC)/GO) nanosorbent	GC-FID	0.3–1.5 μg L^{-1}	91.6–102	ND	[41]
Metal ions	water	d-SPME	Microcrystalline cellulose	EAAS	6 ng L^{-1}	96–106	ND	[37]
PAHs	tea infusion	d-μSPE	carbon fibers (CFs)	GC-MS	0.012–0.014 μg L^{-1}	85.0–93.5	ND	[36]
BPs	drinking water, plastic food container and sea water	MDSPE	hollow porous nanospheres-decorated cellulose-based carbon fibers NiMn2O4 - CCFs	LC-UV	0.56–0.83 μg L^{-1}	84.3–103.5	YES (7)	[33]
PAEs	fruit juices, mineral water, injection solution, cola, and yoghourt drink packed in plastic containers	MDSPE	carbonized cellulose–ferromagnetic nanocomposite	GC-FID	0.15–0.50 μg L^{-1}	57–80	ND	[40]
OPPs	water	MSPE	magnetic-carboxymethyl cellulose nanofiber (Fe3O4-cmCNF)	GC-μECD	0.03 μg L^{-1}	81.8–119.6	ND	[25]
OPPs	fruit juice and agricultural water	MSPE	Magnetic carbonized cellulose-MIL101(Fe) nanoparticles	LC-UV	0.06–0.15 μg L^{-1}	89–101	YES (11)	[26]

Abbrevitions:DSPE - dispersive SPE, d-μSPE - dispersive micro-solid phase extraction, EAAS - electrothermal atomic absorption spectrometry, FAAS - flame atomic absorption spectroscopy, GC-EDC - gas chromatography with electron capture detector, GC-FID - gas chromatography with flame ionization detection, GC-MS - gas chromatography with mass spectrometrydetection,LC-DAD - liquid chromatography with diode-array detection, LC–FLD - liquid chromatography with fluorescence detection, LC-UV - liquid chromatography with ultraviolet detection, MDSPE - magnetic dispersive solid phase extraction, ND – no data, PANI/PPY - polyaniline/polypyrrole.

block). The physical properties of alginate depend on the distribution of the M- and G-block units along the chain, which is influenced by the extraction source. Alginate can form viscous and biocompatible hydrogels when crosslinked with different agents, with divalent cations being the most commonly used [49].

The adsorption mechanisms of chitin and alginate-based sorbents for EDC removal involve physical interactions (e.g., hydrophobic interactions and π–π stacking) and chemical interactions (e.g., hydrogen bonding and electrostatic interactions) between the sorbent and EDCs. The presence of functional groups on the sorbent surface further enhances the adsorption affinity [53].

3.1. Applications of Chitin and alginate polymer-based sorbents in extraction of EDCs

Chitin- and alginate-based sorbents have demonstrated excellent performance in extraction of EDCs from various sample matrices, including water, wastewater, soil, sediment, and biological samples. Sorption efficiency can be influenced by factors such as pH, temperature, contact time, sorbent dosage, and the presence of competing substances [11–13].

Chitin is a highly suitable option for adsorbing toxic metal ions from water because it contains multiple chelation sites, as well as amino and hydroxyl groups that attract metal ions through coordination bonds or ion exchange [11–13]. Numerous studies have focused on evaluating the adsorption capabilities of chitosan and its modified forms for the removal of various heavy metals [14–16].

Chitin-based nanomaterials have been investigated for their ability to adsorb or remove dye molecules, with hydroxyl groups being effectively utilized in dye adsorption, while amine groups play a significant role in influencing other biopolymer activities. Menkiti and Onukwuli [54], have shown that diminishing the acetylation degree of chitosan increases the relative proportion of amine groups available for protonation, thus favoring the adsorption of dyes such as Acid Green 25. However, the alteration in these adsorption features is not proportional to the degree of deacetylation or acetylation, but varies with the nature of the dyes [55] and the repartitioning of acetyl groups in the macromolecular chains [50], depending largely on the preparative process. Chitin nanocrystal-decorated biohybrid aerogels based on CNFs have been shown to be efficient for wastewater treatment [56].

In the case of pesticide removal from water, the use of low-cost materials such as nanomaterials, nanosorbents, and polysaccharide-based sorbents has proven to be effective. Chitin have demonstrated high performance for biosorbing pesticides. The presence of hydroxyl groups in chitin influences their conformations, chemical transformations, and kinetics. It has been found to remove over 90 % of the herbicide oxadiazine from water through strong binding (chemisorption) [57]. Modified chitosan nanomaterial matrices can be employed for biosorbing organic and inorganic contaminants and their sustainability can be enhanced by incorporating reinforcement and supporting matrices such as crosslinkers and polymers [58].

Alginate has been used in sorbent-based microextraction techniques, offering desirable analytical features and applications. Recently, several studies have reported the incorporation of this biopolymer in sorbent-based microextraction techniques [59]. In all documented instances of using alginate in microextraction techniques, calcium chloride ($CaCl_2$) was employed as a crosslinking agent to create an alginate hydrogel. In addition, alginate acts as a matrix to disperse supplementary solid materials, thereby increasing the surface area. This contributed to the enhanced interaction between the target compounds and the sorbent. The preparation method for sorbents containing alginate varies depending on the specific sorbent-based approach and the additional materials incorporated into the sorbent [23,24]. Alginate has been extensively employed in wastewater remediation because of its stability, high water permeability, biodegradability, and non-toxicity. It has been proven effective in adsorbing contaminants, particularly heavy metal cations [25–27].

Alginate-based sorbents have gained attention for their ability to form stable bio-hydrogel beads and serve as catalytic support materials, providing advantages such as a high surface area, network structure, and rich surface functionalities [28,29].

Chitin- and alginate-based sorbents have be considered as promising greener extractive materials for the removal of EDCs from samples with different matrix compositions. Their renewable nature, biodegradability, and adsorption capability make them attractive alternatives to conventional sorbents. Further research and development efforts are required to optimize their performance and overcome the existing challenges, ultimately enabling their widespread application in EDC extraction and environmental remediation. A summary of chitin-based sorbents that have been applied to extract and determine EDCs in different sample matrices is presented in Table 3.

4. Chitosan-based sorbents

A linear β-1,4-linked polysaccharide generally produced by the deacetylation of chitin, chitosan is a natural polymer. Being non-toxic, readily biodegradable and totally environment friendly, it is a polymer that has attracted attention in many applications. As a sorbent for sample preparation, chitosan can be chemically modified to introduce new functions that improve the extraction of target analytes.

Chitosan can be integrated with a wide range of materials to produce sorbents that extract organic compounds. The polymer skeleton contains amino ($-NH_2$) and hydroxyl (-OH) groups which can be covalently crosslinked to form chitosan hydrogel [60]. The adsorption of EDCs is enabled by hydrogen bonding between the $–NH_2$ or –OH groups of chitosan and phenolic –OH groups of the target [61]. The hydrophilic property of chitosan-based materials improves the dispersibility of the sorbent in aqueous samples, which increases the contact rate between the sorbent and the analyte and boosts extraction efficiency [60].

Various modification strategies have been implemented to enhance the adsorption capacity of chitosan-based sorbents. Chemical crosslinking effectively improves the mechanical strength and chemical stability of chitosan but occupies amino or hydroxyl groups, reducing adsorption [62]. The properties of sorbents have also been enhanced by grafting, coating or compositing chitosan with materials such as multiwalled carbon nanotubes [60], polyaniline [61], *m*-phenylenediamine [63], and graphene oxide [64]. The choice of materials and modification strategy for a chitosan-based sorbent for EDCs depends on the possible interactions between the sorbent and the target. Chitosan-based sorbents have been designed as magnetic materials, microspheres, cryogel, foam or composite-based sorbents, and coatings (Fig. 3). A summary of chitosan-based sorbents that have been applied to extract and determine EDCs in different sample matrices is presented in Table 4.

4.1. Magnetic chitosan sorbents

Magnetic chitosan ($Chi@Fe_3O_4$) particles have been prepared to extract bisphenol A and 4-tert-butylohenol from water in adsorption processes that involve π-π interaction, n-π interaction and hydrogen bonding. Bisphenol A and 4-tert-butylohenol were efficiently extracted by $Chi@Fe_3O_4$ particles with recoveries ranging from 95.6 % to 101.2 % [65]. To improve the extraction of some EDCs, magnetic chitosan particles have been integrated with affinity materials such as polyaniline, graphene oxide and *m*-phenylenediamine. Chitosan-functionalized magnetite (Fe_3O_4) nanoparticles were fabricated and composited with polyaniline ($PANI@Chi@Fe_3O_4$) for the magnetic solid-phase extraction (MSPE) and enrichment of the EDCs bisphenol A, triclosan and 2, 4-dichlorophenol. The co-precipitation of Fe_3O_4 and chitosan produced hydrophilic chitosan layers on the Fe_3O_4 nanoparticles. Recoveries in the range of 85–107 % were achieved [61]. A magnetic chitosan, also coated with polyaniline, was successfully applied to extract trace PAEs from diapers and baby wipes [67]. In an earlier work,

Table 3
The applications of chitin-based sorbents for the extraction and determination of EDCs.

Target analytes	Sample	Sample preparation technique	Sorbent	Determination technique	LOD	Recovery [%]	Reusability (cycles)	Reference
SDP	Coal washery effluent (CWE) medium Crab Shell	Coag-flocculation	Chi@Fe_3O_4	LC-UV	ND	94.8–99.9	ND	[54]
Methyl orange (MO)	Aqueous solution	MLPE	Chitosan 10B	UV-spectrophotometer	5.0 ng mL^{-1}	90.8–99.9	ND	[55]
Bio-aerogels	Water	MSPE	Cellulose nanofibers (CNFs) and chitin nanocrystals (CNCs)	Electron microscope	ND	80.1–92.9	YES (5)	[56]
Oxadiazon	Water	LPE	Activated carbon and chitosan	GC-MS/MS	1.89–2.27 ng L^{-1}	72.6–97.6	ND	[57]
$CuFe_2O_4$	Lithium batteries	MSPE	Cubic $CuFe_2O_4$ and tetragonal $CuFe_2O_4$ nanoparticles	Cyclic voltammetry	0.01 V	87.0–104.0	ND	[58]

Abbreviations: SDP - Suspended and Dissolved Particles; MLPE – micro-liquid phase extraction; LPE – liquid phase extraction.

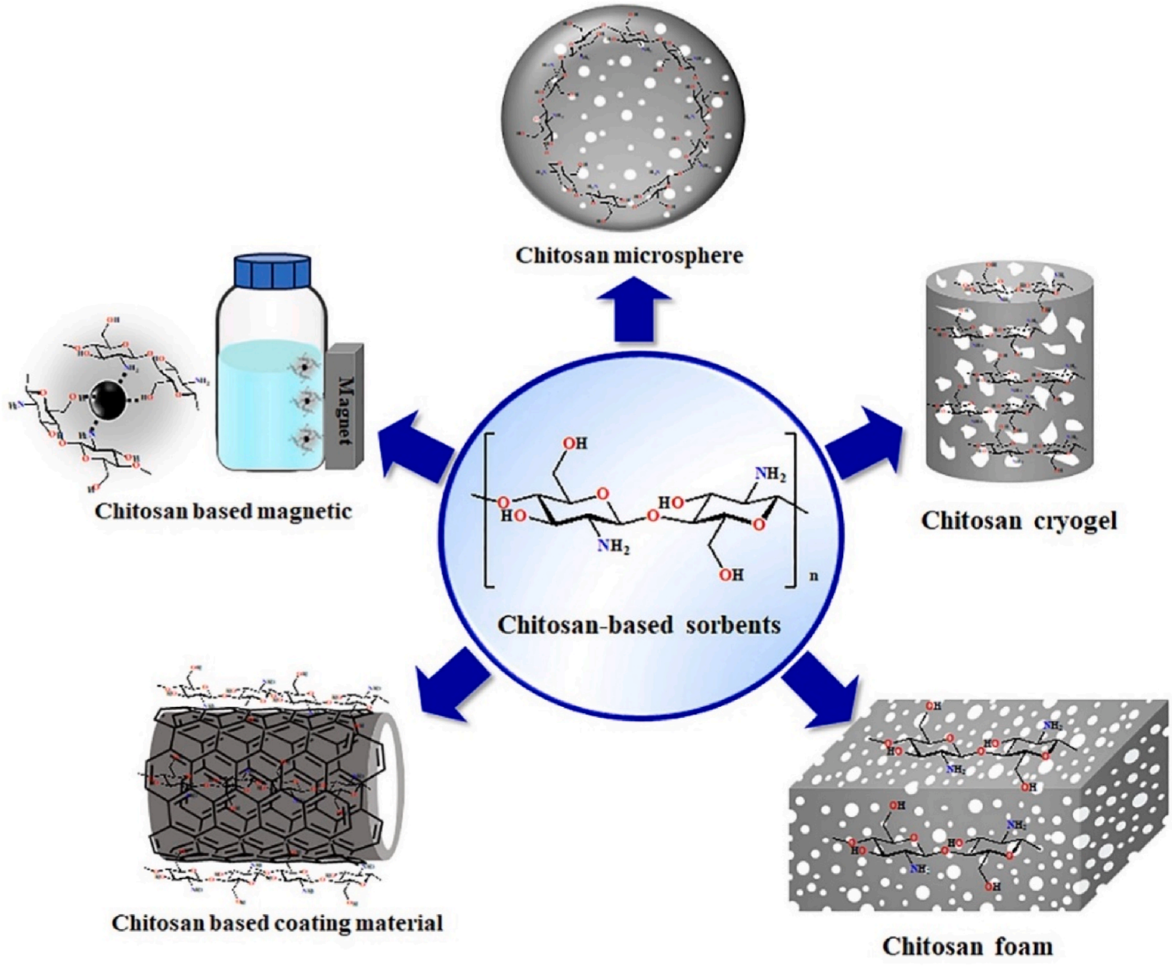


Fig. 3. The fabrication and application of chitosan-based sorbents for the extraction of EDCs.

a polyaniline-grafted chitosan sorbent (PANI@Chi) was synthesized for the dispersive solid-phase extraction (d-SPE) and enrichment of PAEs. The PANI@Chi sorbent recovered PAEs in the range of 82.0–103.0 % [66].

Other affinity materials have also been used successfully with chitosan. Chitosan-functionalized Fe_3O_4 was grafted with graphene oxide (Chi-Fe_3O_4-GO) to extract EDCs from water samples. The sorbent achieved recoveries in the range of 85.6–97.7 % [64]. A composite sorbent of chitosan-coated Fe_3O_4 and *m*-phenylenediamine (PPD@Chi@Fe_3O_4) extracted PCBs from water samples, achieving recoveries of 94.0–108.0 % [63]. Magnetic chitosan sorbents generally exhibit good stability and can be reused (Table 4).

4.2. *Chitosan-based microspheres*

Chitosan microspheres were prepared by a simple precipitation

Table 4
The applications of chitosan-based sorbents for the extraction and determination of EDCs.

Target analytes	Sample	Sample preparation technique	Sorbent	Determination technique	LOD	Recovery [%]	Reusability (cycles)	Reference
BPA, 4-tert-BP, 4-tert-OP	River water and wastewater	MSPE	MCGO	LC-UV	4.69–18.34 ngL^{-1}	85.6–97.7	YES (5)	[64]
BPA, 2,4-DCP, TCS	Water	MSPE	PANI@Chi@Fe$_3$O$_4$	LC-DAD	0.10–0.13 ng mL^{-1}	85.0–106.7	YES (6)	[61]
BPA, 4-tert-BP	Water	MSPE	Chi@Fe$_3$O$_4$	LC-UV	ND	87.6–101.2	YES (5)	[65]
PCBs	Water	MSPE	PPD@Chi@ Fe$_3$O$_4$	GC-MS/MS	0.11–0.32 ng L^{-1}	94.0–108.0	YES (10)	[63]
PAEs	Milk	d-SPE	PANI@Chi	LC-UV	0.1–0.3 ng mL^{-1}	82.0–103.0	ND	[66]
PAEs	Diapers and wet paper	MSPE	PANI@Chi@Fe$_3$O$_4$	GC-FID	0.0002–0.0005 μgmL^{-1}	ND	ND	[67]
Parabens	Water	UA-SPE	MOF@Chi	LC-MS/MS	0.09–0.45 μg L^{-1}	78.8–102.1	YES (10)	[68]
PCBs, PBDEs	Water	μ-SPE	Chi-MWCNTs-Me	GC-MS	0.12–0.60 ng L^{-1}	82.4–104.1	ND	[60]
BTEX-S	Water	μ-SPE	Chitosan microspheres	GC-MS	0.01–0.04 μg L^{-1}	59.0–97.0	YES (10)	[69]
Parabens	Water	SPE	Chitosan-coated activated carbon	LC-DAD	6–15 ng L^{-1}	96.7–107.0	ND	[70]
PAEs	Contact lens storage solution and artificial saliva in contact with baby teethers	μ-SPE	PPY-Chi cryogel stir bead	LC-DAD	3.9–4.4 ngmL^{-1}	81.3–106.3	YES (3)	[71]
Chlorophenols	Water	SPME	Chi-ZnO	LC-UV	0.1–2 μg L^{-1}	93.0–102.0	ND	[72]

Abbreviations: 2,4-DCP - 2,4-dichlorophenol; 4-tert-BP - 4-tertiary butylphenol, 4-tert-OP - 4-tertiary octylphenol; BPA - bisphenol A; BTEX-S - benzene, tuoluene, ethylbenzene, xylene and styrene; Chi-MWCNTs-Me - chitosan functionalized multiwall carbon nanotubes coated polypropylene membrane; Chi-ZnO - chitosan-ZnO nanorod; MCGO - magnetic chitosan graphene oxide; MS/MS –tandem mass spectrometer; PBDEs - polybrominated diphenyl ethers; PPY-Chi cryogel stir bead - polypyrrole-chitosan cryogel stirbead; TCS – triclosan; LC - liquid chromatography.

process involving chitosan solution in sodium hydroxide and cross-linking with glutaraldehyde [69], which formed a porous structure in the microspheres by inter-molecular cross-linking interactions. The porous structure trapped target molecules adsorbed on the surface of the sorbent. Extraction efficiency ranged from 59 to 97 % for BTEX-S (benzene, toluene, ethylbenzene, xylenes and styrene). The cross-linked chitosan microspheres showed good mechanical stability and could be reused up to 10 times.

4.3. *Chitosan cryogel*

Chitosan cryogel is highly elastic and has a sponge-like macroporous structure. It can be used as a supporting material to entrap adsorption materials such as nanoparticles or polymers. Cryogel is normally prepared by freezing a chitosan solution. Chitosan cryogel is simple to fabricate, can be easily prepared in various formats, is environmentally friendly, and has good physical and chemical stability as a supporting material for sorbent applications. Furthermore, when chitosan cryogel is applied as an SPE sorbent, the highly porous structure of the cryogel can reduce back pressure, allowing samples to be loaded at high flow rates that reduce extraction time. Chitosan cryogel sorbents have been designed in different forms and utilized effectively as stir-bead MSPE [71], and SPE sorbents [73]. Polypyrrole was incorporated into chitosan cryogel beads to extract four PAEs. The extraction recoveries of the four PAEs were in the range of 81.2–106.6 % [71]. Elsewhere, a chitosan cryogel monolith SPE sorbent was successfully applied to extract pesticides [73]. The proposed monolith chitosan cryogel sorbent could also be applied to extract EDCs if suitable affinity materials were incorporated.

4.4. *Chitosan foam or composite-based chitosan sorbents*

A composite chitosan sorbent was fabricated to extract EDCs in aqueous samples. The different formats have included a composite foam. A highly porous composite of a metal organic framework and chitosan foam (MOF/Chi) was fabricated using an ice-templating process. The fabricated MOF/Chi foam exhibited excellent adsorption ability and reusability for the extraction of parabens. The MOF/Chi foam extracted parabens from water with recoveries in the range of 78.8–102.1 % [68].

4.5. *Chitosan-based coatings*

Chitosan composite sorbents have been designed as coatings for the micro-solid-phase extraction (μSPE) of EDCs. A composite of chitosan and multi-walled carbon nanotubes was functionalized by acid oxidation and coated on the surface of a polypropylene membrane (Chi-MWCNTs-Me) to extract EDCs from water. The sorbent had a hydrophobic interior of MWCNTs and a hydrophilic chitosan exterior coating. The chitosan polymer helped to improve the wetting of MWCNTs while MWCNTs provided a large surface for the adsorption of analytes. The Chi-MWCNTs-Me demonstrated good extraction efficiency for polychlorinated biphenyls and polybrominated diphenyl ethers, with recoveries from spiked water that ranged from 86 to 104 % [60]. Chitosan-coated activated carbon (Chi-activated CA) was utilized for the extraction of parabens in water samples. Using chitosan as a supporting material, mechanical and chemical properties of the sorbent were improved. The Chi-activated CA extracted parabens in water samples efficiently, producing recoveries between 96.7 and 107.0 % [70].

5. Agricultural waste-based sorbents

Agricultural waste contains organic materials that humans discard during agricultural production. This category includes plant residues, livestock and poultry waste, byproducts from agricultural and related processing, as well as rural household waste. Primarily coming from our daily lives, agricultural waste specifically includes crop stalks and animal manure. It is produced in large quantities from many sources. Moreover, it is generally environmentally friendly and biodegradable. The huge production of agricultural waste also presents a challenge of its proper disposal to reduce its environmental impacts. Since these materials are naturally enriched with various kinds of functional groups they can be utilized as sorbents for adsorptive removal of pollutants and there is a long history of such applications [74,75]. Of course, these materials are preferred over synthetic sorbents because of their easy availability, abundance, environmentally friendliness, low-cost, and minimal secondary pollution. The most important aspects in exploring new sorbents revolve around enhancing the selectivity, extraction capacity, and finally, the thermal, chemical, and mechanical stability. The new trends indicate utilization of agricultural waste-based sorbents in analytical sample preparation as a sorbent media. Although such applications are not large in number, some exciting results have been reported.

In this regard, the following materials have been discussed: i) diatomaceous earth, ii) biochar, iii) carbon aerogels, iv) silk and cotton fibers and their carbonized forms, v) crop waste.

Diatomaceous earth is an amorphous silicate sediment which forms from the accumulation of unicellular carapaces of microorganisms on tiny algae in lakes and oceans. It is generally comprised of minute particles in hollow cylindrical shapes and acts as a sponge that can absorb significant quantities of liquids. In addition to silica, it includes aluminum, iron, calcium, magnesium, sodium, and potassium in its composition. One of its applications includes filtration of beer, after which it can be regenerated by thermal treatment. The recycled diatomaceous earth was used as a sorbent for extraction of endocrine disrupting compounds (BPA, benzophenone, triclocarban, 4-methylbenzylidene camphor and 2-ethylhexyl-p-methoxycinnamate) from environmental waters by employing it in TF-SPME combined with 96 well-plate system [76]. The use of recycled material as sorbent in SPME further enhances the greenness of the procedure. In addition, its combination with 96 well-plate system provides significant advantages for high throughput analysis. SEM and FTIR characterization supported the adsorption properties of the material. SEM images revealed high porosity and large superficial area, while the presence of OH groups was observed by FTIR, which can play a significant role in extraction. When the desorption step is performed using various solvents, it is important to evaluate the stability of the sorbents in such media after repeated extraction/desorption steps. As shown in Fig. 4, recycled diatomaceous earth sorbent retained a significant extraction performance even after 20 extraction-desorption cycles. Acetonitrile: methanol (50:50) was an optimum desorption solvent in this study [76].

In another study, chemically modified biochar obtained from coconut husk was used as dispersive solid-phase extraction sorbent to remove interferences from acetonitrile extract of PAEs from the breast milk and urine samples. It was found to be effective and environmentally friendly compared to other synthetic cleanup sorbents [77].

Aerogels as emerging nanomaterials are known for their three-dimensional network, highly porous and controllable structures, low densities, large specific surface areas, and exceptional thermal and chemical stabilities. Inorganic, organic, and modified aerogels have been used for extraction purposes. Carbon aerogels are very famous in this regard because of their excellent adsorption capabilities. They are mostly prepared from organic polymers, carbon nanomaterials, and other synthetic substances. Tedious synthesis procedures and consumption of large volumes of hazardous solvents is a common issue with silica, carbon, and organic aerogels. However, recently there is growing interest in biocharcoal aerogels because of their synthesis from low-cost and environmentally friendly natural materials. Thus, a biocharcoal aerogel was directly synthesized via freeze-drying and carbonizing the inner spongy layer of pomelo peel under high temperature and oxygen-limited environment (Fig. 5). This was employed as coating for in-tube SPME (IT-SPME) to extract PAHs from different water and soft drink samples. IT-SPME device showed excellent extraction performance and reusability which was evident from the obtained %RSDs after 1st, 50th and 100th tests were less than 4.2 %. The chemical stability was demonstrated by performing extraction before and after treatment with different chemicals while the peak areas were slightly changed for PAHs with %RSDs 3.6 % [78].

Silk fiber, cotton fiber, and carbonized silk fibers have also been used for extraction applications. Silk fiber contains hydroxyl, carboxyl, amino, and other hydrophilic groups, along with lot of internal pores, which are supportive to its adsorption properties. The surface properties and large specific surface area also highlight their potential as extractants for different analytes. Silk fibers were packed inside the PEEK tube which was connected to LC system and utilized for extraction of derivatized aldehydes from various samples. Silk fibers packed PEEK tube were utilized for IT-SPME. The extraction was attributed to hydrogen bonding and electrostatic interactions [79]. In another work, IT-SPME was used for extraction of PAHs from water samples by employing carbonized silk fibers as a sorbent. The carbon material obtained from biomass exhibited a good affinity toward PAHs [80]. The carbonized cotton fibers were also employed for extraction of analytes, and they showed better extraction efficiency for PAHs than PAEs and estrogens [81].

Oilseed rape straw (OSRS) crop waste was used for synthesis of hierarchical porous carbon by a straightforward hydrothermal reaction and KOH activation. The resulting material had a very high specific surface area of 2551 m^2/g, high pore volume, good poor distribution, and most importantly very high thermal stability (>450 °C). All these features indicate this material can be utilized for extraction of analytes, also in conditions where thermal stability is needed. Thus, it was utilized as a SPME coating for extraction of chlorobenzenes, polychlorinated biphenyls, PAHs, and PAEs and it showed extraction capacity higher than commercial PDMS fiber [82].

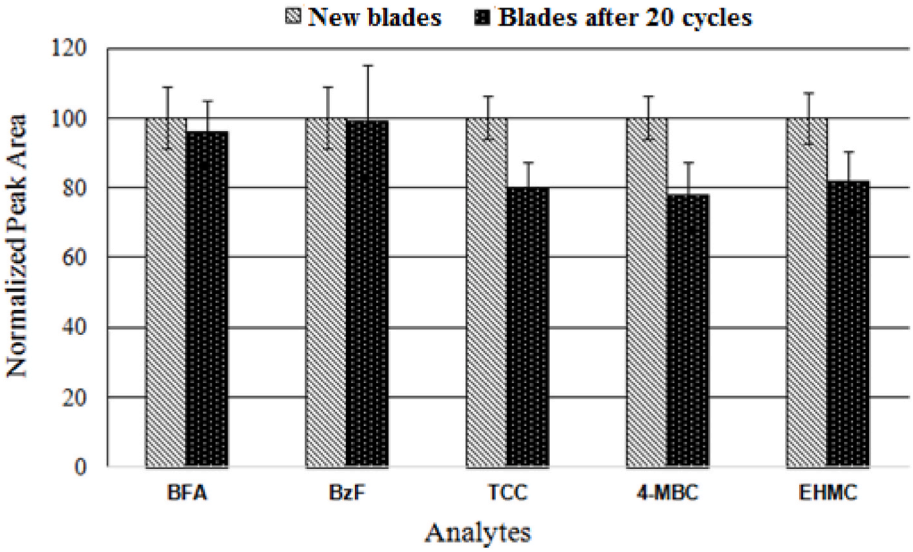


Fig. 4. Stability evaluation of diatomaceous earth as sorbent phase for TF-SPME after 20 extraction/desorption cycles. Reused from Ref. [76] with permission. Copyright (2017) Elsevier B.V. The figure is taken from supplementary data.

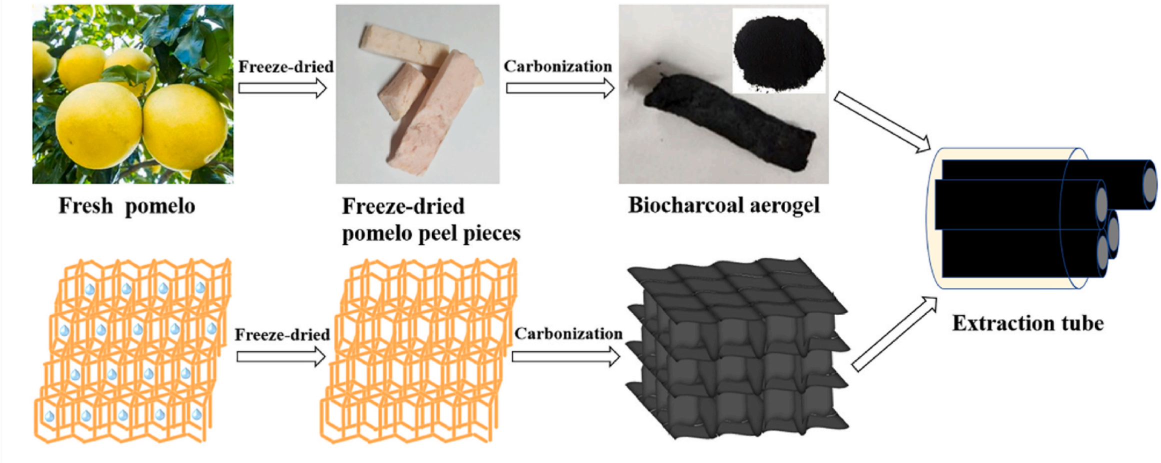


Fig. 5. Schematic illustration of the procedure adopted for the preparation of biocharcoal aerogel and the extraction tube. Reused from the supplementary information of [78] with permission. Copyright (2020) Wiley-VCH GmbH.

6. Conclusions and future perspectives

Concluding, the use of biopolymers as greener extraction materials for EDCs appears to be a promising strategy for a smaller environmental footprint. Biopolymers present many advantages over synthetic polymers, such as biodegradability, low cost, low toxicity, and abundant availability. In addition, they present a high number of desirable features, including high thermal, chemical, and structural stability and controllable porosity. Furthermore, they can have a wide field of applications due to the presence of a variety of functional groups enabling them to bind with various compounds, while more importantly, their adsorption performance may be easily increased by further functionalization.

For the removal of EDCs cellulose-based extraction materials exhibit high efficiency in their removal compared to commercially available sorbents. Moreover, the majority of them exhibit also reusability, reducing by this way the overall cost of the extraction material. Although the production or cleaning specific sorbents may require the application of chemicals, they seem to be better solution for systematic analytical performances. Moreover, they are biodegradable, which minimizes production of wastes.

Chitin- and alginate-based sorbents present also many advantages like renewable nature and biodegradability, combined with high adsorption efficiency for EDCs. However, despite their potential, the utilization of chitin- and alginate-based sorbents for EDC extraction still faces challenges, including limited reusability, scalability, and the need for optimization in complex sample matrices. Future research should focus on addressing these challenges, exploring novel modifications, and investigating the potential of hybrid sorbents and composites for enhanced EDC extraction.

Chitosan based materials exhibit also high extraction efficiency for EDCs. Being non-toxic, readily biodegradable and totally environment friendly the chitosan-based sorbents can be powerful candidates for environmental analysis. Moreover, chitosan can be easily chemically modified to introduce new functions that can improve the extraction of target analytes while its hydrophilic property can improve the dispersibility of the sorbent in aqueous samples, increasing by this way the contact rate between the sorbent and the analyte and boosting the extraction efficiency.

Finally, agricultural waste-based sorbents present many advantages such as easy availability, abundance, environmentally friendliness, ease of synthesis and modification, low-cost, and minimal secondary pollution. Up to now, they exhibit high sorption efficiency for EDCs in combination with high stability offering the potential of reuse for many consecutive cycles. However more work is needed to be done in order to enhance their selectivity, extraction capacity, and their thermal, chemical, and mechanical stability.

To sum up, natural biopolymers are an attractive alternative for EDCs extraction, however further research efforts are required to optimize their performance, increase their selectivity and reusability thus enabling their widespread application in EDCs removal and environmental remediation.

CRediT authorship contribution statement

Justyna Płotka-Wasylka: Writing – review & editing, Writing – original draft, Supervision, Project administration, Investigation, Conceptualization. **Aneta Chabowska:** Writing – original draft, Investigation. **Suwijak Pantanit:** Writing – original draft, Investigation. **Opas Bunkoed:** Writing – review & editing, Writing – original draft, Investigation. **Michel Y. Fares:** Writing – original draft. **Muhammad Sajid:** Writing – review & editing, Writing – original draft, Investigation. **Dimitra Lambropoulou:** Writing – review & editing, Writing – original draft, Funding acquisition. **Aleksandra Kurowska-Susdorf:** Writing – review & editing. **Natalia Jatkowska:** Writing – original draft, Visualization, Project administration, Conceptualization.

Declaration of competing interest

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

Data availability

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

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