

# 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 chemistry

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- $\mu$ SPE), 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).

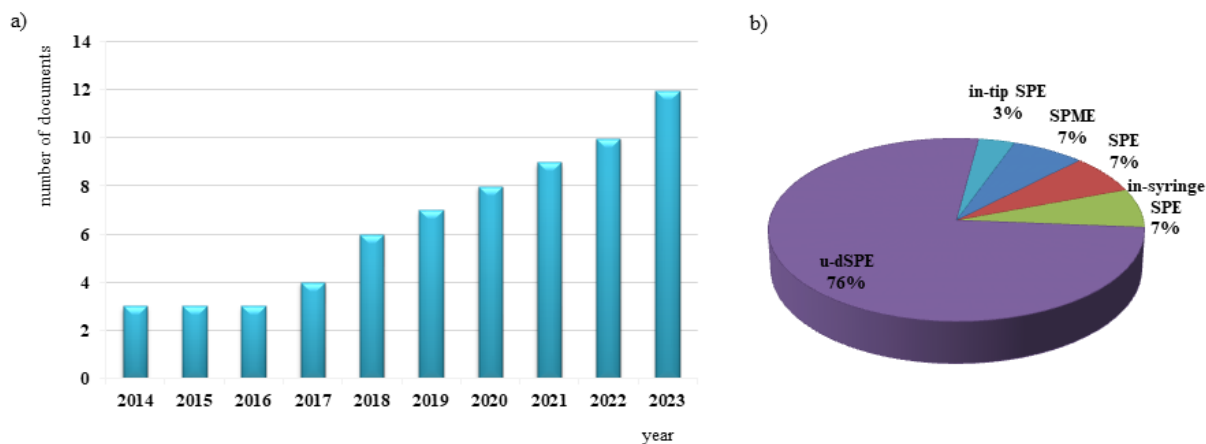


Fig.1.a) Number of publications focused on alginate-based sorbents application in microextraction approaches based on Web of science database (searched keywords: alginate-based sorbent; microextraction, accessed on June 2024);  
b) the distribution of articles among various sorbent-based microextraction 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- $\mu$ SPE. 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 strictly 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 seems to be a 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].

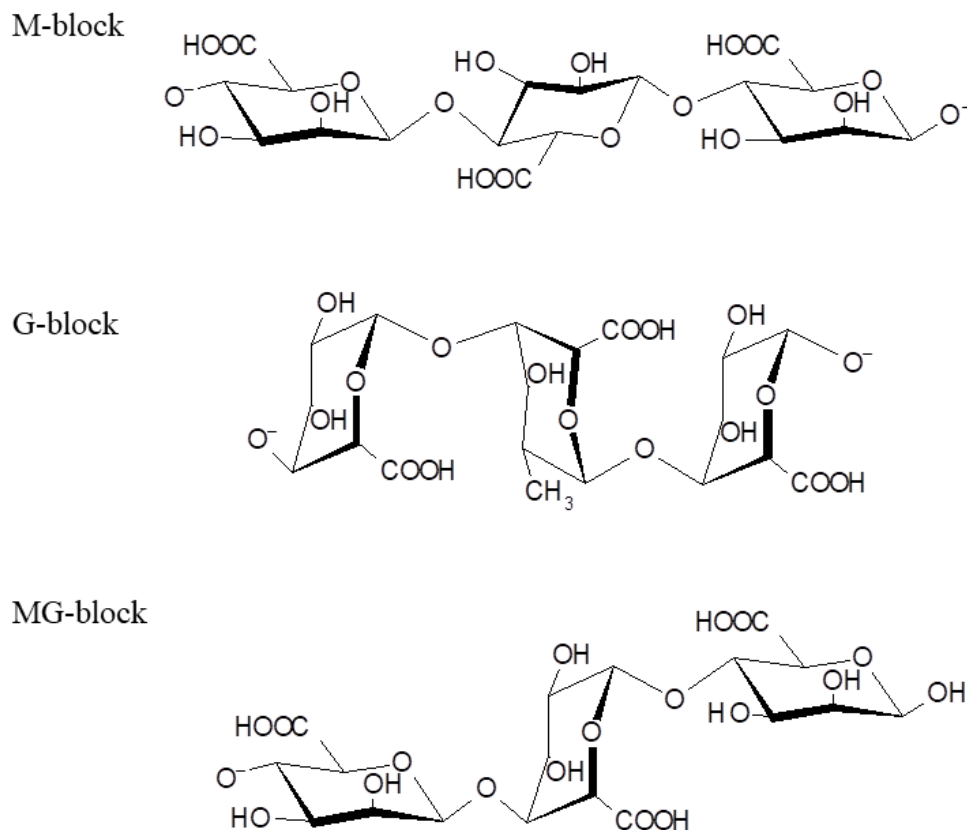


Fig.2. The molecular structures of possible sequences of L-guluronic and D-mannuronic units in alginate polymer.

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

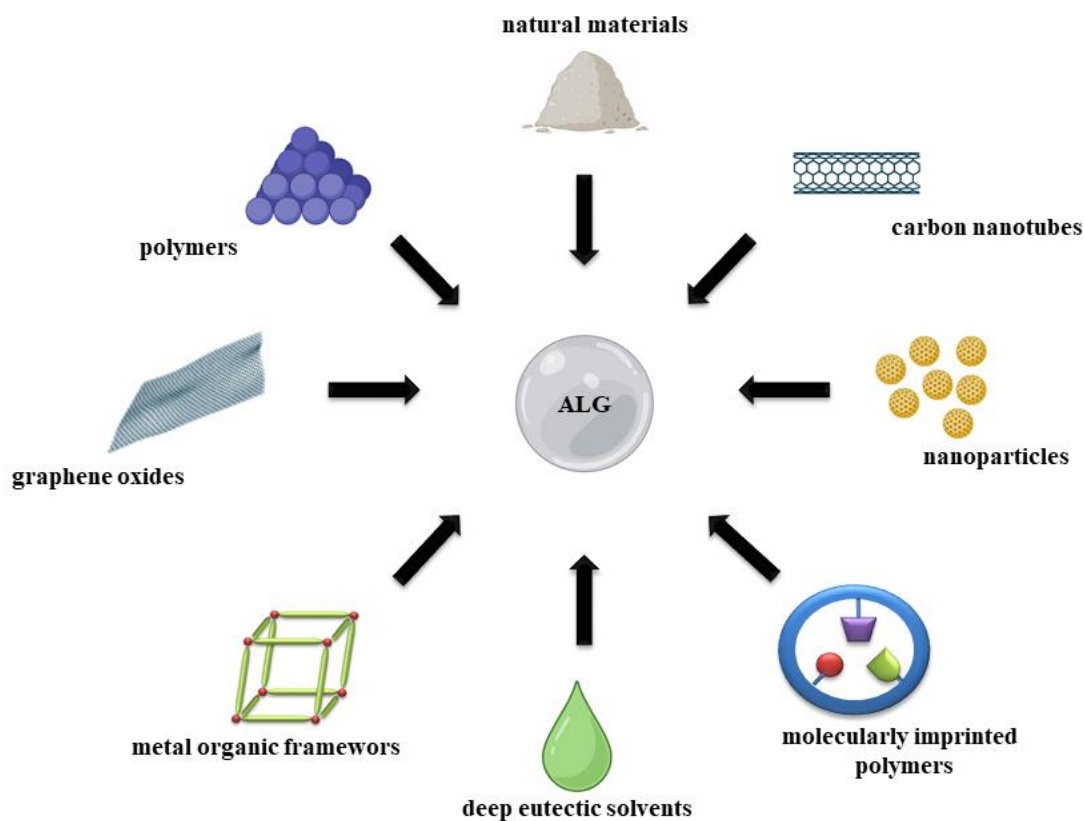


Fig.3. Main groups of sorbents combined with alginate hydrogel and used in solid-phase microextraction techniques.

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90 3. Application of alginate-based sorbents in microextraction techniques

91 So far, alginate-based sorbents have been applied as a sorptive material in some of the miniaturized  
 92 extraction techniques, such as SPE, SPME, and D- $\mu$ SPE. In general, regardless of the microextraction  
 93 mode, the sorbent preparation process is relatively simple and easy to operate. As shown in Fig. 4,  
 94 four main stages can be distinguished. In the first step, an alginate solution is prepared by dissolving  
 95 alginate in water. The alginate content in an aqueous solution usually ranges from 1 to 2% (w/v). The  
 96 second step involves adding specific material to the alginate solution to improve surface and  
 97 adsorption properties of the sorbent. In the next step, alginate solution is added to the crosslinker agent  
 98 to obtain the alginate-based solid sorbent. Depending on the microextraction approach, the procedure  
 99 for obtaining the sorbent shape/format is different. To prepare sorbent beads, the alginate solution is  
 100 added dropwise into the crosslinking solution, while for fiber formation, a certain amount of the  
 101 alginate solution is added continuously. However, in order to obtain covered fiber, the device is  
 102 immersed directly in a crosslinking solution. In almost all of the reported procedures, calcium chloride  
 103 ( $\text{CaCl}_2$ ) solution was used as a crosslinker. This stage is the most time-consuming of the entire  
 104 procedure. Achieving complete formation of the sorbent requires keeping it in the  $\text{CaCl}_2$  solution from  
 105 30 minutes to even 2 hours. Then the formed sorbent is separated from the solution, washed by  
 106 distilled water and, in most applications, dried. Following these steps, the sorbent becomes ready for  
 107 use in the chosen microextraction procedure.

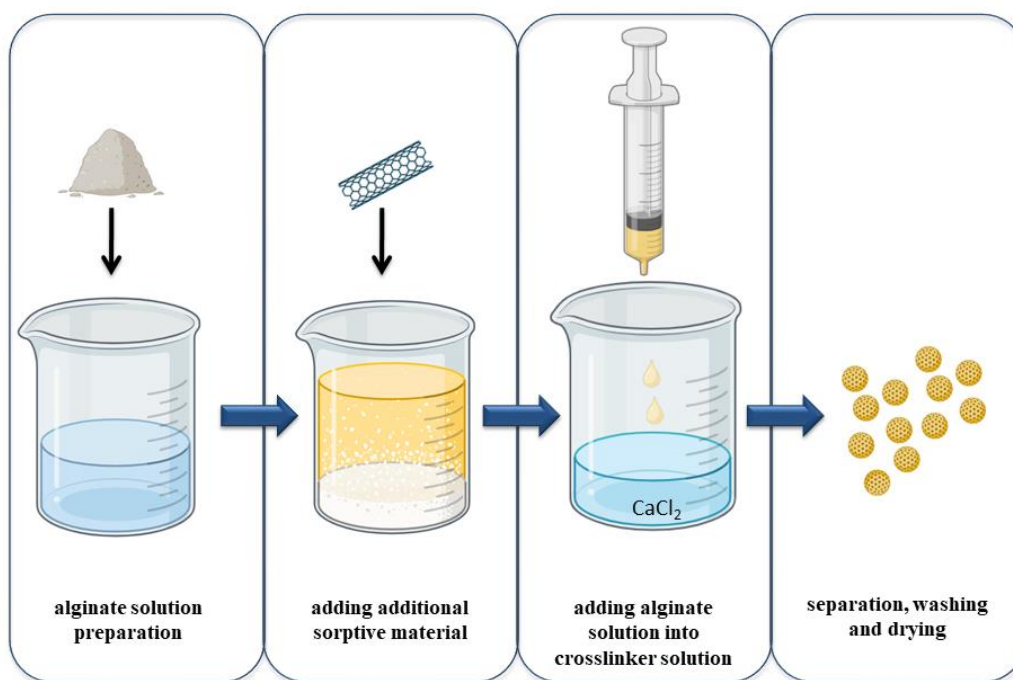


Fig.4. Main steps of alginate-based sorbent preparation.

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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- $\mu$ SPE. 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  $\text{CaCl}_2$  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  $\text{HNO}_3$  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  $\mu\text{m}$ , 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  $\text{HNO}_3$  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),  $\text{C}_{18}$ -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  $\text{CaCl}_2$  solution to obtain MIL-101/CTAB/ALG/CF. The 500 mg of synthesized sorbent was packed  
184 into a 1000  $\mu\text{L}$  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  $\mu\text{L}$  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  $\text{m}^2/\text{g}$ ), resulting in a high recovery rate (85.2–97.8%). Furthermore, the method  
191 exhibited a low limit of detection (0.15  $\mu\text{g}/\text{L}$ ) 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 ( $K_{ow}$ ), such as estriol, estrone, 17- $\alpha$ -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- $\mu$ SPE) 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- $\mu$ SPE, 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<sub>2</sub> 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 with 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-D $\mu$ -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<sup>2</sup>/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.

#### 329 3.4. Magnetic dispersive micro-solid phase extraction (MD- $\mu$ SPE)

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  $\mu$ SPE is the preferred choice of researchers. The iron oxide, namely magnetite (Fe<sub>3</sub>O<sub>4</sub>) 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<sub>3</sub>O<sub>4</sub> 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<sub>3</sub>O<sub>4</sub> consisting of  
340 polyaniline (PANI) coated Fe<sub>3</sub>O<sub>4</sub> 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<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>/alginate sorbents,  
345 PANI/alginate/Fe<sub>3</sub>O<sub>4</sub> exhibited much higher adsorption capability (more than 4 times) of the target  
346 analytes via  $\pi$ - $\pi$  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  $\mu$ g/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<sup>2</sup>/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,  $\beta$ -estradiol, and bisphenol A,  
355 without significant loss even after 16 regeneration cycles [34]. A polypyrrole-based sorbent named  
356 porous nanostructured polypyrrole, reduced GO, magnetite nanoparticle alginate hydrogel  
357 microspheres (PPy-rGOx-Fe<sub>3</sub>O<sub>4</sub>) was also applied for phthalate extraction from bottled water and  
358 beverage samples. PPy-rGOx-Fe<sub>3</sub>O<sub>4</sub> 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<sub>3</sub> in  
362 the hydrogel microspheres with the hydrochloric acid, bubbles of CO<sub>2</sub> 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  $\mu\text{g/L}$  [35]. Another sorbent applied to magnetic D- $\mu\text{SPE}$  was proposed by  
367 Sereshti et. al. [36], who synthesized a three-component eutectogel, composed of a crosslinked  
368 copolymeric DES and polyvinylpyrrolidone-coated  $\text{Fe}_3\text{O}_4$  nanopowder (PVP- $\text{Fe}_3\text{O}_4$ ). 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  $\mu\text{L}$ ).  
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  $-\text{O}^-$   
378 and  $-\text{COO}^-$  groups in sorbent and  $-\text{NH}_3^+$  groups in melamine. One more magnetic eutectogel beads  
379 composed of a polymeric DES, carboxylated multiwall carbon nanotubes and polyvinylpyrrolidone  
380 coated- $\text{Fe}_3\text{O}_4$  nanocrystals ( $\text{Fe}_3\text{O}_4@/\text{CA}/[\text{PNVP}]:[\text{BA}]/\text{MWCNT-COOH}$ ) 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  $\text{ZnO}/\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-NH}_2/\text{MIP}/\text{alginate}$  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  $\text{CaCl}_2$  solution,  
398 the commonly used crosslinking agent,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution, was used. The combination of sodium  
399 hydrogel and MGO (MGO-ALG) yielded a sorbent with a large specific surface of 303.68  $\text{m}^2/\text{g}$ .  
400 Significantly higher than these calculated for GO and MGO, equal to 43.64  $\text{m}^2/\text{g}$  and 274.67  $\text{m}^2/\text{g}$ ,  
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  $\text{ng/L}$ , 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/ $\text{Fe}_3\text{O}_4\text{-SiO}_2$  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-101 and significantly boosted the adsorption  
411 capacity of the sorbent, almost 2 times compared to MIL-101/ $\text{Fe}_3\text{O}_4\text{-SiO}_2$ , and 1.2 times compared to



412 GOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>. Moreover, the sorbent demonstrated thermal stability and allowed for up to 16  
413 reuses without significantly decreasing its extraction performance.

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Table 1. 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
<b>SPE</b>											
NFL/ALG (n.d.)	18.86	Pb <sup>2+</sup>	water, beverages (2 mL)	3 M HNO <sub>3</sub> (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 <sub>3</sub> (1)	ICP-MS	0,01-0,03 [ng/L]	n.d.	81-101	n.d.	50 cycles	[25]
<b>in-syringe SPE</b>											
P – ZrO <sub>2</sub> CeO <sub>2</sub> ZnO nanoparticles/ALG (150)	62.89 292.93	Ca, Li	environmental water (100 mL)	1 M HNO <sub>3</sub> (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]
<b>in-tip SPE</b>											
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]
<b>SPME</b>											
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]
<b>μ-dSPE</b>											
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 <sup>2+</sup>	corn cereal	1 M HNO <sub>3</sub>	MIP OES	n.d.	n.d.	100	n.d.	10 cycles	[42]



PAAM/MWCNT-f (10)		Cd <sup>2+</sup>		(10)							
SFE/ALG beads (200)	n.d.	Pb <sup>2+</sup>	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/DC M (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 [ug/kg]	7.49 [ug/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]
GO <sub>x</sub> /MIL-101/Fe <sub>3</sub> O <sub>4</sub> -SiO <sub>2</sub> (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 <sub>3</sub> O <sub>4</sub> @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 [ug/kg]	2 [ug/kg]	77.4-105	<6.9	3 cycles	[36]
HP-PEDOT@Fe <sub>3</sub> O <sub>4</sub> @ALG (250)	n.d.	PAHs	meat (5 g)	IPA (1)	GC-MS/MS	0.2-0.4 [ug/kg]	0.5-1 [ug/kg]	81.5-99.4	<7	9 cycles	[44]
Fe <sub>3</sub> O <sub>4</sub> @C <sub>18</sub> @Ba <sup>2+</sup> -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 <sub>3</sub> O <sub>4</sub> /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 <sub>3</sub> O <sub>4</sub> @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 <sub>3</sub> O <sub>4</sub> (400)	1.15-1.25	PAHs	environmental water (10 mL)	ACN (1 mL)	HPLC-FLD	0.01 [µg/L]	0.04 [µg/L]	86-98	<6	6 cycles	[32]
PPy-rGOx-Fe <sub>3</sub> O <sub>4</sub> ALG hydrogels (750)	n.d.	phthalates	beverages (20 mL)	EtOAc (3)	GC-MS/MS	0.005-0.01 [µg/L]	0.02-0.04 [µg/L]	87.5-99.1	0.6-7.7	18 cycles	[35]
ZnO/Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub> /MIP/ALG (500)	n.d.	sulfonamides	milk (10 mL)	MeOH/acetic acid (2)	HPLC-DAD	0.03-0.06 [µg/L]	0.1-0.2 [µg/L]	87-98.5	<6	10 cycles	[38]
PANI/GOx/ C <sub>18</sub> -SiO <sub>2</sub> -Fe <sub>3</sub> O <sub>4</sub> (500)	n.d.	fluoroquinolones	honey, milk, eggs (10 mL)	ACN/DCM/acetic acid (3)	HPLC-FLD	0.001-0.01 [µg/L]	0.003-0.04 [µg/L]	80-98	<9	7 cycles	[33]
polypyrrole/Fe <sub>3</sub> O <sub>4</sub> /ALG (n.d.)	n.d.	estriol, β-estradiol, BPA	environmental water (10 mL)	ACN (2)	HPLC-FLD	0.5 [µg/L]	n.d.	90-98	<5	16 cycles	[34]
MIL-101(Cr)-NH <sub>2</sub> (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 detector; GAC- granular activated carbon; GC-Gas Chromatography; HEMA-2-Hydroxyethyl methacrylate; HP- Hierarchically Porous; 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.



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- $\mu$ SPE  
470 group and four from the MD- $\mu$ SPE 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]
$\mu$ -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]
M $\mu$ -dSPE	MIL-101(Cr)-NH <sub>2</sub>	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 <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub> /MIP/ALG	16	5	3	8	68	51	4	3	8	34	[38]
	PANI/GOx/C <sub>18</sub> -SiO <sub>2</sub> -Fe <sub>3</sub> O <sub>4</sub> ALG	12	1	3	8	76	70	4	3	8	15	[33]

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486 As it can be seen in Table 2, a significant majority of the selected analytical procedures obtained total  
487 Eco-scale scores above 75, indicating an excellent green analysis. Only one procedure, with a rating of  
488 68, qualifies as an acceptable green analysis. However, considering the sorbent synthesis approach, it  
489 becomes evident that not all these steps are as environmentally friendly as their analytical application.  
490 Just four of the ten investigated synthesis protocols achieved scores  $\geq 75$ . In these protocols, only a  
491 slight modification of alginate hydrogel was conducted, consisting of compounding with natural  
492 sorbents and DES (references [4, 7, 9, 19]). The other procedures necessitated the use of significantly  
493 more reagents, primarily those hazardous and energy-consuming processes like long-term high-  
494 temperature processes or sonication, thereby increasing the PPs associated with reagents and energy  
495 consumption. The PANI/GO<sub>x</sub>/C<sub>18</sub>-SiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> alginate sorbent synthesis yielded the lowest eco-scale  
496 score rating of 15. This result is mainly influenced by the PPs associated with usage of a significant  
497 amount of reagents (classified as “danger”) at the stage of tedious and involves several steps in the in  
498 the synthesis of individual sorbent components. Similarly, in the case of the other two protocols with  
499 an eco-scale score lower than 40, the main factor affecting the decrease in green profile are PPs  
500 assigned to the reagents used (PPs for reagents greater than 50). This suggests that the main factor  
501 reducing the environmental sustainability of the synthesis is the excessive use of hazardous reagents.

## 502 5. Summary and future trends

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

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708 Figure captions:

709

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

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

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

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

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

719

720 Table captions:

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

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

724

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