Alginate-based sorbents in miniaturized solid phase extraction techniques - step towards greenness sample preparation

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Abstract:

In response to growing concerns about environmental degradation, one of the main areas of research activity in recent years has been to make sample preparation methods more sustainable and eco-friendly. The increasing greenness of this step can be achieved by minimizing the usage of reagents, automating individual stages, saving energy and time, and using non-toxic, biodegradable substances. Therefore, the use of natural materials as sorbents in miniaturized extraction techniques is becoming a main trend. One of the natural material that is increasingly being used, not only due to eco-friendly nature but also because of their easy applicability to various sample preparation techniques, is alginate hydrogel. Following this trend, this review discusses the recent application of alginate-based sorbents in various microextraction techniques, focusing on functionalization approaches that enhance extraction performance. Additionally, the green profile of alginate-based sorbent microextraction approaches, along with the sorbent synthesis, were investigated.

1. Keywords: biosorbents, biopolymers, microextraction, sample preparation, green sorbent, green analytical chemistryIntroduction

Introducing the ideology of Green Analytical Chemistry (GAC) into analytical laboratories was a turning point in the approach to developing analytical procedures. Since then, the main goal of analysts has been to find a balance between high sensitivity, precision, accuracy, and the sustainability of the developing analytical methodology [1]. Sample preparation is usually considered as the step with the largest environmental impact of the entire analytical procedure due to the extensive use of organic solvents in time-consuming procedures [2]. Therefore, special attention has been paid to improving the greenness of this step. The main strategies include: (i) miniaturization and automation; (ii) reducing or completely eliminating harmful and toxic chemicals; (iii) minimizing energy consumption; and (iv) minimizing waste generation. Another strategy to improve the sustainability of analytical sample preparation is to use biodegradable, reusable reagents easily obtained from renewable sources [3]. Therefore, in recent years, most published papers have focused on the replacement of toxic solvents and petroleum-based materials with more eco-friendly substances. One of the main directions in the area of solid phase extraction techniques is the application of materials of natural origin as sorbents. So far, various natural products such as cork, cotton, bamboo, pollen, sponge, seeds, and biowastes [3,4] have been used directly in different modes of solid-phase techniques. Some of these natural products have also served as sources of biopolymers. Depending on the monomer unit, biopolymers can be classified into three categories, such as polysaccharides, polynucleotides, and polypeptides. According to the literature, polysaccharides, are particularly widely used as sorption materials for sample preparation. Due to their high porosity, good mechanical properties, the possibility of easy chemical or physical modification of their surface, high availability, and low price [5,6]. Indeed, polysaccharides, such as cellulose, starch, chitosan, and agarose have been applied in different miniaturized extraction techniques such as solid-phase extraction (SPE), solid phase microextraction (SPME), dispersive micro solid-phase extraction (D-μSPE), thin film microextraction (TFME) and many others. A detailed description of these and other applications can be found in the latest published papers [6–11]. However, in recent years, growing interest in the application of another class of polysaccharides, alginates, for sorbent preparation intended formicroextraction has been observed (Fig.1).

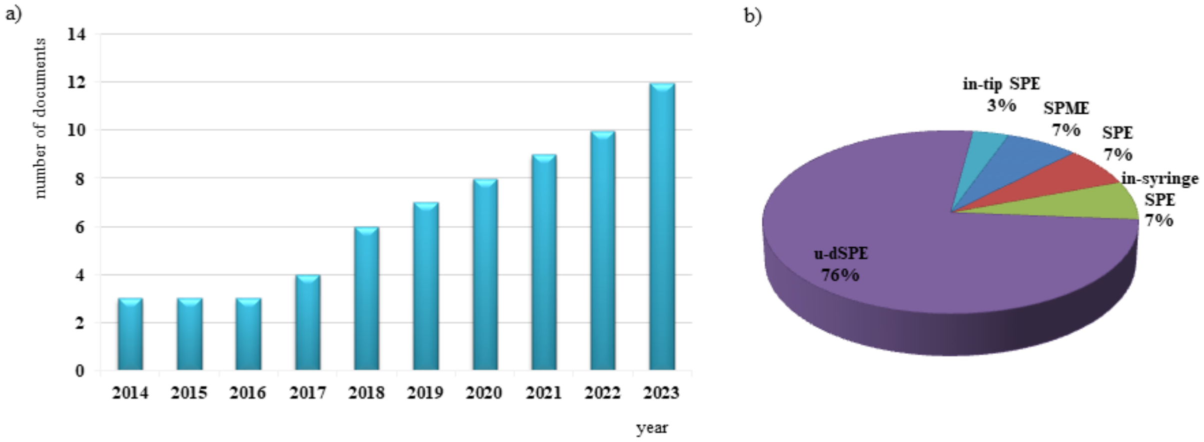

Fig.1a) Number of publications focused on alginate-based sorbents application in microextraction approaches based on Web of science database (searched keywords: alginate-based sorbent; microextraction, accessed on June 2024); b) the distribution of articles among various sorbent-based microextraction techniques.

In the light of the growing interest in the use of alginate-based materials in analytical chemistry, it seems important to collect detailed information about their performance and applicability. Therefore, this literature review presents a comprehensive overview of recent strategies for alginate gel functionalization and their application in microextraction techniques such as SPE, in-syringe SPE, SPME, and D-µSPE. Additionally, environmental and sustainability issues related to preparation and using alginate-based sorbents in the sample preparation step were considered by application of Analytical Eco-scale tool. Although, few review articles focused on application of bio-sorbents in microextraction processes are published, there is no publication stricte focused on the alginate-based sorbents application in miniaturized extraction techniques, therefore, this review gives the comprehensive knowledge in this area. It is believed that this article will motivate researcher to conduct experiments in this area as considering published data, alginate-based sorbents applied in microextraction processes seams be very promising solution.

2. Chemical structure and properties of alginates

Alginates (ALG) are composed of L-guluronic (G) and D-mannuronic (M) units combined with 1,4-glycosidic linkages. The basic structure consists of linear, unbranched units made up of monomers arranged in blocks of M and G in different configurations as homopolymeric blocks of G units (GG), M units (MM), and alternating M and G units (GM), as shown in the Fig. 2 [12].

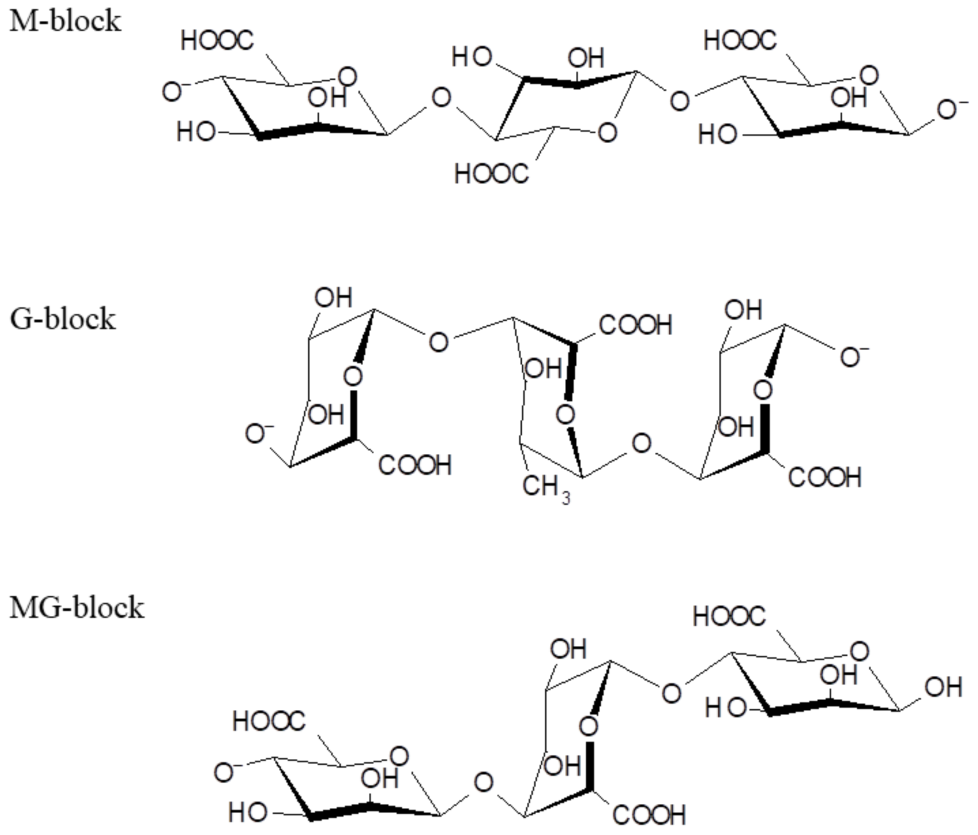

Fig.2.The molecular structures of possible sequences of L-guluronic and D-mannuronic units in alginate polymer.

The main sources of this biopolymer are marine plants and microorganisms. Seaweeds and brown algae such as *Ascophyllumnodosum, Laminariadigitata, Laminariahyperborea,* and *Macrocystispyrifera*, are particularly rich in alginate. The most common form of commercial alginate is sodium salt ($C_6H_9NaO_7$) [12,13]. One of the special features of alginates is their capability of forming gel networks. It can be achieved by two methods: ionic crosslinking with divalent cations or acid precipitation. Furthermore, they are biodegradable, biocompatible, and have not been shown to accumulate in biological systems. Thus, this material is particularly attractive for medical, pharmaceutical, cosmetic and food applications as well as for environmental remediation. The other good feature of alginates is their capability of forming gel independent of temperature, which is unique compared to other polysaccharides such as gelatin or agar [12,13]. Nonetheless, compared to conventional synthetic polymers, this biopolymer exhibits some limitations, such as a strong hydrophilic character, low thermal stability, and weak mechanical properties [14]. Therefore, much effort has been made to improve its physico-chemical properties. It was found that compounding alginates gel with other popular sorbents like metal nanoparticles, graphene oxide (GO), molecularly imprinted polymers, and others contributes to a significant improvement in physico-chemical properties. What is more, by selecting the appropriate material, both sorption capacity and selectivity towards selected groups of analytes can be significantly enhanced. In Figure 3 groups of materials usually combined with alginate gel to improve their sorption properties are presented. The adsorption properties of different alginate composite materials as well as their application in different microextraction modes are detailed discussed in the next subsection.

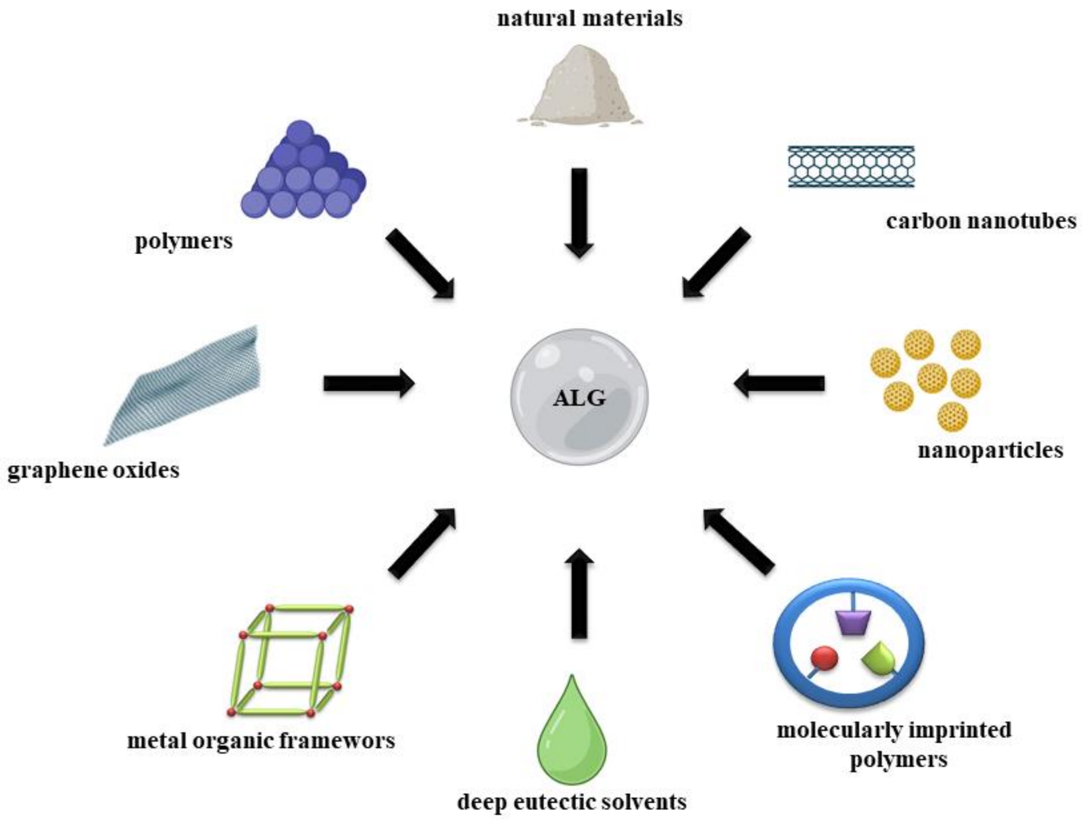

Fig.3. Main groups of sorbents combined with alginine hydrogel and used in solid-phase microextraction techniques.

3. Application of alginate-based sorbents in microextraction techniques

So far, alginate-based sorbents have been applied as a sorptive material in some of the miniaturized extraction techniques, such as SPE, SPME, and D-µSPE. In general, regardless of the microextraction mode, the sorbent preparation process is relatively simple and easy to operate. As shown in Fig. 4, four main stages can be distinguished. In the first step, an alginate solution is prepared by dissolving alginate in water. The alginate content in an aqueous solution usually ranges from 1 to 2% (w/v). The second step involves adding specificl material to the alginate solution to improve surface and adsorption properties of the sorbent. In the next step, alginate solution is added to the crosslinker agent to obtain the alginate-based solid sorbent. Depending on the microextraction approach, the procedure for obtaining the sorbent shape/format is different. To prepare sorbent beads, the alginate solution is added dropwise into the crosslinking solution, while for fiber formation, a certain amount of the alginate solution is added continuously. However, in order to obtain covered fiber, the device is immersed directly in a crosslinking solution. In almost all of the reported procedures, calcium chloride ($CaCl_2$) solution was used as a crosslinker. This stage is the most time-consuming of the entire procedure. Achieving complete formation of the sorbent requires keeping it in the $CaCl_2$ solution from 30 minutes to even 2 hours. Then the formed sorbent is separated from the solution, washed by distilled water and, in most applications, dried. Following these steps, the sorbent becomes ready for use in the chosen microextraction procedure.

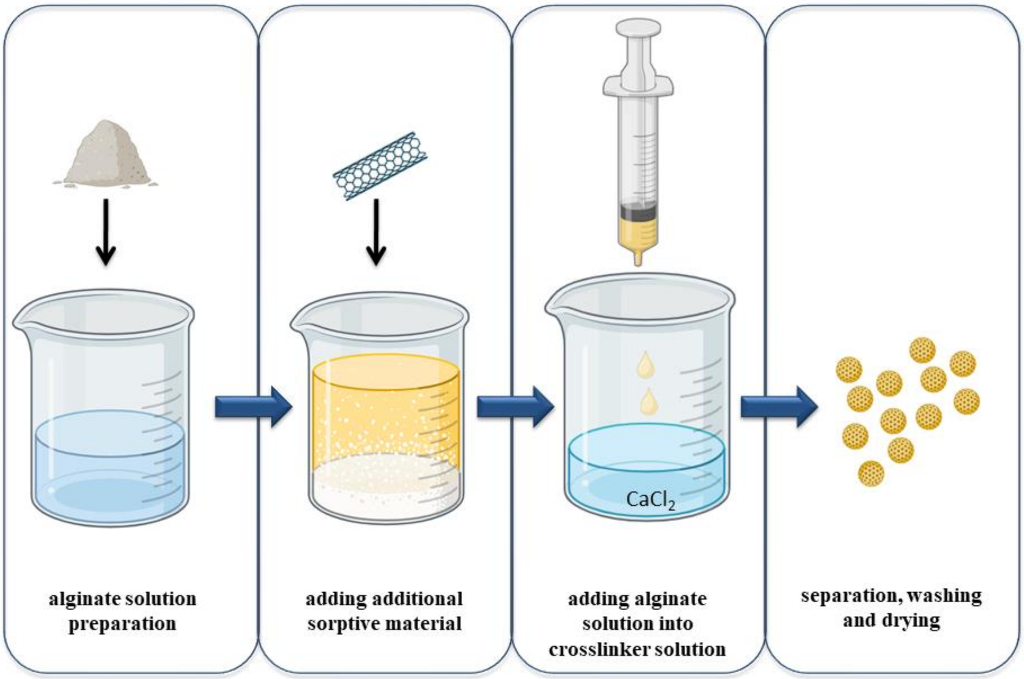

Fig.4. Main steps of alginate-based sorbent preparation.

Based on a literature review, it can be stated that the application of alginate-based sorbents to extract analytes in microextraction procedures is not very popular so far. However, the number of published reports is constantly increasing (as seen in Fig. 1). The vast majority of reports in this field are devoted to the application of this material in D-µSPE. Articles focusing on using it in SPE, or SPME format are much rarer . In this section, the application of alginate-based sorbents in different miniaturized extraction techniques is described in detail. Moreover, specific parameters of the applied procedures are summarized in Table 1.

3.1. column SPE

Column SPE is without any doubt one of the most popular sorbent-based extraction techniques available today. The main reason for its widespread popularity is the possibility of achieving high efficiency in the extraction and clean-up processes in a shorter time and at a lower cost. In standard SPE configuration, the sorbent is placed between two frits in a cartridge or syringe barrel. After the sorbent conditioning, a sample passes through the sorbent, and the compounds of interest are retained in the solid phase. Then, the analytes are desorbed by the appropriate solvent [15].

Nonetheless, the application of an alginate-based sorbent in this format has not been widely adopted so far. There are only two papers in the literature describing the application of this approach. In the first paper, the authors used layered double hydroxides (LDHs) nanosheets-alginate hydrogel to extract and preconcentrate lead ions from tap and mineral water samples as well as juices and liqueur samples. The preparation of monolith columns began with the hydrothermal synthesis of NFLS (nickel–iron layered double hydroxides with laminar structure) nanosheets. Next, the obtained NFLS nanocomposite was mixed with a sodium alginate solution under ultrasonication. Then, NFLS/alginate dispersions were dropped into $CaCl_2$ solution to generate the ionic crosslinked NFLS-gel in the SPE column. Before loading the sample, the sorbent was conditioned with 2 mL of deionized water. After the sample passed through, the cartridges were again cleaned with deionized water, and then the analyte was eluted with 2 mL of HNO_3 and determined by Flame Atomic Absorption Spectrometer

(FAAS). The proposed method showed very good extraction efficiency (91.7–99.8%) and good precision (relative standard deviation, 2.65%). Moreover, it has been shown that the incorporation of sulphide intercalated LDHs nanosheets provides more adsorption sites, contributing to the higher selectivity of Pb (II) and almost six times higher adsorption capacity compared to alginate hydrogel [16]. Another approach based on packing alginate microparticles in polypropylene column was proposed by Arantes De Carvalho et al. [17]. This column was prepared for the extraction and preconcentration of 14 rare earth elements from environmental water samples. Briefly, the spherical calcium alginate (CA) beads were synthesized, washed, and freeze-dried. Then, in order to increase the surface area, dried beads were cryogenically ground and sieved. The obtained sorbent (300 mg), with particle sizes ranging from 10 to 180 µm, was dispersed in deionized water and packed as a slurry into a polypropylene column with a porous polyethylene frit at the bottom and at the top. The column was coupled to a flow injection system and conditioned before loading the sample. After loading a sample, the column was dried, the analytes were eluted with 1.0 mL of 0.5 mol/L HNO_3 and analyzed by ICP-MS. However, the obtained recovery values were slightly lower than those obtained using commercially available resins such as iminodiacetate (IDA), C_{18}-polyacrylonitrile (PAN), or alkyl phosphinic acid resin (APAR). The proposed protocol can be a reliable, environmentally friendly alternative due to the possibility of re-utilization of the CA column, even for up to 50 cycles, low cost, and no need to use relatively highly concentrated acids.

3.1.1. in-syringe SPE

Although SPE is a very effective extraction method, it suffers from a few limitations, including using a larger sample volume, solvents for conditioning and desorption, and a larger sorbent amount. So, following GAC principles, a miniaturized version of traditional cartridge-based SPE in the form of a syringe filter holder was proposed [18]. So far, in the area of alginate-based sorbents application in this technique, only one study has been reported. The researchers prepared the sorbent by dispersing biochar (obtained from herb residue) in the sodium alginate matrix and crosslinking it by immersing in a calcium chloride solution. Then the obtained membrane was cut into a round piece (25 mm) and packed in the syringe filter. To extract the nitroimidazoles from tap water, the sample was passed through the filter six times by pulling and pushing the syringe plunger. Subsequently, the analytes were eluted with 1.5 mL of acetonitrile and analysed by ultrahigh performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS). Under optimal conditions (pH, extraction time, elution solvent, volume, and extraction cycles), the application of the developed material allowed recoveries of metronidazole (80.2 - 92.5%), secnidazole (86.4 - 99.1%), dimetridazole (79.3 - 93.9%), and ornidazole (79.6 - 92.9%) in the analysed samples. The results revealed that immobilization of biochar in alginate gel not only increased analyte adsorption efficiency but also enhanced mechanical properties, allowing it to be reused up to five times. Moreover, the mass of the sorbent used and the limit of detection (LOD) value were significantly lower compared to other solid phase microextraction methods applied for the analysis of nitroimidazoles in water samples. An additional advantage of the proposed methodology was that no additional steps such as centrifugation, filtration, or magnet separation were required, which significantly simplified the entire procedure and reduced the time compared to others [19].

3.1.2. In-tip SPE

In another format of miniaturized SPE that uses the same steps—conditioning, sample loading, washing, and elution—a small amount of sorbent is packed inside a plastic pipette tip[20]. An alginate-based sorbent has also been applied in this approach. Nurerk et al. introduced a micro-pipette tip device consisting of cotton fiber coated with sorbent, which was prepared by integrating metal-organic frameworks (MIL-101) and cetyltrimethylammonium bromide (CTAB) into alginate hydrogel [21]. In the proposed method, the authors first synthesized MIL-101 via the hydrothermal method and mixed it with CTAB and alginate hydrogel. Subsequently, they used epichlorohydrin as a cross-linker in the reaction between sodium alginate and cotton fibers. Then, cotton fibers were immersed in a $CaCl_2$ solution to obtain MIL-101/CTAB/ALG/CF. The 500 mg of synthetized sorbent was packed into a 1000 µL pipette tip and connected to a syringe. The proposed lab-made microextraction device was utilized for the extraction of five phthalates from beverage samples. A 10 mL sample was manually passed through the sorbent. The adsorbed analytes were then eluted from the fibers using 2 mL of acetonitrile and evaporated to dryness. Finally, the dry residue was dissolved in 1 mL of methanol, and 20 µL were injected into the high performance liquid chromatography coupled to diode array detection (HPLC-DAD) system. The proposed approach yielded a sorbent with a large specific surface area (710.02 m^2/g), resulting in a high recovery rate (85.2–97.8%). Furthermore, the method exhibited a low limit of detection (0.15 µg/L) and high precision (RSD less than 4.9%). The obtained parameters were comparable to another HPLC-DAD method using graphene nanoplates as a sorbent in SPE mode. However, it should be highlighted, that the volume of the sample as well as solvent used for sorbent conditioning in the in-tip SPE approach were significantly reduced (approximately 20 times). Moreover, the proposed procedure was much simpler and did not require the use of additional equipment, such as a vacuum pump. Furthermore, the sorbent showed potential to be used multiple times. Even after 15 cycles of sorption-desorption, the analyte recovery remained at 92–93.4%.

3.2. SPME

Among different miniaturized solid extraction techniques, solid-phase microextraction (SPME), introduced by Pawliszyn and Arthur [22] was found to be one of the most popular and powerful tool to separate and enrich analytes from different complex samples. In this green extraction technique, a small quantity of sorbent is coated on a solid support, typically fiber of a specially constructed syringe-like device. There are two ways to perform the extraction: directly immersing the fiber into the sample (DI-SPME) or placing the fiber above the sample (HS-SPME). Currently, numerous commercial SPME fibers are available with different fiber coatings, such as polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacrylate (PA), polyethylene glycol (PEG), and composites such as polydimethylsiloxane/carboxen (PDMS/CAR), polydimethylsiloxane/divinylbenzene (PDMS/DVB) and others. However, some of them exhibited limitations in terms of extraction selectivity, pH tolerance, and thermal durability. Therefore, many novel functional materials (e.g., carbon materials, metal-organic frameworks (MOFs), molecularly-imprinted polymers (MIPs), ionic liquids (ILs), metal nanoparticles (NPs), etc. have been applied as coatings [15].

Alginate-based hydrogels have also been applied as efficient coatings in SPME. The first paper describing the usage of alginate sorbent supported on a fiber was published in 2017 by Castilhos et. al. [23]. The researchers prepared an alginate-based hydrogel modified by the incorporation of corn protein-zein for coating a polypropylene hollow fiber. The fiber preparation procedure consisted of the following steps: (i) cutting the fiber into 1.5 cm long pieces; (ii) conditioning in acetone (5 min); (iii) immersing in the alginate/zein dispersion at 60 °C under magnetic stirring (2 h); (iv) inserting, stainless steel rods into the inner lumen of the hollow fiber; (v) immersing the fiber in calcium chloride solution (2 h); and (vi) washing with ultra-pure water. Then the fiber was immersed in a water sample (30 min) to adsorb thirteen polar compounds including hormones, anti-inflammatory agents, antiseptics and analgesics. After the extraction, analytes were desorbed in methanol using ultrasonic energy for 60 min, then methanolic extract was dried and derivatization reagent was added. Finally, the sample was injected into gas chromatography coupled to mass spectrometry (GC-MS) system. The authors of this work attributed the superior extraction efficiency especially towards compounds with a low n-octanolwater partition coefficient (Kow), such as estriol, estrone, 17-α-ethinylestradiol, progesterone, and 4-nonylphenol. The increase in the extraction efficiency compared to coating prepared without zein addition could be due to reduced initial amount of water absorbed by the hydrogel, which resulted in better interaction between analytes and the sorbent. It should also be highlighted that covering the fiber with alginate-based gel significantly improved the extraction efficiency for some analytes. The peak areas of paracetamol, atrazine, ibuprofen, and 4-octylphenol were significantly higher when fiber supported by hydrogel was used on a sample preparation step than when using polypropylene (PP) fiber with no modification. Which confirmed that the fiber modification by alginate sorbents significantly improved the affinity and selectivity of the sorptive device. However, the approach proposed by researchers is efficient and sensitive, the fiber modification and extraction steps are quite time- and energy-consuming [23]. Another research group suggested using unmodified alginate gel as a covering material for the extraction of fluoxetine and its metabolite, norfluoxetine, from human plasma samples. A similar methodology, as described above, was used for the preparation of hydrogel fiber device. However, the time of fiber immersing in the hydrogel and calcium chloride solution was significantly shortened (240 min versus 4 min). Moreover, the fiber was coated with a second layer of hydrogel. Obtained SPME fiber was used in DI mode, extracted analytes were eluted in methanol and then injected onto high performance liquid chromatography coupled with fluorescence detector (HPLC-FD). Again, the authors obtained much higher peak areas when using a hydrogel-coated fiber than when only PP fiber was applied, which confirms superior sorption capacity of alginate gel. Moreover, it was also proven that alginate hydrogel acted as a restricted access material (RAM), effectively blocking nearly all (96%) plasma proteins presented in the samples. This feature of the hydrogel is particularly advantageous in the context of its use for biological matrices preparation because it allows simplification of the procedure and shortens the sample preparation time by eliminating steps such as protein precipitation or incorporation of additional RAMs into the extraction phase [24]. Despite the analytical figures of merit not being evaluated (making comparisons of selectivity, sensitivity, and efficiency of the extraction process impossible), the proposed methodology appears intriguing and warrants further development, especially in the context of the application of this format in bioanalysis. Reducing sample preparation steps and costs allows for an increase in the greenness in comparison to commercial SPME devices.

3.3. Dispersive micro-solid phase extraction

Without a doubt, dispersive micro-solid-phase extraction (D-μSPE) is technique where alginate-based sorbents are most frequently used. In this sub-mode of traditional SPE method, low sorbent amount (in the low milligram range) is directly introduced into the sample solution and dispersed by vortexing or external energy source such as ultrasounds. Due to the sorbent dispersion in the sample, the contact area between the extractant and analytes increases significantly thus allowing to improve the extraction efficiency and reduced the extraction time. Subsequently, the sorbent containing adsorbed analytes is separated from the sample matrix, typically through centrifugation or filtration. Advantageous features of the D-μSPE, such as simplicity, short sample preparation time, minimized solvent usage, as well as simplicity of alginate-based sorbent preparation have caused so wide interest among analysts. Silva et. al. prepared ALG-MWCNT microbeads by mixing sodium alginate solution with multi-walled carbon nanotubes that were used for the extraction of polycyclic aromatic hydrocarbons (PAHs) from environmental water samples [25]. The procedure entailed adding ALG-MWCNT microbeads to an aqueous sample and thoroughly mixing the entire solution on a platform shaker for 30 minutes. After this time, the microbeads were separated by decantation and dried. The authors tested several solvents and their volumes for analytes desorption. Finally, 0.1 mL of ethyl acetate was used. In order to improve desorption, ultrasonication was applied. Fluorene, phenanthrene, and fluoranthene determination was carried out using an gas chromatography coupled to flame ionization detector (GC-FID) system, resulting in LODs ranging from 0.22 to 0.42 ng/mL. In another work, also aimed at extracting PAHs from real water samples, alginate beads based on granular activated carbon were applied. The authors obtained carbon material from waste polyethylene terephthalate (PET) bottles, which is a very interesting solution in terms of reducing the amount of plastic waste and thus environmental protection. The plastic bottles were first cut into small pieces, washed, and dried. Then a small portion of the material was subjected to carbonization in a cylindrical furnace at 800 ˚C for 1 h under a nitrogen atmosphere. Cooled and powdered activated carbon was mixed with sodium alginate solution, and sorbent beads were formed. The obtained sorbent exhibited a sphere shape with a rough surface and porous structure, which ensured sufficient inner area for PAHs sorption, resulting in recovery rates ranging from 93.5% to 102.22%. 50 mg of sorbent was found to be sufficient for obtaining satisfactory extraction efficiency, and equilibrium was achieved under shaking in just 8 minutes. Moreover, the developed method exhibited very good linearity, and precision (RSD <6.7%), low LOD of 0.01 ng/mL (much lower than other procedures reported in the literature for PAHs extraction) and low LOQ of 0.03 ng/mL [26]. In 2022,Asghari and co-workers introduced an innovative variant of gel-based sorbent composed of an eutectogel derived from the combination of calcium alginate and deep eutectic solvent (DES). In this procedure, a hydrophobic DES consisting of choline chloride (ChCl) and polyethylene glycol (PEG) in molar ratio 1:1 was encapsulated in alginate beads (beads diameter in the range of 414–746 μm). After drying at room temperature, the small portion (30 mg) of sorbent was used for the rapid extraction (completed in 10 min) of 5-hydroxymethylfurfural (HMF) from coffee samples. The analyte desorbed from the sorbent with 200 μL of acetonitrile was determined by HPLC-UV. The introduction of green solvent to the alginate beads provided high recovery (79-102%) due to the formation of dipolar interactions and hydrogen bonding between PEG chains and HMF molecules. The validation results demonstrate broad linear range (7.49–1000 μg/kg), low LOD (2.25 μg/kg), and good precision (RSD < 4.7%) of proposed method. Moreover, the authors assessed the environmental impact of the proposed method using two green analytical matrix tools: the Complex Green Analytical Procedure Index (Complex GAPI) and the Analytical Eco-Scale. The obtained pictogram as well as the final Eco-Scale score of 63 out of 100 indicate that the method can be classified as an acceptable green [27]. A similar approach, involving encapsulation of DES in alginate beads, was proposed by Karami and Seresthi [28]. The researchers combined thymol and methacrylic acid in a 1:1 molar ratio and subjected it to the polymerization process using ammonium persulfate (APS) as a radical initiator and ethylene glycol dimethacrylate (EGDMA) as a crosslinker to obtain a polymer named ([poly(MAA-co EGDMA)]:[Thy] DES). The sorbent was then utilized to extract twenty four pesticides from non-alcoholic malt-based beverages. A comparison between the extraction efficiency of unmodified alginate hydrogel and the eutectogel showed a considerable role of the DES in enhancing extraction capabilities, resulting in 1.5–3.4 times higher chromatographic responses than unmodified ones. As can be seen, the main shape of the alginate-based sorbent used in the D-μSPE is a bead; however, in one report, scientists proposed the use of other structural configuration, such as fiber. They prepared sorbent named zirconia nanoparticles-decorated calcium alginate hydrogel fibers (ZNCAHF) by constant injection with syringe zirconia/sodium alginate suspension into $CaCl_2$ solution. After drying, the sorbent (0.1 g) was immersed in water and juice samples to extract three compounds from organophosphorus pesticides group under stirring for 5 min. Afterward, the sorbent was withdrawn from the solution, washed, dried, and transferred to a small tube wit toluene/dichloromethane mixture to desorb analytes. The method exhibited very high recovery rate (90-105%) and very low LOD (0.001-0.004 μg/L). According to the authors, these excellent results was achieved due to high specific area resulting with sorbent thin fibrous shape and also zirconia nanoparticles content. However, the influence of the sorbent shape on the extraction efficiency has not been investigated [29]. In another study, researchers prepared sorbent by combining activated carbon (AC) and polyvinylpyrrolidone (PVP) and encapsulating it in alginate beads (AC@PVP@ALG) [30]. The synthesized material was employed for ultrasound-assisted dispersive micro-solid phase extraction (UA-Dμ-SPE) of antiretroviral drugs in environmental water samples, and then followed up with HPLC-DAD determination. Due to its high porosity and large specific surface area (372 m^2/g), the developed sorbent exhibited a favourable extraction capability, ranging from 91.6 to 99.1%. Moreover, the application of ultrasounds as an enhancing extraction factor could potentially affect this high recovery factor, but the authors have not conducted any comparison studies. In comparison to SPE-Oasis HLB cartridges, mostly used for nevirapine and zidovudine extraction, the elaborated procedure exhibited a notable higher recovery with a much lower quantity of the sorbent used.

3.4. Magnetic dispersive micro-solid phase extraction (MD-μSPE)

If the sorbent has magnetic properties, it can be separated from the sample matrix using an external magnetic field. Based on the data gathered in Table 1 it can be concluded that this sub-version of D-μSPE is the preferred choice of researchers. The iron oxide, namely magnetite (Fe_3O_4) is one of the most frequently used due to its superparamagnetism and facile synthesis. However, unmodified iron oxide suffers from some drawbacks such as poor selectivity, sensitivity to acids and tendency to aggregation. To overcome these limitations, hybrid materials composed of Fe_3O_4 and other materials of different sizes and physicochemical properties are synthesized [31]. So far, GO, carbon nanotubes (CNTs), silica-based materials, MOFs, and MIPs have been the most frequently used in the preparation of magnetic alginate-based sorbents.

Nurerk et. al. proposed a magnetic composite sorbent named PANI/ALG/Fe_3O_4consisting of polyaniline (PANI) coated Fe_3O_4 nanoparticles entrapped in alginate beads [32]. These sorbent beads were combined with the HPLC-FLD method for the extraction and determination of three PAHs in reservoir, river and wastewater samples. The proposed method showed very good extraction efficiency (86–98%) and good precision (RSD <6%). Moreover, it has been shown that the addition of PANI has a beneficial effect on PAHs adsorption efficiency. Compared to Fe_3O_4, Fe_3O_4/alginate sorbents, PANI/alginate/Fe_3O_4exhibited much higher adsorption capability (more than 4 times) of the target analytes via π-π interactions. The adsorption capacity for benzo[a]anthracene, benzo[b]fluoranthene, and benzo[a]pyrene was determined as 1.25, 1.19, and 1.15 μg/g, respectively and remained constant even after six cycles of sorption-desorption. Similar sorbent, have also been used to extract fluoroquinolones from honey, milk, and egg samples. However, in the case of this study, the core of the sorbent consists, apart from magnetite, also GO and octadecyl-bonded silica. The combination of these high-affinity materials and the formation of a double-pore network in the hydrogel provided a high sorption capacity of 27.84 m^2/g and a good extraction efficiency ranging from 80 to 98% [33]. In the next publication by the same authors, another material, polypyrrole, was used to cover the alginate beads. The sorbent exhibited high adsorption capacity towards estriol, β-estradiol, and bisphenol A, without significant loss even after 16 regeneration cycles [34]. A polypyrole-based sorbent named porous nanostructured polypyrrole, reduced GO, magnetite nanoparticle alginate hydrogel microspheres (PPy-rGOx-Fe_3O_4) was also applied for phthalate extraction from bottled water and beverage samples. PPy-rGOx-Fe_3O_4 was prepared by adding magnetite nanoparticles, GO, and calcium carbonate to an alginate solution. To reduce GO, hydrogel microspheres were immersed in 0.2% w/v ascorbic acid and heated at 85^{o}C for 6 h. While, to obtain the hierarchical porous nanostructure, the composite was added to 20% w/v hydrochloric acid. With the reaction of $CaCO_3$ in the hydrogel microspheres with the hydrochloric acid, bubbles of CO_2 were released, which created a porous double network. The obtained composite were then coated with polypyrrole. The analytes desorbed from the sorbent with ethyl acetate were determined using GC-MS/MS. Under optimized conditions, the elaborated method showed favourable recovery rates ranging from 87.5 to 99.1% and a low LOD of 0.005-0.01 μg/L [35]. Another sorbent applied to magnetic D-μSPE was proposed by Sereshti et. al. [36], who synthesized a three-component eutectogel, composed of a crosslinked copolymeric DES and polyvinylpyrrolidone-coated Fe_3O_4 nanopowder (PVP-Fe_3O_4). The copolymeric DES, consisting of 2-hydroxyethyl methacrylate (HEMA)/thymol (Thy) in a 1:1 M ratio, was prepared through thermally-induced free-radical polymerization with azobisisobutyronitrile, as an initiator, and EGDMA as a crosslinker. The resulting material exhibited excellent and rapid (extraction occurred in 10 min) sorption capability of melamine from milk and dairy products. Additional advantages of the proposed approach include low sorbent mass (10 mg) and low volume of desorption solvent (300 μL). Once again, a significantly greater recovery of analyte was obtained using DES-modified gel beads (66.9%) than that of unmodified calcium alginate beads 33.3%). Furthermore, it was found that the extraction efficiency of the sorbent was significantly influenced by the pH of the sample solution. The highest recovery (87.6%) was obtained at pH adjusted at 6 due to electrostatic interactions between -O$^-$ and -COO$^-$ groups in sorbent and –NH_3^+ groups in melamine. One more magnetic eutectogel beads composed of a polymeric DES, carboxylated multiwall carbon nanotubes and polyvinylpyrrolidone coated-Fe_3O_4 nanocrystals (Fe_3O_4@CA/[PNVP]:[BA]/MWCNT-COOH) was applied for determination of pesticide residues in honey samples [37]. Another interesting sorbent was proposed by Khongkla et. al. [38]. The authors integrated ZnO nanoparticles with magnetic molecularly imprinted polymer and incorporated them into alginate hydrogel beads. This innovative sorbent, known as ZnO/Fe_3O_4@SiO_2-NH_2/MIP/alginate was utilized for determination of two compounds from sulphonamides group in milk samples. Through the application of molecular imprinting technique it was possible to obtain not only efficient, with recovery ranging from 80.7-98.5% but also highly selective material. Only the target sulfonamides have been extracted from such complex sample as milk without interference compounds presented in the matrix. Moreover, the sorbent demonstrated satisfactory reusability for up to ten sorption-desorption cycles. The process of sorbent preparation was also investigated in terms of repeatability. Despite the demonstrated good reproducibility, with RSDs < 1.3%, the unquestionable disadvantage is the long duration of the entire process (almost 52 hours).Sorbent beads containing magnetic graphene oxide (MGO) as a magnetic core were used to extract endocrine disrupting compounds (EDCs) such as bisphenol A (BPA) and epichlorohydrin (ECH) from river water and industrial wastewater [39]. Shah and Jan first synthesized GO, and then, by adding a solution of Fe (II) and Fe (III) in molar ratio 1:2, in alkali conditions, they synthesized MGO. Subsequently, they added to the sodium alginate solution and stirred for 2 h. The procedure of alginate beads preparation was the same as described elsewhere. However, instead of $CaCl_2$ solution, the commonly used crosslinking agent, $FeSO_4\cdot 7H_2O$ solution, was used. The combination of sodium hydrogel and MGO (MGO-ALG) yielded a sorbent with a large specific surface of 303.68 m^2/g. Significantly higher than these calculated for GO and MGO, equal to 43.64 m^2/g and 274.67 m^2/g, respectively. The optimized conditions of the sample preparation step resulted in a very high recovery rate of 97.17% for ECH and 99.46% for BPA. Using an HPLC-UV at the final determination stage, the authors achieved low LODs of 8.25 and 13.99 ng/L, which was lower than in similar reported methods. Nonetheless, regeneration study results showed that five times the use of the sorbent contributed to reducing the recovery to 87% and 83% for BPA and ECH, respectively. In another study, the authors investigated the applicability of a hydrogel sorbent consisting of MGO, MIL-101, and silica-coated magnetite nanoparticles for the selective extraction and quantification of phthalates in water, juice, and tea samples [40]. GOx/MIL-101/Fe_3O_4-SiO_2 sorbent in the form of fiber showed a satisfactory extraction efficiency toward four phthalate esters, ranging from 80.7-89.9%. According to the test results, the synergistic effect of GOx and MIL-101and significantly boosted the adsorption capacity of the sorbent, almost 2 times compared to MIL-101/Fe_3O_4-SiO_2, and 1.2 times compared to

$GOx/Fe_3O_4-SiO_2$. Moreover, the sorbent demonstrated thermal stability and allowed for up to 16 reuses without significantly decreasing its extraction performance.

Table1. Summary of application of alginate-based sorbents in microextraction techniques.

Sorbent (mass [mg])	Adsorption capacity [mg/g]	analyte	Sample (volume/mass)	desorptive solvent (volume [mL])	Final determination	LOD	LOQ	Recovery [%]	RSD [%]	reusability	Ref
SPE											
NFL/ALG (n.d.)	18.86	Pb^{2+}	water, beverages (2 mL)	3 M HNO$_3$ (2)	FAAS	0.39 [ug/L]	1.31 [ug/L]	91.7-99.8	2.65	n.d.	[16]
Calcium ALG microparticles (10)	n.d.	rare earth elements	water (100 mL)	0.5 M HNO$_3$ (1)	ICP-MS	0,01-0,03 [ng/L]	n.d.	81-101	n.d.	50 cycles	[25]
in-syringe SPE											
P − ZrO$_2$CeO$_2$ZnO nanoparticles/ALG (150)	62.89 292.93	Ca, Li	environmental water (100 mL)	1 M HNO$_3$ (10)	ICP-MS	0.03 0.102 [ng/L]	0.099 0.34 [ng/L]	57.0–147.7 33.12–116.5	n.d.	n.d.	[41]
biochar/SA MMM (n.d.)	n.d.	nitroimidazoles	environmental and drinking water (10 mL)	ACN (1.5)	HPLC-MS/MS	0.006-0.014 [ng/mL]	0.021-0.048 [ng/mL]	79-99	7.1-8.2	5 cycles	[19]
in-tip SPE											
MIL-101/CTAB/ALG/CF (500)	3.48, 4.99	phthalates	beverages (10 mL)	ACN (2)	HPLC-DAD	0.15 [ug/L]	n.d.	85.2-97.8	0.1 – 4.9	15 cycles	[21]
SPME											
ALG hydrogel (n.d.)	n.d.	luoxetine, norfluoxetine	plasma (0.32 mL)	MeOH (0.2)	HPLC-FD	n.d.	n.d.	n.d.	n.d.	5 cycles	[24]
ALG/zein hydrogel (n.d.)	n.d.	drugs	water (10 mL)	MeOH (0.19)	GC-MS	1-50 [ng/L]	n.d.	n.d.	n.d.	n.d.	[23]
µ-dSPE											
ALG/GAC hydrogel (n.d.)	n.d.	PAHs	environmental water (100 mL)	toluene (2)	HPLC-UV	0.01-0.07 [ng/mL]	0.03-0.23 [ng/mL]	93.5-102.2	4.2–6.7	n.d.	[26]
CA/[poly(MAA-co-EGDMA)]:[Thy] (n.d.)	n.d.	pesticides	beverages (3 mL)	EtOH (0.15)	GC-MS	0.004-0.069 [ug/L]	0.013-0.23 [ug/L]	68.2-115.6	1.4−10.2	4 cycles	[28]
ALG-g-	n.d.	Pb^{2+}	corn cereal	1 M HNO$_3$	MIP OES	n.d.	n.d.	100	n.d.	10 cycles	[42]

PAAM/MWCNT-f (10)		Cd^{2+}		(10)							
SFE/ALG beads (200)	n.d.	Pb^{2+}	environmental water (200 mL)	0.8 M HCl (2)	FAAS	2 [ug/L]	7 [ug/L]	94.8-100.2	< 5	6 cycles	[43]
ZNCAHF (n.d.)	n.d.	pesticides	beverages (5 mL)	toluene/DCM (0.25)	GC-MS	0.001-0.004 [ng/mL]	0.003-0.012 [ng/mL]	90-105	3.2–7.8	n.d.	[29]
ALG-MWCNT (50)	n.d.	PAHs	environmental water (50 mL)	EtOAc (0.1)	GC-FID	0.22-0.42 [ng/mL]	0.732-1.38 [ng/mL]	71,2-104	0.4-12.4	n.d.	[25]
CA/[ChCl]:[PEG] (30)	n.d.	5-hydroxymethylfurfural	coffee (0.5 g)	ACN (0.2)	HPLC-UV	2.25 [µg/kg]	7.49 [µg/kg]	79-102	<4.7	n.d.	[27]
AC@PVP@alginate (100)	42.2, 44.4	nevirapine, zidovudine	environmental water (20 mL)	ACN (5)	HPLC-DAD	0.20-0.23 [ug/L]	0.67-0.75 [ug/L]	91.3-99,1	≤6.8	6 cycles	[30]
Mµ-dSPE											
Fe-ALG- MGO (5)	6.73, 7.01	BPA, ECH	environmental water (20 mL)	MeOH (n.d.)	HPLC-UV	13.99 [ug/L]	8.25 [ug/L]	97.17-99.46	1.20–6.87	5 cycles	[39]
GOx/MIL-101/Fe_3O_4-SiO_2 (n.d.)	n.d.	phthalates	beverages (10 mL)	ACN (2)	HPLC-DAD	3-5 [ug/L]	10-15 [ug/L]	80.7-89.9	0.1–7.3	16 cycles	[40]
Fe_3O_4@CA/[(HEMA)m-co-(EGDMA)n]:[Thy] (10)	n.d.	melamine	milk and diary products (0.5 g)	MeOH (0.3)	HPLC-UV	0.5 [µg/kg]	2 [µg/kg]	77.4–105	<6.9	3 cycles	[36]
HP-PEDOT@Fe_3O_4@ALG (250)	n.d.	PAHs	meat (5 g)	IPA (1)	GC-MS/MS	0.2-0.4 [µg/kg]	0.5-1 [µg/kg]	81.5–99.4	<7	9 cycles	[44]
Fe_3O_4@C_{18}@Ba^{2+}-ALG (100)	n.d.	PAHs and PAEs	environmental water (20 mL)	ACN (0.5)	HPLC-FLD	2-53 [ng/L]	(n.d.)	72-108	1-9	8 cycles	[45]
Fe_3O_4/MWCNTs/ALG (200)	n.d.	PAHs	environmental water (10 mL)	ACN/toluene (4)	HPLC-FLD	0.05-0.01 [ng/L]	0.02-0.04 [ng/L]	96-98	<10	10 cycles	[46]

Fe_3O_4@CA/[PNVP]:[BA]/MWCNT (10)	n.d.	pesticides	honey	ACN (0.1)	GC-MS	0.007-0.31 [µg/kg]	0.023-1.02 [µg/kg]	73.2-110.8	2.3-8.1	n.d.	[37]
PANI/ALG/Fe_3O_4 (400)	1.15-1.25	PAHs	environmental water (10 mL)	ACN (1 mL)	HPLC-FLD	0.01 [ug/L]	0.04 [ug/L]	86-98	<6	6 cycles	[32]
PPy-rGOx-Fe_3O_4 ALG hydrogels (750)	n.d.	phthalates	beverages (20 mL)	EtOAc (3)	GC-MS/MS	0.005-0.01 [ug/L]	0.02-0.04 [ug/L]	87.5-99.1	0.6–7.7	18 cycles	[35]
ZnO/Fe_3O_4@SiO_2-NH_2/MIP/ALG (500)	n.d.	sulfonamides	milk (10 mL)	MeOH/acetic acid (2)	HPLC-DAD	0.03-0.06 [ug/L]	0.1-0.2 [ug/L]	87-98.5	<6	10 cycles	[38]
PANI/GOx/ C_{18}-SiO_2-Fe_3O_4 (500)	n.d.	fluoroquinolones	honey,milk, eggs (10 mL)	ACN/DCM/ acetic acid (3)	HPLC-FLD	0.001-0.01 [ug/L]	0.003-0.04 [ug/L]	80–98	<9	7 cycles	[33]
polypyrrole/Fe_3O_4/ALG (n.d.)	n.d.	estriol,β-estradiol, BPA	environmental water (10 mL)	ACN (2)	HPLC-FLD	0.5 [ug/L]	n.d.	90-98	<5	16 cycles	[34]
MIL-101(Cr)-NH_2 (300)	n.d.	herbicides	environmental water (10 mL)	ACN (1)	HPLC-MS/MS	0.43–16 [ng/L]	n.d.	75.3-155.3	1.51-9.5	10 cycles	[47]

AC- activated carbon; ALG- alginate; BPA-bisphenol A; CTAB- cetyl trimethyl ammonium bromide; ECH-epichlorohydrin; EGDMA- ethylene glycol dimethacrylate; EtOH-ethanol; FAAS-Flame Atomic Absorption Spectrometer; FID- Flame ionization detektor; GAC- granular activated carbon; GC-Gas Chromatography; HEMA-2-Hydroxyethyl methacrylate; HP- Hierarchically Poros; HPLC-High Performance Liquid Chromatography; ICP- Inductively Coupled Plasma; IPA-2-propanol; MeOH-methanol; MIP OES - Microwave-Induced Plasma Optical Emission Spectrometer; MIL-amino-functionalized metal-organic framework; MIP-molecularly imprinted polymers; MGO-magnetic graphene oxide; MMM- Mixed matrix membrane; MS-Mass Spectrometer; MWCNTs – multiwalled carbon nanotubes; PAAM-poly(acrylamide); PAHs-polyaromatic hydrocarbons; PAEs-phthalate esters; PANI- polyaniline; PEDOT- poly(3,4-ethylenedioxythiophene); PEG-polyethylene glycol; PVP- polyvinylpyrrolidone; Thy-thymol; UV-ultraviolet; ZNCAHF-zirconia nanoparticles-decorated calcium alginate hydrogel fibers.

4. Green profile

Because of their eco-friendly nature, the application of alginate-based sorbents in microextraction techniques is undoubtedly a significant step toward improving the greenness of analytical procedures. Alginates are renewable, non-toxic, and easily biodegradable materials, therefore using them as a sorbent is in line with some of the GAC principles. Based on the data presented in the Table 1, it can be stated that the amount of the sorbent, volume of the sample, and desorption solvent used in various miniaturized alginate-based sorbent approaches are relatively small. Additionally, the sample preparation procedures are usually simple and do not consist of many steps. From a GAC point of view, the possibility of regeneration and multiple reuses of the sorbent is also an undeniable advantage. However, it should be highlighted that in the vast majority of procedures, modified alginate hydrogels were used. The surface modification procedures or combination with other materials mostly require the use of large quantities of additional reagents, solvents, and washing solutions. Whereby the overall amount/volume of chemicals and generated wastes is increased. Moreover, some stages of sorbent modification require the utilization of ultrasound energy or long-term heating, which significantly reduces environmental friendliness of the entire analytical procedure.

To study whether the green profile of the analytical procedure is consistent with that of the alginate-based sorbent synthesis, selected approaches proposed by different researchers were evaluated using one of the tools intended to assess how green the analytical methods are, named Analytical Eco-scale [48]. This green chemistry metric proposed by Gałuszka et al. [49] is based on the penalty points, which are assigned in four main aspects: (i) the amount and hazards of reagents used; (ii) the energy consumption; (iii) occupational hazards; and (iv) waste generation. The Eco-scale score is calculated by subtracting all penalty points from 100. In this evaluation, the higher the score, the greener and more sustainable the analytical procedure is. This metric tool was selected over others such as GAPI, AGEEPrep [50,51], and others because it primarily concentrates on the sample preparation step, disregarding issues related to sample collection, transportation, preservation, or sample throughput that are not relevant to the sorbent synthesis.

Ten representative studies have been selected from those collected in the Table 1. At least one study from each type of microextraction technique was selected. Due to the larger number of publications in the dispersive micro-solid phase extraction techniques section, two publications from the D-μSPE group and four from the MD-μSPE group were selected. Additionally, the diversity of the sorbent composition was taken into account at the stage of reports selection. Table 2 includes the penalty points assigned to a given category and the eco-scale score of the selected studies, considering the analytical procedure (without sorbent preparation process) and the alginate-based sorbent synthesis.

Table. 2. Penalty Points and Analytical Eco-scale scores of the selected reports, with consideration of the analytical procedure and the sorbent synthesis.

Microextraction technique	sorbent	Analytical procedure					Sorbent synthesis					Ref.
		Reagents PPts	Energy PPts	Occupational haz.	Waste PPts	Eco-scale score	Reagents PPts	Energy PPts	Occupational hazard	Waste PPts	Eco-scale score	
SPE	NFL/ALG	2	2	0	6	90	11	3	0	6	80	[16]
in-syringe SPE	biochar/ALG	8	3	3	8	78	5	4	3	6	82	[19]
in-tip SPE	MIL-101/CTAB/ALG/CF	10	2	3	8	77	52	6	0	8	34	[21]
SPME	ALG/zein	11	2	3	8	76	5	1	0	6	88	[51]
µ-dSPE	CA/[poly(MAA-co-EGDMA)]:[Thy]	4	3	0	6	87	18	1	0	6	75	[28]
	ALG-g-PAAc/MWCNT-f	4	3	3	6	84	34	3	0	8	55	[47]
Mµ-dSPE	MIL-101(Cr)-NH$_2$	4	3	3	8	82	43	7	0	8	42	[47]
	Fe-ALG-MGO	11	3	0	8	78	41	3	3	8	45	[39]
	ZnO/Fe$_3$O$_4$@SiO$_2$-NH$_2$/MIP/ALG	16	5	3	8	68	51	4	3	8	34	[38]
	PANI/GOx/C$_{18}$-SiO$_2$-Fe$_3$O$_4$ALG	12	1	3	8	76	70	4	3	8	15	[33]

As it can be seen in Table 2, a significant majority of the selected analytical procedures obtained total Eco-scale scores above 75, indicating an excellent green analysis. Only one procedure, with a rating of 68, qualifies as an acceptable green analysis. However, considering the sorbent synthesis approach, it becomes evident that not all these steps are as environmentally friendly as their analytical application. Just four of the ten investigated synthesis protocols achieved scores ≥ 75. In these protocols, only a slight modification of alginate hydrogel was conducted, consisting of compounding with natural sorbents and DES (references [4, 7, 9, 19]). The other procedures necessitated the use of significantly more reagents, primarily those hazardous and energy-consuming processes like long-term high-temperature processes or sonication, thereby increasing the PPs associated with reagents and energy consumption. The PANI/GOx/C_{18}-SiO_2-Fe_3O_4 alginate sorbent synthesis yielded the lowest eco-scale score rating of 15. This result is mainly influenced by the PPs associated with usage of a significant amount of reagents (classified as “danger”) at the stage of tedious and involves several steps in the in the synthesis of individual sorbent components. Similarly, in the case of the other two protocols with an eco-scale score lower than 40, the main factor affecting the decrease in green profile are PPs assigned to the reagents used (PPs for reagents greater than 50). This suggests that the main factor reducing the environmental sustainability of the synthesis is the excessive use of hazardous reagents.

5. Summary and future trends

Alginates gels seem to be a very attractive material capable of being employed in various miniaturized extraction techniques. In comparison to synthetic polymers, they offer many favourable futures, such as biodegradability, low cost, abundant availability, and easy preparation. These characteristics make alginates ideal green sorptive materials from the GAC point of view. Unfortunately, alginates gels in their pure form show low extraction capacity, which limits their use as a neat extraction material. Nevertheless, their adsorption performance can be easily enhanced by compounding with other sorptive materials, including carbon and magnetic nanoparticles, GO, MIPs, MOFs, DESs, and others. So far, alginate composites sorbents have been successfully applied as efficient adsorbents in SPE, in-syringe SPE, in-tip SPE, SPME, and Dμ-SPE, with the last being the most preferred approach. In all presented methods, the tested sorbents showed effective binding capabilities for specific analytes. Despite the fact that the idea of using biodegradable material as a sorbent contributes to improving the green profile of analytical methodology, some of the sorbent preparation processes are not as green as desirable. As discussed above, in some research, the alginate gel modification step required the use of a large amount of hazardous reagents and energy- and time-consuming processes. Therefore, future efforts should be made to find a balance between sorbent formulation process sustainability and alginate-based sorbent efficiency. This goal could be achieved by using materials coming from natural sources and/or natural deep eutectic solvents as modifiers; replacing organic solvents used during the sorbent synthesis by greener alternatives, and using modifiers that will contribute to increasing the reusability of the sorbent. What is more, it is also important to take sorbent synthesis into consideration when the environmental sustainability of the procedure is considered.

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Figure captions:

Fig.1. Number of publications focused on alginate-based sorbents application in microextraction approaches based on Web of Science database (searched keywords: alginate-based sorbent; microextraction, accessed on June 2024).

Fig.2.The molecular structures of possible sequences of L-guluronic and D-mannuronic units in alginate polymer.

Fig.3. Main groups of sorbents combined with alginine hydrogel and used in solid-phase microextraction techniques

Fig.4. Main steps of alginate-based sorbent preparation.

Fig 5. The distribution of articles among various sorbent-based microextraction techniques.

Table captions:

Table 1. Summary of application of alginate-based sorbents in microextraction techniques.

Table. 2. Penalty Points and Analytical Eco-scale scores of the selected reports, with consideration of the analytical procedure and the sorbent synthesis.