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Review

Returning to Nature for the Design of Sorptive Phases in Solid-Phase Microextraction

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Abstract: Green analytical chemistry principles aim to minimize the negative impact of analytical procedures in the environment, which can be considered both at close (to ensure the safety of the analysts) and global (to conserve our natural resources) levels. These principles suggest, among other guidelines, the reduction/minimization of the sample treatment and the use of renewable sources when possible. The first aspect is largely fulfilled by microextraction, which is considered to be among the greenest sample treatment techniques. The second consideration is attainable if natural products are used as raw materials for the preparation of new extraction phases. This strategy is in line with the change in our production system, which is being gradually moved from a linear model (take–make–dispose) to a circular one (including reusing and recycling as key terms). This article reviews the potential of natural products as sorbents in extraction and microextraction techniques from the synergic perspectives of two research groups working on the topic. The article covers the use of unmodified natural materials and the modified ones (although the latter has a less green character) to draw a general picture of the usefulness of the materials.

Keywords: green chemistry; circular economy; natural products; sorbents; cork; cotton; pollen; seeds; paper; wood

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1. Introduction

The irrational fear of chemicals, called chemophobia, is caused by the negative perspective among the general public of the impact of chemistry in our health and environment [1]. While fighting this chemophobia by intensive teaching at different levels [2,3] (including the general public as a target, too) of the benefits that chemistry provides to our societies, chemists must be aware of the potential risks they deal with, to design effective strategies for their control and minimization. In the environmental protection context, analytical chemistry plays a role, since it allows the detection of environmental pollution and permits the monitorization of the remediation protocols. However, this positive contribution must be complemented by the reduction of the collateral impact of analytical procedures, which is the primary goal of green analytical chemistry (GAC) [4–6].

In 2012, Professor Namieśnik et al. theorized about the main guidelines of GAC, providing 12 general principles to be followed in order to reduce the potentially deleterious effects of analytical procedures [7]. The application of these principles is desirable as long as the main aim of analytical chemistry, providing useful and reliable information, is fulfilled. For example, the first principle recommends the direct analysis of samples avoiding in that way the sample treatment. Although this principle identifies one of the trends of current research in analytical sciences, it is difficult to be applied when complex samples containing the analytes at very low concentrations are processed. In such scenarios, the simplification of the sample treatment and the reduction of the sources applied (reagents, energy) can be a more practical objective, at least currently. Microextraction techniques fulfill the latter criteria [8], and they are considered among the greenest sample treatment techniques [9].

Microextraction techniques have evolved in the last decade following some key trends. Among them, the development of new extraction phases can be highlighted, considering the context of this review article. In this evolution, the tenth (use of renewable resources) and eleventh (replace or remove toxic reagents) principles of GAC are especially relevant [7]. In the liquid microextraction context, environmentally friendly solvents [10,11] such as CyreneTM [12] and deep eutectic solvents [13] are clear examples of this progress.

The paradigm of our production system, which up to now has been based on a linear "take–make–dispose" model, is progressively changed to a circular model [14] where reusing, repairing, refurbishing, and recycling appear as key terms. The use of surpluses of natural products as raw materials for the preparation of new sorbents is an interesting contribution of analytical chemistry for changing the production model. This review article, which combines the vision of two research groups working in the topic, tries to draw the general picture of the potential of natural products for the synthesis of new sorptive phases in solid phase extraction and solid phase microextraction. The article will cover strategies with different green characteristics, as some of the natural materials can be used with minimal modifications, but others require a chemical adjustment depending on the analytes to be extracted.

2. Cork

Cork is defined as the outside bark of the *Quercus suber* L., which is commonly known as cork oak tree. This evergreen oak can be found in southwest Europe and northwest Africa and grows up to 20 m height. Due to its cellular structure and chemical composition, cork exhibits some physical properties such as a high coefficient of friction, resilience, high energy absorption, excellent insulation properties, impermeability, low conductivity, and low density, which makes it an excellent material for a variety of applications. It is mainly used as wine bottle stopper; nevertheless, various other applications have been attributed to cork and its derivatives such as flooring and walls coverings, acoustic and vibrating insulation, ecoceramics, and ecodesign [15,16].

Cork has unique microscopic features compared to other lignocellulosic materials. Its hollow polyhedral prismatic cells may present honeycomb or brick wall structures when observed from radial or axial directions, respectively. On average, cork cells are 45 mm tall and have 15–20 mm of face and 1–2 mm of thickness. The chemical composition of cork varies according to seasonality and territory but mainly consists of hydrophobic biopolymers such as suberin (±40%) and lignin (±24%), the hydrophilic polysaccharides cellulose and hemicellulose (±20%), and 15% of other extractives e.g., waxes and tannins. The main cork constituent comprises phenolic, long-chain, and hydroxy fatty acids, which are linked by ester groups framing a polyester structure [17]. Moreover, granules and cork powders exhibit surface charge according to the environment pH. The point of zero-charge values between 2.1 and 4.6 can be reached, corresponding to acidic range. Meanwhile, about 40% of the total acid groups correspond to strong acids and 50% correspond to the overall phenolic OH groups. Therefore, its formidable characteristics are promising resources with potential application on adsorption technologies [18]. Herewith cork is a natural, cheap, renewable, fully sustainable, and biodegradable raw material with a very relevant advantage over other carbonaceous materials to be explored as a sorbent in many applications [19].

Since it was first described as an adsorbent in 2005, [20] its use in environmental applications for the removal of a variety of organic and inorganic pollutants has gained considerable attention, and a large number of research articles, as well as reviews, covering this approach have been published [17,21–26]. The cork employment in sample preparation for microextraction purposes was firstly reported in

2011 [27] and has been increasing over the years. In the first study, powdered activated carbons (AC) from cork waste were supported for bar adsorptive microextraction (BAµE) as novel adsorbent phases for the determination of clofibric acid and ibuprofen in environmental and biological matrices [27]. The ACs were prepared by the chemical and physical activation of raw waste cork with K_2CO_3 at 700 °C for 1 h and steam at 750 °C for 1 h, respectively. For the concentrations used in the study, both carbons completely removed the two target compounds.

Further, cork was successfully applied as a coating for solid phase microextraction (SPME) devices in the determination of ultra-trace levels of organochlorine pesticides and polycyclic aromatic hydrocarbons (PAHs) in water samples, respectively, by gas chromatography [28,29]. The preparation of the fibers was performed as follows: the cork powder (200 mesh) was immobilized into wires of NiTi (0.2 mm thickness and 2 cm length) containing epoxy glue. Then, the devices were placed into a heating block for 90 min at 180 °C and conditioned at 260 °C for 60 min in the gas chromatograph (GC) inlet port before using. The natural features of the cork were modified due the heating indicating that the biosorbent suffered thermal decomposition at high temperatures. According to the chemical analysis, at 200 °C the partial decomposition of suberin, waxes and other extractives occurred. Over 90% of the polysaccharides were degraded at 250 °C, and lignin started to decompose between 250 and 300 °C. Nevertheless, the cork coatings showed similar or better extraction efficiencies than polydimethylsiloxane/divinylbenzene (PDMS/DVB) and divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) commercial fibers.

Regarding the recent publications, raw cork-based approaches have been highlighted in microextraction methodologies whereas they exhibit some unique analytical features that allow for "green", sustainable, and efficient procedures that are relevant to the current environmental concerns [30–38]. Table 1 points out the analytical features of the recent applications using raw cork-based methodologies for the extraction of different analytes from various matrices. Raw powder cork is produced from cork stoppers after cleaning with ultrapure water and overnight drying at 110 °C. Further, the powder is prepared using a sandpaper, and the resulting material is sifted to ensure 200 mesh granulometry. Afterward, the resulting powder is conditioned with acetonitrile, and it is ready to be applied as sorbent phase.

Table 1. Applications of raw cork-based microextraction techniques for different analytes and matrices. (Reference period: 2015–2019).

Technique	Raw Cork Format	Analytes	Matrix	Desorption Volume (µL)	LOQ (µg/L)	Instrumentation	Ref.
BAµE	Powder	Benzophenone, Trichlocarban and Parabens	Lagoon water	250	1.6–20	LC-DAD	[30]
BAµE	Powder	Cancer biomarkers	Urine	100	250–300	LC-DAD	[31]
DPX	Powder	10 Pharmaceuticals	Urine	85	5–10	LC-DAD	[32]
TF-SPME	Powder	Endocrine Disruptors Compounds	River water	300	0.8–15	LC-DAD	[33]
RDSE	Powder	Parabens	River water	3000	0.8	LC-MS/MS	[34]
DPX	Powder	Pb and Cd	Water	300	0.3–4.1	HR-CS GFAAS	[35]
DPX	Powder	Parabens and UV filters	Lake water	100	2.0–4.3	LC-DAD	[36]
RDSE	Laminar	Hormones	Wastewater	5000	0.01–0.062	GC-MS	[37]
RDSE	Laminar	20 Pesticides, PAHs and UV filters	River water	1000	0.3–4.8	GC-MS	[38]

BAµE: Bar Adsorptive Microextraction; **DPX**: Disposable Pipette Extraction; **TF-SPME**: Thin-Film Solid Phase Microextraction; **RDSE**: Rotating Disk Sorptive Extraction; **PAHs**, polycyclic aromatic hydrocarbons; **LC**, liquid chromatography; **DAD**, diode array detection; **HR-CS GFAAS**, high resolution continuum source graphite furnace atomic absorption spectrometer; **GC**, gas chromatography; **MS**, mass spectrometry.

Raw cork powder has been successfully applied in different microextraction approaches such as bar adsorptive microextraction [30,31], disposable pipette extraction [32,35,36], thin film-solid phase microextraction [33], and rotating disk sorptive extraction [34] as a biosorbent for the reliable determination of organic micropollutants, toxic metals, UV filters, endocrine disruptors, and compounds in aqueous samples as well as pharmaceuticals and lung cancer biomarkers in human urine. Cork exhibits significant hydrophobicity and a number of aromatic rings that can undergo effective π–π interactions with the analytes and substantially enhance the preconcentration ability of the extraction procedures. The last cork-based applications have been focused on improving the mass transfer using laminar cork for rotating disk sorptive extraction (RDSE) methodologies, demonstrating an interesting new configuration for high-throughput procedures [37,38].

Studies comparing the extraction efficiency of cork-based microextraction techniques with commercial sorbents such as C18, nylon, Oasis® HLB (Hydrophilic-Lipophilic Balance), and DVB have been proposed in some applications. In a recent study, the recovery results showed that the cork reaches higher sorption efficiency than C18, DVB, and nylon, and achieves very similar recoveries to those of Oasis® HLB in which recoveries were between 67% and 98% for Oasis® HLB, while the cork reached values between 63% and 89% [37]. In another study, on applying the optimized conditions for all sorbents, positive results were obtained for the cork-based methodology where using the same amount of sample and sorbent, the renewable sorbent provided better results when compared with the commercial C18 [34]. Therefore, cork proved to be an excellent alternative to the synthetic phases, presenting the advantage of achieving similar efficiency with a cost-effective benefit. Moreover, cork-based devices have been demonstrating an incredible performance regarding reproducibility and reusability. On Dispersive Pipette Extraction (DPX) applications, studies were conducted to evaluate the cleaning step of the pipette tip and the cork stability under several extraction cycles. The results showed that a single DPX cork-based tip maintained around 80% of the extraction efficiency with good precision (relative standard deviation lower than 20%) for all analytes with up to 15 extraction/desorption cycles [32]. In addition, an efficient cleaning of the DPX device was achieved after four cycles with the desorption solvent, enabling the reutilization of the device without carryover [36].

The advances in cork-based techniques have led to remarkable improvements with regard to environmentally friendly aspects, in particular because cork harnessed as biosorbent is originated from cork stoppers that would be discarded and are reused for the development of several analytical methodologies. Moreover, the strategy of combining this cheap and natural biosorbent with high-throughput strategies [33,38] that are able to perform fast and efficient extractions are promising trends that should be further investigated.

3. Cotton

Raw cotton fibers are mainly composed of cellulose (about 95% of the naturally occurring material). Cellulose is a plentiful, inexpensive, and biodegradable material that has been used for many purposes. The non-cellulosic constituents comprise proteins, amino acids, other nitrogen-containing compounds, wax, pectic substances, organic acids, sugars, inorganic salts, and a minimal amount of pigments. Raw fibers may be treated with selective solvents to remove the naturally occurring non-cellulosic materials, resulting in a material with cellulose content over 99% [39].

Cellulose, found in plant walls, is the most abundant raw material on Earth. It is a 1→4 linked linear polymer of ß-ᴅ-glucopyranose, which is interlinked with strong intermolecular/intramolecular hydrogen bonds besides hydrophobic bonds. This fact is possible due to the high content of hydroxyl groups on the polymer surface, providing a hydrophilic character. For this reason, the functionalization of the fibers with different groups is compulsory for being used in the microextraction context as sorbent as well as a support for nanocomposites [40]. The chemical structure indicates that the 2-OH, 3-OH, and 6-OH are the potentially available sites for the same chemical reactions that occur with alcohols. However, it must be noted that in cotton, not all the OH groups are accessible for reaction. Besides, the reactivity of the hydroxyl groups of cellulose may change depending on the swelling pretreatment, the reagents employed, and the reaction conditions. Some procedures have been carried out to achieve the correct functionalization of the fibers and therefore the applicability of the material. Etherification reactions, particularly condensation reactions, produce the most stable cotton derivatives. Hydroxyl groups of cotton cellulose may be functionalized with carboxylic acid, acyl halides, anhydrides, isocyanates, and ketenes to produce cellulose esters [41–43]. This variation provides wrinkle resistance, water repellence, flame resistance, and antimicrobial action, as well as resistance to alkaline and acidic conditions. In this way, cotton fibers may be modified with biologically active conjugates such as proteins or peptides by glycine esterification [44,45]. Accordingly, Edwards et al. employed the peptide-cellulosic material as a biosensor of human serine protease, monitoring the fluorescence produced by the reaction. Furthermore, cotton fibers have been treated with 4-formylphenylboronic acid to obtain a boronate affinity adsorbent for the determination of nucleosides from urine samples. In this case, the microextraction process was simplified drawing upon the in-pipette-tip solid phase extraction (SPE), exhibiting good selectivity, capacity, and accuracy [46]. On the other hand, cotton has been altered through graft copolymerization with polyacrylonitrile (PAN) for selective extraction via the imprinting process of copper ions from aqueous solutions [47]. In the same way, carbon-based nanomaterials such as carbon nanotubes or graphene have been incorporated into cotton fibers, being the last one employed as sorbent for the determination of multiclass pesticide residues from water samples [48], along with a large number of applications. Apart from the strategies mentioned above, many attempts, including sulfonation of the cotton, modification of the cotton surface with ion-imprinted polymers, organic ligands, and surfactants have been made to overcome the lack of selectivity of the material [49].

On another note, raw cotton has been commonly employed in the production of activated carbon fibers (ACFs or CFs) as an alternative to synthetic precursors such as PAN, viscose/rayon, phenolic, asphalt, and polyamide fibers. Typically, this green and easy modification of raw cotton consists of the pyrolysis of the cellulose fibers in an inert atmosphere, approximately at 400–700 °C, being used for many years to remove dyes and oil from environmental samples [50,51]. Figure 1 shows the macroscopic appearance of raw cotton (Figure 1a) and CFs (Figure 1b), which maintain the fibrous structure (Figure 1c) of the original substrate. Denoted as carbon fibers aerogels (CFAs) in some cases, these materials have been employed in various fields including energy storage, adsorption, thermal insulation, and flame retardancy [52]. In the microextraction context, CFAs are usually modified following the carbonization process in order to enhance the selectivity of the sorbent material. For this reason, CFAs coated with chitosan and dopamine–polyethylenimine complex were used to remove nanopollutants such as citrate-capped gold and silver nanoparticles from water samples [53]. In some cases, activation agents such as $ZnCl_2$ [54], H_3PO_4 [55], KOH or NaOH [56], K_2CO_3, $AlCl_3$, and Na_2HPO_4 [57] are used for the obtention of fibers with better strength, yield, and adsorption capacities. ACFs were used for the isolation of dyes (methylene blue, crystal violet, or Alizarin Red S) and nitrobenzene from aqueous samples [58–61], in addition to the determination of chlorophenols from urine samples [62]. In the last case, the material was immobilized in a syringe barrel allowing the dispersion of the sorbent in the sample matrix, resulting in good accuracy, sensitivity, and precision values in a simple extraction procedure. Moreover, magnetic CFs have been employed for the determination of bisphenol compounds from environmental samples [63]. On the other hand, a relation between the pyrolysis degree (concerning time and temperature) with the polarity of the resulting CFs has been recently accomplished. Thereby, the pyrolysis parameters may be tailored according to the analytical problem, increasing in this way the selectivity of the extraction process [64].

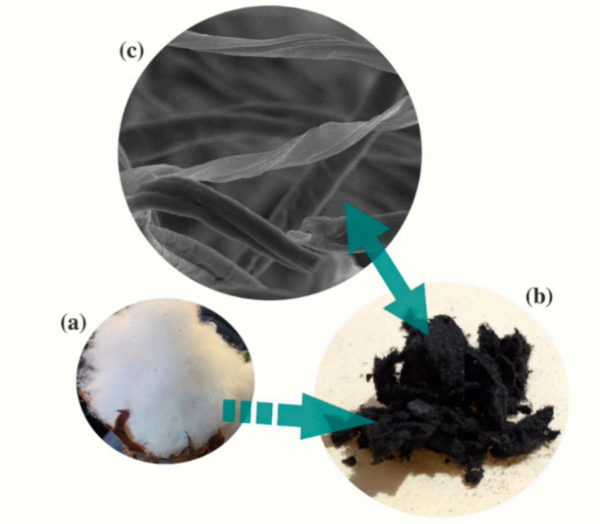

Figure 1. (**a**) Raw cotton; (**b**) Carbon fibers; (**c**) Scanning electron microscopy picture of carbon fibers where the fibrous structure is observable.

In recent years, cotton waste has been employed as a novel source in the development of cellulosic-based sorbents in order to obtain a high-added-value product at low cost. A million tons of cotton cloths are produced annually, increasing at the same time the generation of their waste. Nowadays, environmental concern has gained great importance, arising the consciousness about recycling and resource utilization. For this reason, microextraction applications using waste products, such as cotton cloths waste, are increasingly appearing in scientific publications [65–67]. Cotton cloths waste has been used for the production of nanocellulose materials [68], including activated and porous carbon [69,70]. There are two main types of nanocellulose materials arising from cotton fibers, viz. cellulose nanofibers (CNF) and cellulose nanocrystals (CNC), which differ in their dimensions, functions, and preparation methods. Generally, the production of CNF consists of mechanical treatments, while acid hydrolysis is the primary chemical process used to produce CNC [71]. These nanomaterials reveal a host of advantages such as high surface area-to-volume ratio, large aspect ratio (typically 20–70), high strength, and thermal stability, due to their nanometric dimensions together with a high degree of molecular order [72]. For this reason, CNC and CNF have been used in the microextraction context, among other applications, for isolating fluoroquinolones from egg samples as well as crystal violet dyes and magnetic nanoparticles from water samples, respectively [73,74].

The main applications of cotton in the microextraction context are summarized in Table 2.

Table 2. Applications of cotton as sorbent material in microextraction techniques for different analytes and matrices. (Reference period: 2015–2018).

Technique	Material	Analytes	Matrix	LOD	Instrumentation	Ref.
In-pipette-tip SPE	Cotton fibers modified with 4-formylphenylboronic acid	Nucleosides	Urine	5.1 and 6.1 ng/mL	LC-UV	[46]
SPE under stirring	Graphene-coated cotton fibers	Multiclass pesticide residues	Water	Low µg/L	GC-MS	[48]
D-µSPE	Carbon fibers	Chlorophenols	Urine	0.1–0.9 µg/L	GC-MS	[62]
D-µSPE	Magnetic cellulose-based carbon fibers	Bisphenol analogues	Environmental samples	0.56–0.83 ng/mL	LC-UV	[63]
D-µSPE	Carbon fibers	Pollutants of different polarities	Water	Low ng/mL	HS-GC-MS	[64]
Magnetic D-µSPE	Fe_3O_4@CCNs@MIPs	Fluoroquinolones	Egg	3.6–18.4 ng g^{-1}	LC-DAD	[73]

SPE: solid phase extraction; **D-µSPE**: dispersive micro-solid phase extraction; **Fe_3O_4@CCNs@MIPs**, molecularly imprinted polymers coated on magnetic carboxylated cellulose nanocrystals, **LC**: liquid chromatography; **UV**: Ultraviolet detection; **GC**: gas chromatography; **MS**: mass spectrometry; **HS**: head space; **CCNs**: carboxylated cellulose nanocrystals; **MIPs**: molecularly imprinted polymers.

4. Pollen

Pollen grains are produced by higher plants to contain and spread the male genetic material [75]. The grains, which have a size in the 10–150 µm depending on the species, present a very resistant outer wall (called exine) to protect the genetic content. The resistance to non-oxidative deterioration procedures is mainly provided by sporopollenin [76]. The particle size, the superficial area, and the OH-rich surface make pollen grain a sustainable, cheap, and green sorbent.

Although pollen was proposed as a sorbent for environmental application in 2011 [77], its use for analytical sample preparation was firstly reported in 2014 by Professor Feng's research group [78]. In this initial approach, pine pollen instead of bee pollen was selected, since it can be obtained in a higher amount, cheaper, and cleaner (free of hormones and pesticides). The untreated pollen, for which only a washing step was necessary, was packed in a conventional SPE cartridge. The size (30–40 µm) allowed a good but not excessive packaging of the sorbent. The highly hydrophilic surface of pollen made its application as hydrophilic interaction sorbent possible in such a way that the water that adsorbed over the outer surface was actually responsible for the analyte extraction. In this initial approach, 16 plant growth regulators were extracted from different fruit and vegetables. Then, this extraction format was extrapolated to the extraction of trans-resveratrol in peanut oils [79].

The OH-rich surface of pollen, which is responsible for its hydrophilic nature, opens the door to their easy chemical modification to include special extractive groups that broaden its applicability as sorbent. Mohamad et al. have proposed a double derivatization of sporopollenin spores to synthesize magnetic and selective sorbents [80]. In an initial step, β-cyclodextrin (β-CD) is immobilized over the surface of the spore using toluene diisocyanate as the linker. These β-CDs, which develop a host–guest interaction mechanism with different compounds according to their chemical structure and size, provide a selective interaction with several drugs. In addition, the porous surface of sporopollenin, which is crossed with abundant channels, was exploited to entrap magnetic nanoparticles, which are synthesized by the simple precipitation of Fe (II) and Fe (III) in an alkaline medium. A similar approach, but using cyanopropyltriethoxysilane as the extractive group, has been recently proposed for the isolation of some drugs from water samples [81]. However, in this case, the double derivatization is done in a different order. The spore (Figure 2a) is initially covered with the magnetic nanoparticles (Figure 2b), and the sorptive phase is finally coated over the magnetic spore (Figure 2c).

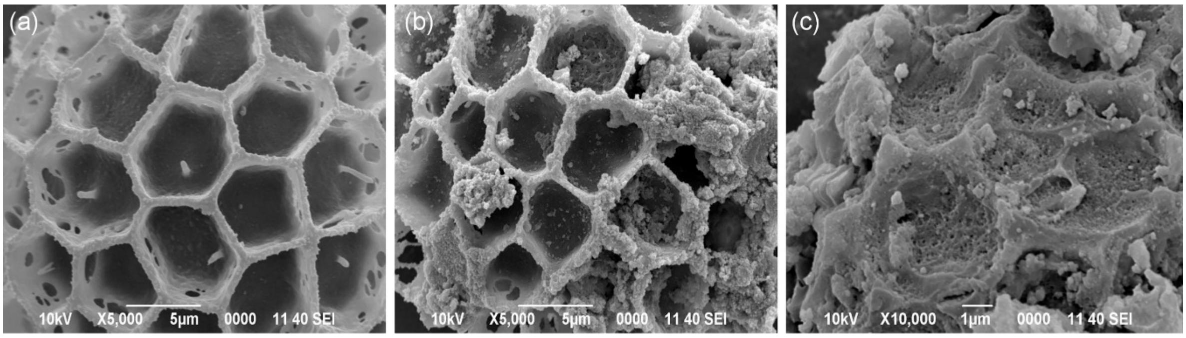

Figure 2. (**a**) Spore; (**b**) Spore covered with magnetic nanoparticles; (**c**) Final composite after the coating with the sorptive phase. Reproduced from reference [81] with permission of Elsevier, 2019.

The main applications of pollen and related materials in the microextraction context are summarized in Table 3.

Table 3. Applications of pollen as sorbent material in microextraction techniques for different analytes and matrices. (Reference period: 2015–2018).

Technique	Material	Analytes	Matrix	LOD	Instrumentation	Ref.
HILIC-SPE	Raw pollen	Plant growth regulators	Fruit and vegetables	0.01–1.1 μg/kg	UHPLC-MS/MS	[78]
NP-SPE	Raw pollen	Trans-resveratrol	Peanut oil	2.7 ng/g	LC-UV	[79]
Magnetic SPE	Sporollenin modified with cyclodextrin	Non-steroidal autoinflammatory drugs	Water	0.16–0.37 ng/mL	LC-UV	[80]
Magnetic SPE	Sporollenin modified with CNPrTEOS	Non-steroidal autoinflammatory drugs	Water	0.21–0.51 μg/L	LC-UV	[81]

HILIC-SPE: hydrophilic interaction solid phase extraction; **NP-SPE**: normal phase solid phase extraction; **CNPrTEOS**: cyanopropyl-triethoxysilane; **UHPLC**: Ultra high-pressure liquid chromatography, **MS**: mass spectrometry; **LC**: liquid chromatography; **UV**: Ultraviolet detection.

5. Agricultural By-Products

As previously noticed, the use of biomass as an extractant for inorganic and organic compounds is considered as a promising alternative to conventional sorbents. Among the existing choices, the use of natural products usually considered as waste such as fruit peels for cations and anions removal from waters has been extensively described [82,83]. These sorbents are effective and economical with a clear beneficial effect on reducing the amount of waste to be eliminated.

The retention is based on the presence of residual hydroxyl, carboxyl, or amine groups of cellulose or lignin, which exhibit chelating or ion-exchange properties. It has been further demonstrated that once retained, the metal ions can be removed from the sorbent by an acidic treatment, opening the door to evaluate their use as extractant phases with analytical aims. This section will describe the potential of agricultural by-products such as fruit and vegetable peels as a sorbent for the isolation and preconcentration of inorganic and organic compounds from waters.

Vegetable old cell walls are enriched with lignin, which is a phenolic polymer of hydrophobic nature whose aromatic moieties have been identified as responsible for interacting with metals [84]. Amine groups of cellulose proteins and glycoproteins synergically contribute to adsorption [85]. Increasing the superficial area of any sorbent results in a better capacity for analytes retention. In the case of fruit and vegetable peels, chemical treatment such as mercerization can be used to modify the surface of the peel to increase the number of hydroxyl groups available for interaction, thus enhancing the chelating/ion exchange capacity [86]. Concerning the solid-phase extraction of cationic species from waters, banana peel and Sophia seeds have been proposed as sorbents. Cadmium (II) has been extracted from environmental and industrial wastewaters [87]. In this specific application, once dried and crushed, the peels were passed through a 120-mesh sieve (125 μm). Then, activation of the superficial carboxylic groups was carried out using acidic methanol. The esterification of the acidic groups was corroborated by infrared spectroscopy. Only 100 mg of the banana peel was needed to efficiently preconcentrate cadmium (II) by ion exchange with an up to 10 times reusability cycle. Untreated banana peel has also been proposed for the solid-phase extraction of copper and lead from river waters [88]. In this application, dried banana peel was pulverized using a ball mill and further sieved to select the fraction between 35 and 45 μm for metals preconcentration using 20 mg of solid. To minimize potential interferents, the organic fraction of the sample was eliminated by oxidation, being the extraction procedure carried out at acidic pH. An enrichment factor of 20 was achieved in this case, this being value corroborated by the analysis of a standard reference material. Descurania Sophia seeds have also been proposed as sorbent for the isolation and preconcentration of cadmium (II) from water and rice flour [89]. Seeds were commercially available and utilized as received, with the only requirements being washing and sieving. The extraction of cadmium was accomplished in acidic medium using 150 mg of sorbent. The selectivity study carried out by the authors demonstrated that no interference from other divalent and trivalent ions was identified. Electrostatic and coordinative interactions between carboxylic groups and cadmium were responsible for the isolation. The enrichment factor obtained after the analytical method was 20. Accuracy was corroborated by analyzing a certified reference material.

The interaction of organic compounds with biopeels has also been described in the literature. In fact, methylene blue [90] and direct red 12B [91] were removed from water samples using garlic peel. However, the use of these materials for the solid-phase extraction of organic compounds usually requires an additional treatment of the biopeel. In this context, Zhao et al. have proposed the oxidation of the garlic peel with nitric acid to increase the surface acidic functional groups [92]. In this way, the sorption capacity was increased by a factor of 10 for quinolone antibiotics. The authors systematically studied the effect of the oxidation of garlic peel in terms of porosity and functional group distribution. Concerning the superficial morphology, the scanning electron microscopy analysis demonstrated that while the garlic peel exhibits a compact net structure, the oxidized one showed a corroded one and smaller pore irregularly distribution on the surface. The infrared spectra pointed out that after the acidic treatment, some unreactive groups were transformed into carboxylic moieties, while a weaker absorption band was observed in the aromatic ring region, which indicates their decomposition during the treatment. Moreover, the evaluation of the cellulose, hemicellulose, and lignin contents also indicates an increase of the former in the oxidized garlic peel, this fact correlatating with the higher retention for quinolones on the modified sorbent.

The elimination of dyes, pigments, and other colorants using activated carbon is probably the most effective remediation procedure due to the almost irreversible interaction established between the sorbent and the analyte. Agricultural by-products have been identified as an environmentally friendly source of activated carbon, which is usually generated by carbonization at high temperatures [93]. Following this idea, several carbon-based sorbents have been prepared using banana and pomelo peels as starting materials. Four relevant examples will be briefly presented.

Li et al. prepared a hierarchical porous carbon by the treatment of banana peels at 160 °C and further carbonization at 900 °C under an inert atmosphere [94]. The solid showed an intrinsic microporous structure with the presence of meso and macropores, which provides a high surface area (561.8 m^2/g). The formation of graphitized carbon during the synthesis allows the interaction with aromatic compounds via π-stacking. Therefore, the authors evaluate the potential of the hierarchical porous carbon synthesized as a sorbent for carbamate pesticides potentially present in cucumber and watermelon samples. Cartridge SPE was selected as an extraction mode by packing 10 mg of the solid. The enrichment factors obtained were in the range of 80–114 depending on the carbamate and the sample, which resulted in detection limits between 0.05 and 0.30 ng/g.

Pomelo peels have also been used as a precursor material to obtain nanoporous carbon [95]. In this approach, chemical activation with KOH was applied. The grounded and dried pomelo peel was precarbonized at 450 °C for 2 h in an inert atmosphere and thoroughly mixed with 1 M KOH aqueous solution. After a thermal threaten (up to 800 °C), the nanoporous carbon was activated being ready to use as a sorbent phase in SPME fiber. For this aim, the solid was immobilized onto a stainless-steel wire via physical coating approach and further protected with a silicone sealant. The SPME fiber was evaluated for the headspace extraction of benzene homologs from waters and soil before their determination by gas chromatography-mass spectrometry. As evaluated by the authors, their approach resulted in better sensitivity and comparable selectivity as regards reported methods for the same analytical problem.

Probably, dispersive microextraction can be identified as the simplest and most efficient approach among miniaturized sample treatment techniques [96]. The use of an extractant phase dispersed in the sample matrix facilitates the interaction with the analytes, thus enhancing the efficiency of the whole process. However, the recovery of the extractant enriched with the analytes is challenging. Dispersive micro solid-phase extraction usually requires the implementation of filtration and centrifugation steps, which are usually tedious and negatively affect the method sample throughput. This limitation can be overcome by using superparamagnetic sorbents which can be separated from the sample matrix by means of an external magnet, which clearly simplifies the whole analytical process. Magnetic carbon sorbents can also be prepared using agricultural by-products. Two approaches have been very recently proposed based on the use of pomelo peels. The one-pot synthesis pathway is very similar, using either a mixture of $FeCl_3$–$FeCl_2$ [97] or $FeCl_3$–urea [98] as precursors of the Fe_3O_4 magnetic core of the nanocomposite. Both methods are characterized by the mild conditions used during the synthesis, with temperatures not exceeding 80 °C or 180 °C, respectively. Once obtained, the solids are activated with an organic media and used for the extraction of fluoroquinolones and parabens from waters [97] or triazole fungicides from fruits [98]. The amount of sorbent required for the extraction was in the low milligram level (20–50 mg) with excellent sensitivity and precision. Besides, the results of the proposed approaches showed that they were more competitive in terms of costs, time, and greener considerations.

The main applications of agriculture by-products in the microextraction context are summarized in Table 4.

Table 4. Application of agricultural by-products as sorbent material in microextraction techniques for different analytes and matrices. (Reference period: 2008–2018).

Technique	Material	Analytes	Matrix	LOD	Instrumentation	Ref.
Dispersive SPE	Banana peel	Cadmium	Environmental and industrial wastewaters	1.7 µg/L	FAAS	[87]
SPE	Banana peel	Copper, Lead	River water	–	FAAS	[88]
SPE	Descurainia Sophia seeds	Cadmium	Water rice flour	1.0 µg/L	FAAS	[89]
SPE	Garlic peel	Quinolone antibiotics	Water	0.65–0.85 µg/L	LC-DAD	[92]
SPE	Banana peel	Carbamate pesticides	Cucumber watermelon	0.05–0.20 ng/g	LC-DAD	[94]
SPME	Pomelo peel	Benzene homologues	Water Soil	0.05–0.18 ng/L 0.11–0.18 ng/Kg	GC-MS	[95]
Magnetic-SPE	Pomelo peel	Parabens Fluoroquinolones	Water	0.011–0.053 µg/L 0.012–0.46 µg/L	LC-DAD	[97]
Magnetic-SPE	Pomelo peel	Triazoles fungicides	Fruits	0.12–0.55 µg/Kg	GC-MS	[98]

SPE: solid phase extraction; **SPME**: solid phase microextraction; **FAAS:** flame atomic absorption spectroscopy; **LC**, liquid chromatography; **DAD**, diode array detection; **GC**, gas chromatography; **MS**, mass spectrometry.

6. Trends, Natural Products for Simplifying the Analytical Workflow

The classical analytical workflow comprises the isolation/enrichment of the targets from the sample matrix to obtain a clean extract that is finally analyzed by chromatography. This approach provides a high level of sensitivity and selectivity, but the sample throughput is usually limited by the chromatographic cycle. The elimination of the chromatographic separation, by the direct combination of the microextraction step with the instrumental technique, appears as an attractive alternative. However, avoiding the chromatographic separation compromises the method selectivity, and this loss can be offset by improving the selectivity on the analyte isolation by using a selective instrumental technique such as high-resolution mass spectrometry (MS) or by combining both strategies. Gómez-Ríos and Mirabelli have recently reviewed the potential of the SPME-MS combination promoting as well, changing the classic perspective about chemical analysis [99]. This comprehensive and inspiring review divides this combination into four main groups, depending on the sorptive phase employed namely: fiber/tip, in-tube, mesh, and substrate spray. SPME substrate spray approaches are very versatile, comprising different supports such as coated blades [100–102], paper [103,104], or wooden tips [105,106]. The latter configurations, which make use of natural substrates, are named as paper spray and wooden tip spray, respectively. In both approaches, the substrate can be used for the direct ionization of the sample [107] or the off-line coupling with a microextraction technique [108]. However, the substrate can also be modified with a sorptive phase for the isolation of the target analytes prior to their direct analysis by MS [103]. Although the discussion of the microextraction–MS coupling is beyond the scope of this article, the description of the synthesis of sorptive phases based on paper and wood is relevant and it will be briefly discussed below. The selected developments have been used under the classical or direct analytical workflows.

Paper is a cellulose-processed material that shares some of the characteristics of cotton but presents a flat configuration. This geometry opens the door to its application under the thin film microextraction technique. Although bare paper can be used for extraction [109], it is usually modified to boost its extraction capability. This modification can be done by the covalent bonding [110] or by the deposition of a thin layer of sorptive phase [111]. The coating of paper with polymers of both synthetic [112] and natural origins [113] appears as an interesting way to synthesize versatile sorptive phases. Conventional coatings in microextraction, such as PDMS [114], have been recently complemented by other approaches.

In 2017, Ríos-Gómez et al. proposed the simple modification of paper by dip coating for the extraction of methadone from biological samples [111]. This process is based on the previous dissolution of a polymer in a volatile solvent and the immersion of paper in this solution. The evaporation of the solvent creates a thin film of the polymer over the paper whose thickness depends on the polymer concentration in the original solution and the number of dips developed during the synthesis. The use of polyamides in combination with a template molecule has been used for the fabrication of molecularly imprinted papers [115]. If some nanoparticles are included in the polymer solution, they can be incorporated into the coating, providing additional characteristics [116]. Also, the dip coating has been proposed to cover paper with a pure film of carbon nanohorn suprastructures that can be used for the extraction of drugs from biological matrices [117]. The SEM micrograph of Figure 3 shows how the dahlias (the ordered aggregates of carbon nanohorns) are combined to form a homogeneous coating over the paper.

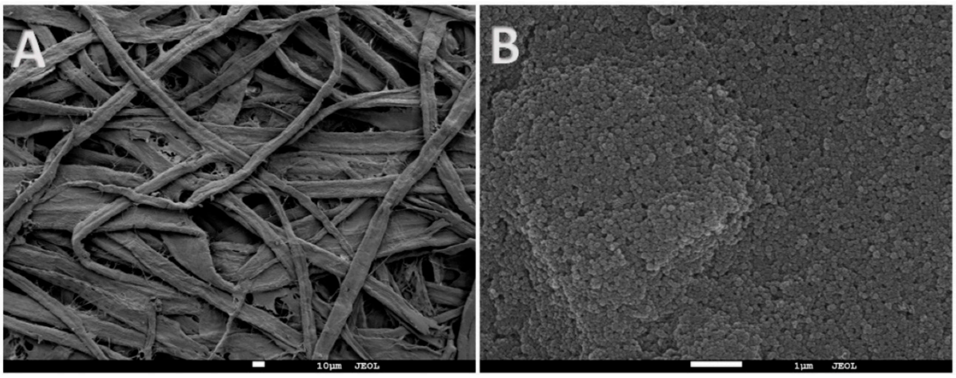

Figure 3. SEM images obtained for (**A**) a bare paper and (**B**) a paper modified with suprastructures of carbon nanohorns. Reprinted from [117].

Wood is a mixture of natural materials such as lignin, cellulose, and hemicellulose [118]. This lignocellulosic material, in the form of a tip or stick, has been used for the development of microextraction phases. The OH-rich surface of wood opens the door to its easy modification by anchoring appropriate groups in order to enhance the interaction with the analytes. Deng et al. proposed a simple silanization, followed by a sulfonation, of wooden tip to prepare a mixed-mode extractant phase that is capable of extracting acidic drugs for water samples [119]. The silanization mechanism also permits the introduction of C18 (using trimethoxyoctadecylsilane) and amine groups (using 3-aminopropyltriethoxysilane), increasing the versatility of these phases [106]. These sorptive phases are not selective at all, and their applicability to complex matrices can be somewhat limited. In this sense, the coating of the wooden tips with molecularly imprinted polymers has allowed the determination of analytes in complex samples such as fish [120] and milk [121]. Recently, Abdel-Rehim et al. have proposed the modification of wooden sticks with a composite based on graphene oxide, making the applicability of these materials even broader [122].

7. Conclusions

Green chemistry tries to minimize the impact of chemicals in the environment, considering both the local and global context. This main objective can be extended to all the chemistry fields, including analytical chemistry, and it requires the previous identification of the impacts in order to provide some alternatives to minimize or avoid these deleterious effects. The principles of GAC provide general guidelines that can be applied to different stages of the analytical process. Some of these principles suggest the simplification of the sample treatment and the use of renewable resources. Both topics have been considered in this review article.

The description of the potential of natural materials as sorbents or substrates in solid-phase microextraction has been the main aim of this article. The principal materials, their characteristics, and their applications have been presented to inspire the readers for further research. Some of the described developments, especially those based on bare natural material, can be used for environmental remediation if they are adapted for a large scale.

In order to avoid green marketing, some challenges in this field must be indicated. The use of renewable sources for the design of new sorbents only reduces the environmental impact if these materials are applied without any chemical modification. However, if this chemical derivatization is required (for example to improve the sorption capacity or selectivity), it must involve no reagents (this is the case of pyrolysis) or a low amount of them. In addition, the proposed materials should be compared with commercial existing products to clearly demonstrate their superiority.

In the next years, intensive research on the topic is expected. This research will cover the use of natural materials as precursors but also the use of natural materials as inspiration for the design of smart and environmentally friendly materials.

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