**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

44 microextraction (TFME) and many others. A detailed description of these and other applications can
45 be found in the latest published papers [6–11]. However, in recent years, growing interest in the
46 application of another class of polysaccharides, alginates, for sorbent preparation intended
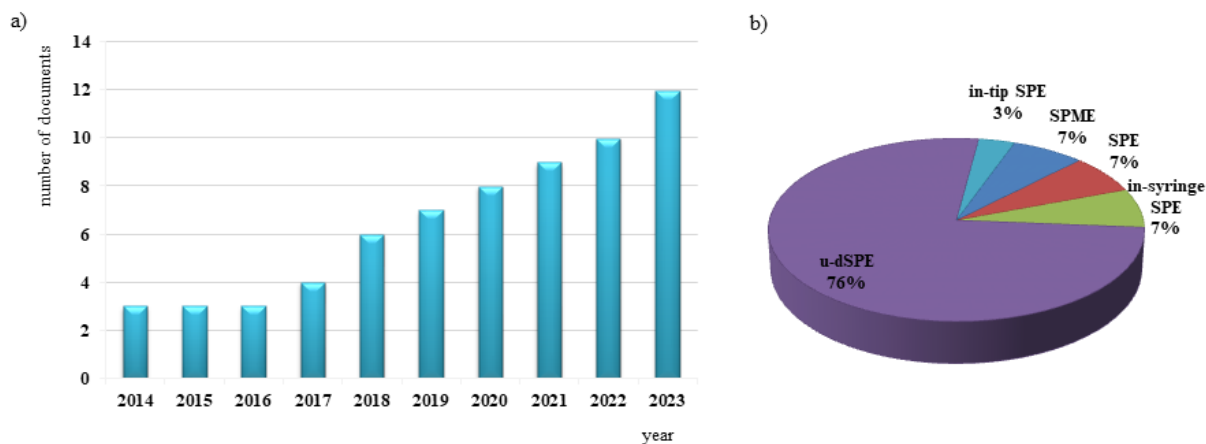47 formicroextraction has been observed (Fig.1).



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.

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

61

62    2. Chemical structure and properties of alginates

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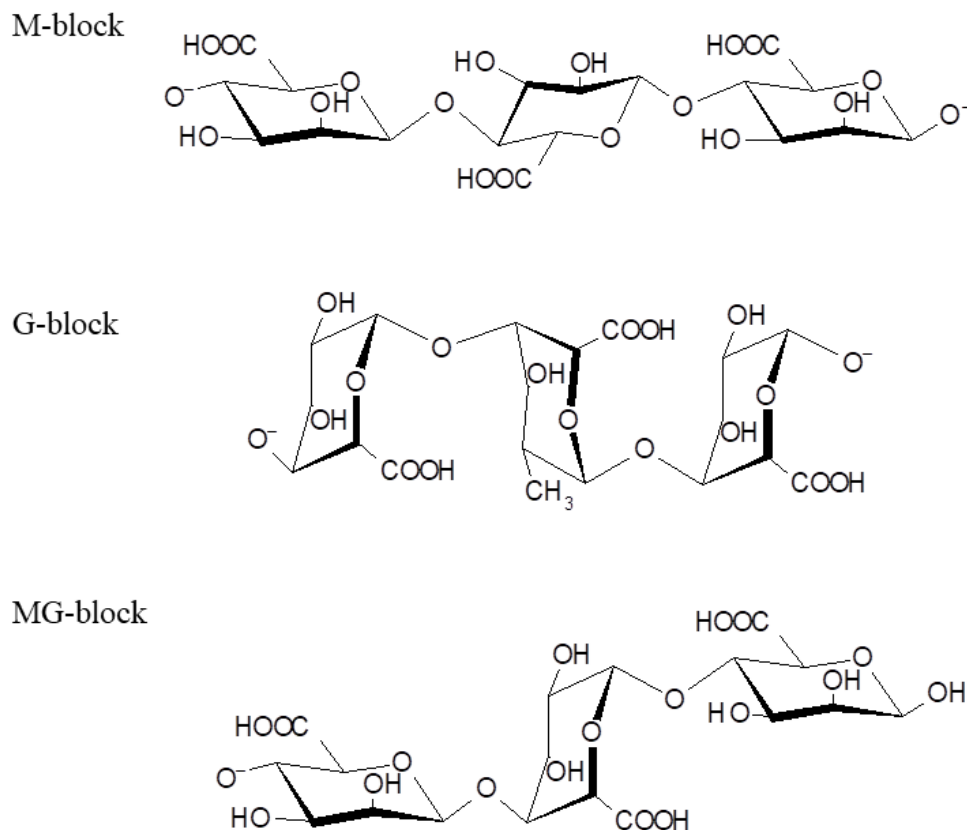
M-block

G-block

MG-block

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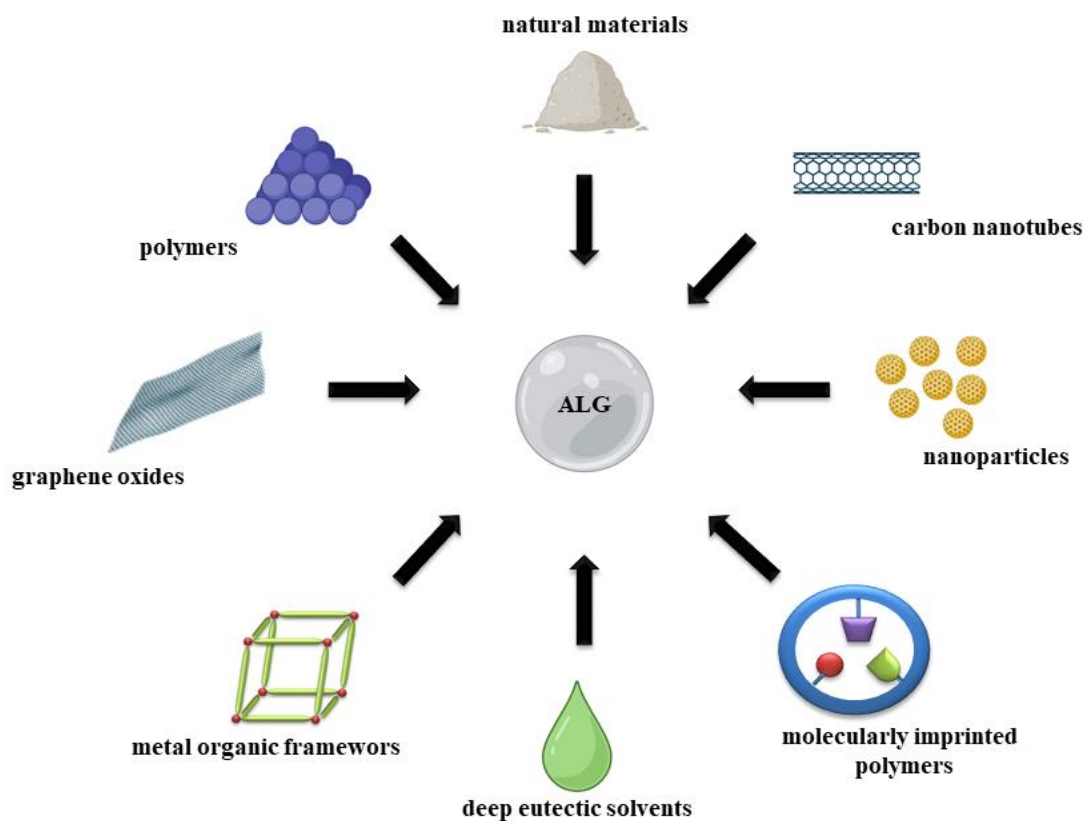
Fig.3. Main groups of sorbents combined with alginine hydrogel and used in solid-phase microextraction techniques.

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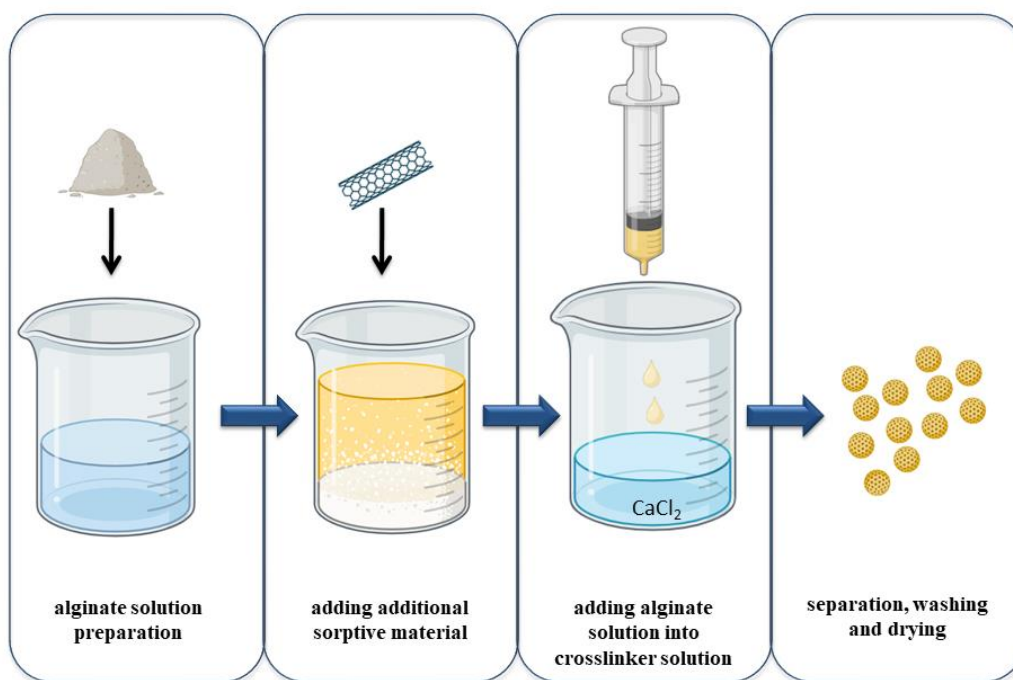
Fig.4. Main steps of alginate-based sorbent preparation.

108

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

116       3.1. column SPE

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

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

134 (FAAS). The proposed method showed very good extraction efficiency (91.7–99.8%) and good
135 precision (relative standard deviation, 2.65%). Moreover, it has been shown that the incorporation of
136 sulphide intercalated LDHs nanosheets provides more adsorption sites, contributing to the higher
137 selectivity of Pb (II) and almost six times higher adsorption capacity compared to alginate hydrogel
138 [16]. Another approach based on packing alginate microparticles in polypropylene column was
139 proposed by Arantes De Carvalho et al. [17]. This column was prepared for the extraction and
140 preconcentration of 14 rare earth elements from environmental water samples. Briefly, the spherical
141 calcium alginate (CA) beads were synthesized, washed, and freeze-dried. Then, in order to increase
142 the surface area, dried beads were cryogenically ground and sieved. The obtained sorbent (300 mg),
143 with particle sizes ranging from 10 to 180 μm, was dispersed in deionized water and packed as a slurry
144 into a polypropylene column with a porous polyethylene frit at the bottom and at the top. The column
145 was coupled to a flow injection system and conditioned before loading the sample. After loading a
146 sample, the column was dried, the analytes were eluted with 1.0 mL of 0.5 mol/L $HNO_3$ and analyzed
147 by ICP-MS. However, the obtained recovery values were slightly lower than those obtained using
148 commercially available resins such as iminodiacetate (IDA), $C_{18}$-polyacrylonitrile (PAN), or alkyl
149 phosphinic acid resin (APAR). The proposed protocol can be a reliable, environmentally friendly
150 alternative due to the possibility of re-utilization of the CA column, even for up to 50 cycles, low cost,
151 and no need to use relatively highly concentrated acids.

152 ### 3.1.1.    in-syringe SPE

153 Although SPE is a very effective extraction method, it suffers from a few limitations, including using a
154 larger sample volume, solvents for conditioning and desorption, and a larger sorbent amount. So,
155 following GAC principles, a miniaturized version of traditional cartridge-based SPE in the form of a
156 syringe filter holder was proposed [18]. So far, in the area of alginate-based sorbents application in
157 this technique, only one study has been reported. The researchers prepared the sorbent by dispersing
158 biochar (obtained from herb residue) in the sodium alginate matrix and crosslinking it by immersing in
159 a calcium chloride solution. Then the obtained membrane was cut into a round piece (25 mm) and
160 packed in the syringe filter. To extract the nitroimidazoles from tap water, the sample was passed
161 through the filter six times by pulling and pushing the syringe plunger. Subsequently, the analytes
162 were eluted with 1.5 mL of acetonitrile and analysed by ultrahigh performance liquid chromatography
163 coupled to tandem mass spectrometry (UHPLC-MS/MS). Under optimal conditions (pH, extraction
164 time, elution solvent, volume, and extraction cycles), the application of the developed material
165 allowed recoveries of metronidazole (80.2 - 92.5%), secnidazole (86.4 - 99.1%), dimetridazole (79.3 -
166 93.9%), and ornidazole (79.6 - 92.9%) in the analysed samples. The results revealed that
167 immobilization of biochar in alginate gel not only increased analyte adsorption efficiency but also
168 enhanced mechanical properties, allowing it to be reused up to five times. Moreover, the mass of the
169 sorbent used and the limit of detection (LOD) value were significantly lower compared to other solid
170 phase microextraction methods applied for the analysis of nitroimidazoles in water samples. An
171 additional advantage of the proposed methodology was that no additional steps such as centrifugation,
172 filtration, or magnet separation were required, which significantly simplified the entire procedure and
173 reduced the time compared to others [19].

174 ### 3.1.2.    In-tip SPE

175 In another format of miniaturized SPE that uses the same steps—conditioning, sample loading,
176 washing, and elution—a small amount of sorbent is packed inside a plastic pipette tip[20]. An
177 alginate-based sorbent has also been applied in this approach. Nurerk et al. introduced a micro-pipette
178 tip device consisting of cotton fiber coated with sorbent, which was prepared by integrating metal-

179    organic frameworks (MIL-101) and cetyltrimethylammonium bromide (CTAB) into alginate hydrogel
180    [21]. In the proposed method, the authors first synthesized MIL-101 via the hydrothermal method and
181    mixed it with CTAB and alginate hydrogel. Subsequently, they used epichlorohydrin as a cross-linker
182    in the reaction between sodium alginate and cotton fibers. Then, cotton fibers were immersed in a
183    $CaCl_2$ solution to obtain MIL-101/CTAB/ALG/CF. The 500 mg of synthetized sorbent was packed
184    into a 1000 µL pipette tip and connected to a syringe. The proposed lab-made microextraction device
185    was utilized for the extraction of five phthalates from beverage samples. A 10 mL sample was
186    manually passed through the sorbent. The adsorbed analytes were then eluted from the fibers using 2
187    mL of acetonitrile and evaporated to dryness. Finally, the dry residue was dissolved in 1 mL of
188    methanol, and 20 µL were injected into the high performance liquid chromatography coupled to diode
189    array detection (HPLC-DAD) system. The proposed approach yielded a sorbent with a large specific
190    surface area (710.02 m²/g), resulting in a high recovery rate (85.2–97.8%). Furthermore, the method
191    exhibited a low limit of detection (0.15 µg/L) and high precision (RSD less than 4.9%). The obtained
192    parameters were comparable to another HPLC-DAD method using graphene nanoplates as a sorbent in
193    SPE mode. However, it should be highlighted, that the volume of the sample as well as solvent used
194    for sorbent conditioning in the in-tip SPE approach were significantly reduced (approximately 20
195    times). Moreover, the proposed procedure was much simpler and did not require the use of additional
196    equipment, such as a vacuum pump. Furthermore, the sorbent showed potential to be used multiple
197    times. Even after 15 cycles of sorption-desorption, the analyte recovery remained at 92–93.4%.

198         3.2. SPME

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

212    Alginate-based hydrogels have also been applied as efficient coatings in SPME. The first paper
213    describing the usage of alginate sorbent supported on a fiber was published in 2017 by Castilhos et. al.
214    [23]. The researchers prepared an alginate-based hydrogel modified by the incorporation of corn
215    protein-zein for coating a polypropylene hollow fiber. The fiber preparation procedure consisted of the
216    following steps: (i) cutting the fiber into 1.5 cm long pieces; (ii) conditioning in acetone (5 min); (iii)
217    immersing in the alginate/zein dispersion at 60 °C under magnetic stirring (2 h); (iv) inserting, stainless
218    steel rods into the inner lumen of the hollow fiber; (v) immersing the fiber in calcium chloride solution
219    (2 h); and (vi) washing with ultra-pure water. Then the fiber was immersed in a water sample (30 min)
220    to adsorb thirteen polar compounds including hormones, anti-inflammatory agents, antiseptics and
221    analgesics. After the extraction, analytes were desorbed in methanol using ultrasonic energy for 60
222    min, then methanolic extract was dried and derivatization reagent was added. Finally, the sample was
223    injected into gas chromatography coupled to mass spectrometry (GC-MS) system. The authors of this
224    work attributed the superior extraction efficiency especially towards compounds with a low n-octanol-

225  water partition coefficient (Kow), such as estriol, estrone, 17-α-ethinylestradiol, progesterone, and 4-
226  nonylphenol. The increase in the extraction efficiency compared to coating prepared without zein
227  addition could be due to reduced initial amount of water absorbed by the hydrogel, which resulted in
228  better interaction between analytes and the sorbent. It should also be highlighted that covering the
229  fiber with alginate-based gel significantly improved the extraction efficiency for some analytes. The
230  peak areas of paracetamol, atrazine, ibuprofen, and 4-octylphenol were significantly higher when fiber
231  supported by hydrogel was used on a sample preparation step than when using polypropylene (PP)
232  fiber with no modification. Which confirmed that the fiber modification by alginate sorbents
233  significantly improved the affinity and selectivity of the sorptive device. However, the approach
234  proposed by researchers is efficient and sensitive, the fiber modification and extraction steps are quite
235  time- and energy-consuming [23]. Another research group suggested using unmodified alginate gel as
236  a covering material for the extraction of fluoxetine and its metabolite, norfluoxetine, from human
237  plasma samples. A similar methodology, as described above, was used for the preparation of hydrogel
238  fiber device. However, the time of fiber immersing in the hydrogel and calcium chloride solution was
239  significantly shortened (240 min versus 4 min). Moreover, the fiber was coated with a second layer of
240  hydrogel. Obtained SPME fiber was used in DI mode, extracted analytes were eluted in methanol and
241  then injected onto high performance liquid chromatography coupled with fluorescence detector
242  (HPLC-FD). Again, the authors obtained much higher peak areas when using a hydrogel-coated fiber
243  than when only PP fiber was applied, which confirms superior sorption capacity of alginate gel.
244  Moreover, it was also proven that alginate hydrogel acted as a restricted access material (RAM),
245  effectively blocking nearly all (96%) plasma proteins presented in the samples. This feature of the
246  hydrogel is particularly advantageous in the context of its use for biological matrices preparation
247  because it allows simplification of the procedure and shortens the sample preparation time by
248  eliminating steps such as protein precipitation or incorporation of additional RAMs into the extraction
249  phase [24]. Despite the analytical figures of merit not being evaluated (making comparisons of
250  selectivity, sensitivity, and efficiency of the extraction process impossible), the proposed methodology
251  appears intriguing and warrants further development, especially in the context of the application of
252  this format in bioanalysis. Reducing sample preparation steps and costs allows for an increase in the
253  greenness in comparison to commercial SPME devices.

254  ### 3.3. Dispersive micro-solid phase extraction

255  Without a doubt, dispersive micro-solid-phase extraction (D-µSPE) is technique where alginate-based
256  sorbents are most frequently used. In this sub-mode of traditional SPE method, low sorbent amount (in
257  the low milligram range) is directly introduced into the sample solution and dispersed by vortexing or
258  external energy source such as ultrasounds. Due to the sorbent dispersion in the sample, the contact
259  area between the extractant and analytes increases significantly thus allowing to improve the
260  extraction efficiency and reduced the extraction time. Subsequently, the sorbent containing adsorbed
261  analytes is separated from the sample matrix, typically through centrifugation or filtration.
262  Advantageous features of the D-µSPE, such as simplicity, short sample preparation time, minimized
263  solvent usage, as well as simplicity of alginate-based sorbent preparation have caused so wide interest
264  among analysts. Silva et. al. prepared ALG-MWCNT microbeads by mixing sodium alginate solution
265  with multi-walled carbon nanotubes that were used for the extraction of polycyclic aromatic
266  hydrocarbons (PAHs) from environmental water samples [25]. The procedure entailed adding ALG-
267  MWCNT microbeads to an aqueous sample and thoroughly mixing the entire solution on a platform
268  shaker for 30 minutes. After this time, the microbeads were separated by decantation and dried. The
269  authors tested several solvents and their volumes for analytes desorption. Finally, 0.1 mL of ethyl
270  acetate was used. In order to improve desorption, ultrasonication was applied. Fluorene, phenanthrene,

271 and fluoranthene determination was carried out using an gas chromatography coupled to flame
272 ionization detector (GC-FID) system, resulting in LODs ranging from 0.22 to 0.42 ng/mL. In another
273 work, also aimed at extracting PAHs from real water samples, alginate beads based on granular
274 activated carbon were applied. The authors obtained carbon material from waste polyethylene
275 terephthalate (PET) bottles, which is a very interesting solution in terms of reducing the amount of
276 plastic waste and thus environmental protection. The plastic bottles were first cut into small pieces,
277 washed, and dried. Then a small portion of the material was subjected to carbonization in a cylindrical
278 furnace at 800 °C for 1 h under a nitrogen atmosphere. Cooled and powdered activated carbon was
279 mixed with sodium alginate solution, and sorbent beads were formed. The obtained sorbent exhibited a
280 sphere shape with a rough surface and porous structure, which ensured sufficient inner area for PAHs
281 sorption, resulting in recovery rates ranging from 93.5% to 102.22%. 50 mg of sorbent was found to
282 be sufficient for obtaining satisfactory extraction efficiency, and equilibrium was achieved under
283 shaking in just 8 minutes. Moreover, the developed method exhibited very good linearity, and
284 precision (RSD <6.7%), low LOD of 0.01 ng/mL (much lower than other procedures reported in the
285 literature for PAHs extraction) and low LOQ of 0.03 ng/mL [26]. In 2022,Asghari and co-workers
286 introduced an innovative variant of gel-based sorbent composed of an eutectogel derived from the
287 combination of calcium alginate and deep eutectic solvent (DES). In this procedure, a hydrophobic
288 DES consisting of choline chloride (ChCl) and polyethylene glycol (PEG) in molar ratio 1:1 was
289 encapsulated in alginate beads (beads diameter in the range of  414–746 μm). After drying at room
290 temperature, the small portion (30 mg) of sorbent was used for the rapid extraction (completed in 10
291 min) of 5-hydroxymethylfurfural (HMF) from coffee samples. The analyte desorbed from the sorbent
292 with 200 μL of acetonitrile was determined by HPLC-UV. The introduction of green solvent to the
293 alginate beads provided high recovery (79-102%) due to the formation of dipolar interactions and
294 hydrogen bonding between PEG chains and HMF molecules. The validation results demonstrate broad
295 linear range (7.49–1000 μg/kg), low LOD (2.25 μg/kg), and good precision (RSD < 4.7%) of proposed
296 method. Moreover, the authors assessed the environmental impact of the proposed method using two
297 green analytical matrix tools: the Complex Green Analytical Procedure Index (Complex GAPI) and
298 the Analytical Eco-Scale. The obtained pictogram as well as the final Eco-Scale score of 63 out of 100
299 indicate that the method can be classified as an acceptable green [27]. A similar approach, involving
300 encapsulation of DES in alginate beads, was proposed by Karami and Seresthi [28]. The researchers
301 combined thymol and methacrylic acid in a 1:1 molar ratio and subjected it to the polymerization
302 process using ammonium persulfate (APS) as a radical initiator and ethylene glycol dimethacrylate
303 (EGDMA) as a crosslinker to obtain a polymer named ([poly(MAA-co EGDMA)]:[Thy] DES). The
304 sorbent was then utilized to extract twenty four pesticides from non-alcoholic malt-based beverages. A
305 comparison between the extraction efficiency of unmodified alginate hydrogel and the eutectogel
306 showed a considerable role of the DES in enhancing extraction capabilities, resulting in 1.5–3.4 times
307 higher chromatographic responses than unmodified ones. As can be seen, the main shape of the
308 alginate-based sorbent used in the D-μSPE is a bead; however, in one report, scientists proposed the
309 use of other structural configuration, such as fiber. They prepared sorbent named zirconia
310 nanoparticles-decorated calcium alginate hydrogel fibers (ZNCAHF) by constant injection with
311 syringe zirconia/sodium alginate suspension into $CaCl_2$ solution. After drying, the sorbent (0.1 g) was
312 immersed in water and juice samples to extract three compounds from organophosphorus pesticides
313 group under stirring for 5 min. Afterward, the sorbent was withdrawn from the solution, washed,
314 dried, and transferred to a small tube wit toluene/dichloromethane mixture to desorb analytes. The
315 method exhibited very high recovery rate (90-105%) and very low LOD (0.001-0.004 μg/L).
316 According to the authors, these excellent results was achieved due to high specific area resulting with
317 sorbent thin fibrous shape and also zirconia nanoparticles content. However, the influence of the
318 sorbent shape on the extraction efficiency has not been investigated [29]. In another study, researchers

319 prepared sorbent by combining activated carbon (AC) and polyvinylpyrrolidone (PVP) and
320 encapsulating it in alginate beads (AC@PVP@ALG) [30]. The synthesized material was employed for
321 ultrasound-assisted dispersive micro-solid phase extraction (UA-Dμ-SPE) of antiretroviral drugs in
322 environmental water samples, and then followed up with HPLC-DAD determination. Due to its high
323 porosity and large specific surface area (372 $m^2$/g), the developed sorbent exhibited a favourable
324 extraction capability, ranging from 91.6 to 99.1%. Moreover, the application of ultrasounds as an
325 enhancing extraction factor could potentially affect this high recovery factor, but the authors have not
326 conducted any comparison studies. In comparison to SPE-Oasis HLB cartridges, mostly used for
327 nevirapine and zidovudine extraction, the elaborated procedure exhibited a notable higher recovery
328 with a much lower quantity of the sorbent used.

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

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

339 Nurerk et. al. proposed a magnetic composite sorbent named PANI/ALG/$Fe_3O_4$consisting of
340 polyaniline (PANI) coated $Fe_3O_4$ nanoparticles entrapped in alginate beads [32]. These sorbent beads
341 were combined with the HPLC-FLD method for the extraction and determination of three PAHs in
342 reservoir, river and wastewater samples. The proposed method showed very good extraction efficiency
343 (86–98%) and good precision (RSD <6%). Moreover, it has been shown that the addition of PANI has
344 a beneficial effect on PAHs adsorption efficiency. Compared to $Fe_3O_4$, $Fe_3O_4$/alginate sorbents,
345 PANI/alginate/$Fe_3O_4$exhibited much higher adsorption capability (more than 4 times) of the target
346 analytes via π-π interactions. The adsorption capacity for benzo[a]anthracene, benzo[b]fluoranthene,
347 and benzo[a]pyrene was determined as 1.25, 1.19, and 1.15 μg/g, respectively and remained constant
348 even after six cycles of sorption-desorption. Similar sorbent, have also been used to extract
349 fluoroquinolones from honey, milk, and egg samples. However, in the case of this study, the core of
350 the sorbent consists, apart from magnetite, also GO and octadecyl-bonded silica. The combination of
351 these high-affinity materials and the formation of a double-pore network in the hydrogel provided a
352 high sorption capacity of 27.84 $m^2$/g and a good extraction efficiency ranging from 80 to 98% [33]. In
353 the next publication by the same authors, another material, polypyrrole, was used to cover the alginate
354 beads. The sorbent exhibited high adsorption capacity towards estriol, β-estradiol, and bisphenol A,
355 without significant loss even after 16 regeneration cycles [34]. A polypyrole-based sorbent named
356 porous nanostructured polypyrrole, reduced GO, magnetite nanoparticle alginate hydrogel
357 microspheres (PPy-rGOx-$Fe_3O_4$) was also applied for phthalate extraction from bottled water and
358 beverage samples. PPy-rGOx-$Fe_3O_4$ was prepared by adding magnetite nanoparticles, GO, and
359 calcium carbonate to an alginate solution. To reduce GO, hydrogel microspheres were immersed in
360 0.2% w/v ascorbic acid and heated at 85°C for 6 h. While, to obtain the hierarchical porous
361 nanostructure, the composite was added to 20% w/v hydrochloric acid. With the reaction of $CaCO_3$ in
362 the hydrogel microspheres with the hydrochloric acid, bubbles of $CO_2$ were released, which created a
363 porous double network. The obtained composite were then coated with polypyrrole. The analytes
364 desorbed from the sorbent with ethyl acetate were determined using GC-MS/MS. Under optimized

365  conditions, the elaborated method showed favourable recovery rates ranging from 87.5 to 99.1% and a
366  low LOD of 0.005-0.01 µg/L [35]. Another sorbent applied to magnetic D-µSPE was proposed by
367  Sereshti et. al. [36], who synthesized a three-component eutectogel, composed of a crosslinked
368  copolymeric DES and polyvinylpyrrolidone-coated $Fe_3O_4$ nanopowder (PVP-$Fe_3O_4$). The copolymeric
369  DES, consisting of 2-hydroxyethyl methacrylate (HEMA)/thymol (Thy) in a 1:1 M ratio, was prepared
370  through thermally-induced free-radical polymerization with  azobisisobutyronitrile, as an initiator, and
371  EGDMA as a crosslinker. The resulting material exhibited excellent and rapid (extraction occurred in
372  10 min) sorption capability of melamine from milk and dairy  products. Additional advantages of the
373  proposed approach include low sorbent mass (10 mg) and low volume of desorption solvent (300 µL).
374  Once again, a significantly greater recovery of analyte was obtained  using DES-modified gel beads
375  (66.9%) than that of unmodified calcium alginate beads 33.3%). Furthermore, it was found that the
376  extraction efficiency of the sorbent was significantly influenced by the pH of the sample solution. The
377  highest recovery (87.6%) was obtained at pH adjusted at 6 due to electrostatic interactions between $-O^-$
378  and $-COO^-$ groups in sorbent and $-NH_3^+$ groups in melamine. One more magnetic eutectogel beads
379  composed of a polymeric DES, carboxylated multiwall carbon nanotubes and polyvinylpyrrolidone
380  coated-$Fe_3O_4$  nanocrystals  ($Fe_3O_4$@CA/[PNVP]:[BA]/MWCNT-COOH)  was  applied  for
381  determination of pesticide residues in honey samples [37]. Another interesting sorbent was proposed
382  by Khongkla et. al. [38]. The authors integrated ZnO nanoparticles with magnetic molecularly
383  imprinted polymer and incorporated them into alginate hydrogel beads. This innovative sorbent,
384  known as ZnO/$Fe_3O_4$@$SiO_2$-$NH_2$/MIP/alginate was utilized for determination of two compounds from
385  sulphonamides group in milk samples. Through the application of molecular imprinting technique it
386  was possible to obtain not only efficient, with recovery ranging from 80.7-98.5% but also highly
387  selective material. Only the target sulfonamides have been extracted from such complex sample as
388  milk without interference compounds presented in the matrix. Moreover, the sorbent demonstrated
389  satisfactory reusability for up to ten sorption-desorption cycles. The process of sorbent preparation
390  was also investigated in terms of repeatability. Despite the demonstrated good reproducibility, with
391  RSDs < 1.3%, the unquestionable disadvantage is the long duration of the entire process (almost 52
392  hours).Sorbent beads containing magnetic graphene oxide (MGO) as a magnetic core were used to
393  extract endocrine disrupting compounds (EDCs) such as bisphenol A (BPA) and epichlorohydrin
394  (ECH) from river water and industrial wastewater [39]. Shah and Jan first synthesized GO, and then,
395  by adding a solution of Fe (II) and Fe (III) in molar ratio 1:2, in alkali conditions, they synthesized
396  MGO. Subsequently, they added to the sodium  alginate solution and stirred for 2 h. The procedure of
397  alginate beads preparation was the same as described elsewhere. However, instead of $CaCl_2$ solution,
398  the commonly used crosslinking agent, $FeSO_4 \cdot 7H_2O$ solution, was used. The combination of sodium
399  hydrogel and MGO (MGO-ALG) yielded a sorbent with a large specific surface of 303.68 $m^2$/g.
400  Significantly higher than these calculated for GO and MGO, equal to 43.64 $m^2$/g and 274.67 $m^2$/g,
401  respectively. The optimized conditions of the sample preparation step resulted in a very high recovery
402  rate of 97.17% for ECH and 99.46% for BPA. Using an HPLC-UV at the final determination stage,
403  the authors achieved low LODs of 8.25 and 13.99 ng/L, which was lower than in similar reported
404  methods. Nonetheless, regeneration study results showed that five times the use of the sorbent
405  contributed to reducing the recovery to 87% and 83% for BPA and ECH, respectively. In another
406  study, the authors investigated the applicability of a hydrogel sorbent consisting of MGO, MIL-101,
407  and silica-coated magnetite nanoparticles for the selective extraction and quantification of phthalates
408  in water, juice, and tea samples [40]. GOx/MIL-101/$Fe_3O_4$-$SiO_2$ sorbent in the form of fiber showed a
409  satisfactory extraction efficiency toward four phthalate esters, ranging from 80.7-89.9%. According to
410  the test results, the synergistic effect of GOx and MIL-101and significantly boosted the adsorption
411  capacity of the sorbent, almost 2 times compared to MIL-101/$Fe_3O_4$-$SiO_2$, and 1.2 times compared to

412 GOx/Fe$_3$O$_4$-SiO$_2$. Moreover, the sorbent demonstrated thermal stability and allowed for up to 16
413 reuses without significantly decreasing its extraction performance.

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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] |

| Sorbent (mg) | | Analyte | Sample (volume) | Eluent (mL) | Detection | LOD | LOQ | Recovery | RSD | Reusability | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 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$_3$O$_4$@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$_3$O$_4$ (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$_3$O$_4$ 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$_3$O$_4$@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$_3$O$_4$ (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$_3$O$_4$/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.

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441    4.  Green profile

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

456    To study whether the green profile of the analytical procedure is consistent with that of the alginate-
457    based sorbent synthesis, selected approaches proposed by different researchers were evaluated using
458    one of the tools intended to assess how green the analytical methods are, named Analytical Eco-scale
459    [48]. This green chemistry metric proposed by Gałuszka et al. [49] is based on the penalty points,
460    which are assigned in four main aspects: (i) the amount and hazards of reagents used; (ii) the energy
461    consumption; (iii) occupational hazards; and (iv) waste generation. The Eco-scale score is calculated
462    by subtracting all penalty points from 100. In this evaluation, the higher the score, the greener and
463    more sustainable the analytical procedure is. This metric tool was selected over others such as GAPI,
464    AGEEPrep [50,51], and others because it primarily concentrates on the sample preparation step,
465    disregarding issues related to sample collection, transportation, preservation, or sample throughput that
466    are not relevant to the sorbent synthesis.

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

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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] |

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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.