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Additional Information

Determination of benzomercaptans in environmental complex samples by combining zeolitic imidazolate framework-8-based solid-phase extraction and high-performance liquid chromatography with UV detection

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Abstract

In this work, the synthesis of zeolitic imidazolate framework-8 (ZIF-8) crystals and their subsequent application as effective sorbents for extraction and preconcentration of several benzomercaptans from environmental complex samples is described. These materials were prepared by solvothermal approach varying the concentration of n-butylamine modulator to modify the surface of the metal-organic framework. The resulting materials were characterized by scanning and transmission electron microscopy, powder X-ray diffraction and Fourier transform infrared spectroscopy. The ZIF-8 material that gave the best features was selected as extractive phase and the influence of various parameters (sample pH and elution solvent composition, among others) on the extraction efficiency of target compounds were investigated. Under the optimal conditions of the method, the tested analytes (2-mercaptobenzothiazole, 2-mercaptobenzoxazole and 2-mercapto-6-nitrobenzothiazole) were retained and eluted quantitatively with alkaline 50:50 (v:v) methanol-water mixture. Using the proposed method, low limits of detection, in the range of 16-21 ng L^{-1} for aqueous samples and 0.4-0.5 µg kg^{-1} for soil samples, were achieved whereas the precision (expressed as relative standard deviation) was lower than 7%. The resulting solid-phase extraction protocol, using the zeolitic material as sorbent, was combined with liquid chromatography and ultraviolet-vis detector and successfully applied to determine traces of these organic pollutants in environmental samples.

Keywords: Metal-organic frameworks; environmental pollutants; soil and aqueous samples; solid-phase extraction; sorbent; sample preparation

1. Introduction

Metal-organic frameworks (MOFs) have aroused a great interest over the last decades. These coordination polymers are a class of highly porous materials composed of metal ions or clusters linked by organic ligands. Their crystalline structures, including their pore sizes and surfaces, can be controlled by a careful selection of their precursors. MOFs are characterized by a large specific surface area and intrinsic porosity, as well as profuse active sites [1]. Many applications have been proposed for this type of materials, and surely, their number will grow in the coming years. Some of those applications include gas/electrical storage and catalysis [2], removal of contaminants in air or water by adsorption and separation [3-4], sensors [5] and sorbents for sample preparation [6]. In particular, zeolitic imidazolate frameworks (ZIFs) are a subfamily of MOFs consisting of Zn or Co metal ions tetrahedrally coordinated by anionic imidazolate ligands [7, 8]. ZIF-8 [Zn(2-methylimidazolate)$_2$] has been widely used due to its easy synthesis, high thermal and chemical stabilities [9, 10], great pore volume and surface area [9]. ZIF-8 shows a very large adsorption capacity, which is attributed to its high porosity and the different ways in which it can interact with adsorbates, such as π-stacking, hydrogen bonding and ionic interactions [11, 12]. Such good features have become this material in one of the most attractive MOFs for the extraction and preconcentration of analytes. Related to this, solid-phase microextraction (SPME) [6] has been commonly reported as a suitable sample preparation technique in the extraction of amines [13], polycyclic aromatic hydrocarbons [14], BTEX [15] and fluoroquinolones [16] from environmental water samples. Despite its advantages, SPME has certain disadvantages such as the limited fiber lifetime, its fragility and its relatively high cost. In this sense, other alternatives based on conventional solid-phase extraction (SPE) format (syringe/cartridges) [17], magnetic SPE [18] or the use of membrane as support medium [19-21] have been developed. However, the preparation of homogenous ZIF-8 membranes is a difficult task presenting some drawbacks such as possible sedimentation phenomena of MOF crystals during the preparation stage, the formation of bubbles during stirring (poor reproducibility) and limited reusability (blockage of pores of membrane). Besides, in most of these works, the selectivity of sorbent has been attributed to the hydrophobic and π-interactions of solutes with the 2-methylimidazole ligands instead of taking advantages of their tunable pore size and feasible chemical functionalization [22].

The pollution of the environment by organic compounds is always of great concern due to the toxicity risks for aquatic organisms and human posed by their occurrence and

3

80   increasing concentration in water bodies. Among organic pollutants, benzomercaptans,

81   such as 2-mercaptobenzothiazole (MBT) and 2-mercaptobenzoxazole (MBO), deserve

82   special attention due to their broad use in many industrial processes. These compounds

83   are commonly used as vulcanization accelerators in the rubber industry, as biocorrosion

84   inhibitors, as coating agents of metallic surfaces, and as biocides in medical applications

85   [23-24]. As consequence, such compounds have been found in different environmental

86   compartments such as surface waters, wastewater effluents, sewage treatment plants,

87   soils, roadsides, etc. These poorly biodegradable pollutants may cause allergic reactions,

88   induce tumours, and be toxic to aquatic organisms [25-26]. According to the NSF

89   International Standard/American National Standard (NSF/ANSI 60-2016), the drinking

90   water criteria (Annex C) for MBT is maximum contamination levels or maximum

91   allowable concentration, respectively of total allowable concentration is $20 \, \mu g \, L^{-1}$, single

92   product allowable concentration is $2 \, \mu g \, L^{-1}$ [27]. In order to reach these low

93   concentrations, determination techniques mainly based on LC combined with mass

94   spectrometry detectors have been reported [28-31]. In any case, sample preparation

95   techniques are required in order to reduce matrix interferences and to improve sensitivity

96   to benzomercaptans in environmental complex samples, being SPE the most common

97   technique used for extraction and preconcentration of these kind of analytes [23, 24, 28,

98   30, 31]. However, SPE shows some disadvantages, such as limited selectivity and poor

99   reusability.

100 In order to overcome the above-mentioned drawbacks, there is a recent interest concerned

101 to functionalized MOFs, which are obtained by incorporation of ligands including

102 additional functional groups (–OH, –NH$_2$, …). Particularly, amine-functionalized MOFs

103 have mainly attracted attention since they improved MOF water stability and provided

104 the possibility of forming hydrogen bonds and even electron transfer capability towards

105 analytes [32]. Recently, these materials have applied for capturing of several polar guests

106 from different matrices. Thus, NH$_2$-MIL-101(Fe) and NH$_2$-MIL-53(Al) have been used

107 for the removal of imidacloprid in water [33] and to selectively recognize tetracyclines

108 from milk [34], respectively. Also, amino-functionalized UiO-66 combined with

109 magnetic Fe$_3$O$_4$ microspheres has been used for the selective extraction of bisphenols in

110 river water samples [35]. In these works, the introduction of amino moieties is

111 accomplished by one-pot solvothermal synthesis MOFs, which has the advantage of

112 avoiding the complicated steps required in post-modification approach. Alternatively,

113 amino moieties can be incorporated through the addition of organic amines as modulators

4

114 in the synthesis mixture of MOF [22]. However, this approach has not been explored in

115 literature with sample treatment purposes.

116 In this work, amine-modulated ZIF-8 (nano)crystals (NH$_2$-ZIF-8) was used as sorbent for

117 the extraction of these target compounds (MBO, MBT and its nitro derivative) in

118 environmental samples. The incorporation of n-butylamine molecules to the framework

119 structure resulted appropriate to tailor the surface properties improving the selectivity of

120 the extraction of these polar compounds. Although this type of material has been

121 previously used in hydrophobic compounds in dispersive mode with sophisticated

122 technique (GC-MS) [36], its application to hydrophilic compounds in cartridge format

123 with accessible instrumentation (LC-UV) has not been explored. Taking into account the

124 key role of butylamine (BA) as modulator, in this work, its content on crystal structure

125 and posterior interaction with analytes was studied. The resulting MOF that provided the

126 best features was selected as SPE sorbent and parameters affecting the extraction process

127 such sample pH and eluent solvent composition (among others) were investigated.

128 Finally, the applicability of the method for the analysis of these compounds by HPLC-

129 UV was evaluated in environmental samples obtained from different sources.

130

131 **2. Experimental section**

132 *2.1. Reagents and materials*

133 Zinc nitrate hexahydrate, 2-methylimidazole (Hmim), n-butylamine (BA), ethylamine

134 and hexylamine were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Sodium

135 hydroxide was obtained from Panreac Química SA (Barcelona, Spain). Acetonitrile

136 (ACN), methanol (MeOH), acetic acid (HAcO) and hydrochloric acid were from VWR

137 International Eurolab (Barcelona, Spain). The benzomercaptans selected in this work

138 were: 2-mercaptobenzoxazole (MBO), 2-mercaptobenzothiazole (MBT) and 6-

139 nitrobenzo[d]thiazole-2-thiol (NMBT), all purchased from Sigma-Aldrich. The structures

140 of these compounds are given in Table S1. Deionized water was prepared in Crystal B30

141 EDI Adrona deionizer (Riga, Latvia). All other reagents were of analytical grade unless

142 otherwise stated. 1 mL empty propylene disposable SPE cartridge and frits (1/16′, 20 μm)

143 were from Análisis Vínicos (Tomelloso, Spain). Individual standard solutions of

144 benzomercaptans (1000 mg L^{-1}) were prepared in MeOH and stored at 4 ºC until its use.

145 Working standard solutions were done daily by appropriate dilution from these stock

146 solutions.

147

148   *2.2. Instrumentation*

149   Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800

150   electron microscope (Ibaraki, Japan) equipped with a retrodispersive electron detector

151   and an energy dispersive spectrometer (EDAX Genesis 4000). A transmission electron

152   microscope (TEM) coupled to a digital camera AMT RX80 model JEM-1010 JEOL

153   (Akishima, Japan) was used to obtain the transmission electron micrographs. Adsorption-

154   desorption isotherms of nitrogen were registered in a S5 Micromeritics ASAP2020

155   instrument (Norcross, USA) at 77 K. The Brauner-Emmet-Teller (BET) model was used

156   to calculate the specific surface area using the low-pressure range. Powder X-ray

157   Diffraction (p-XRD) patterns were obtained in a D8 Advance A25 diffractometer

158   (Bruker). Attenuated total reflection Fourier-transform infrared (FT-IR) spectra of

159   powdered materials were registered with a DuraSamplIR II accessory from Smiths

160   Detection Inc. (Warrington, UK) equipped with a nine reflection diamond/ZnSe

161   DuraDisk plate, installed on a Bruker FT-IR spectrometer (Bremen, Germany) model

162   Tensor 27. The zeta potential measurements were performed with Zetasizer Nano ZS

163   equipment (Malvern Instruments, Malvern, UK). NH_2-ZIF-8-BA 1 was dispersed in

164   distilled water at a concentration of 1 g L^{-1} and sonicated during 1 min. Measurements

165   were carried out per triplicate at 25 °C. The final zeta potential value was estimated from

166   the particle mobility using the Smoluchowski model.

167   Chromatographic separation of standards and samples was performed on a 1260 Infinity

168   II HPLC from Agilent Technologies (Waldbronn, Germany) with a UV-Vis diode-array

169   detector. The separation conditions of benzomercaptans were adapted from Parham *et al*.

170   [30]. The chromatographic column was a Kromasil C18 (250 × 4.0 mm, 5 µm particle

171   size, Análisis Vínicos). Separation was done under gradient elution mode (at flow rate of

172   1.0 mL min^{-1}) using as solvents: (A) water and (B) ACN containing both 0.1% (v/v) of

173   HAcO. The gradient elution and the detection wavelength programs are given in

174   supplementary information (see Table S2).

175

176   *2.3. Synthesis of ZIF-8 crystals*

177   ZIF-8 materials were synthesized following protocols reported in the literature by

178   Cravillon *et al.* [22, 37]. To obtain ZIF-8 (nano)crystals (without modulator), two

179   methanolic solutions were needed. Solution (A) composed of $Zn(NO_3)_2 \cdot 6H_2O$ (9.87

180   mmol) in MeOH (200 mL) and solution (B) of 2-methylimidazole (79.04 mmol) in MeOH

181   (200 mL). The later solution was added to the former under stirring. After keeping at

6

182   room temperature for 24 h, a white dispersion of ZIF-8 was formed, and separated by

183   centrifugation at 6000 rpm for 10 min. Then, the resulting solid was washed with MeOH

184   three times and dried at 40°C overnight. On the other hand, ZIF-8 nanocrystals using BA

185   (NH_2-ZIF-8-BA) as modulator agent were prepared as given elsewhere [22]. A ligand

186   solution (B) (9.874 mmol of Hmim in 50 mL MeOH) including the modulator agent

187   (9.874 mmol of n-BA) was poured slowly into a solution (A) containing the metallic

188   cation (2.469 mmol of $Zn(NO_3)_2 \cdot 6H_2O$ in 50 mL of MeOH) under stirring and left at

189   room temperature for 24 h. The resulting white solid (namely, NH_2-ZIF-8-BA 1) was

190   recovered and washed with the same protocol that is described above for ZIF-8

191   (nano)crystals. Also, different molar contents of BA as modulator (5 and 20 mmol, NH_2-

192   ZIF-8-BA 2 and 3, respectively) were tested by keeping constant the molar ratio of other

193   starting reagents. Additionally, other alkyl amines (ethyl- and hexylamine) were

194   investigated as modulator agent (at 10 mmol) following the abovementioned protocol for

195   NH_2-ZIF-8-BA materials.

196

197   *2.4. Sample collection and treatment*

198   The sampling of water was performed from different locations in Valencia.

199   Approximately, 500 mL were collected in dark containers and refrigerated at 4ºC until

200   their use.

201   Several soil samples from different sources were collected, air-dried at room temperature,

202   crushed and then sieved through a 1 mm sieve. These samples were stored on

203   polypropylene bags in darkness at 25°C. The pH, humidity and electrical conductivity of

204   soil samples were measured following ISO rules [38]. pH and electrical conductivity were

205   measured in a 1:5 (soil:deionized water) extract shaken for 5 min and measured after 2 h.

206   For the determination of humidity, 1 g of each sample was heated at 70ºC overnight until

207   constant weight. These soil parameters are listed in Table S3. The extraction of

208   benzomercaptans from soil samples was adapted from Zhang *et al* [39], as follows.

209   Briefly, 0.1 g approx. of each sample was weighed and spiked at 500 µg kg^{-1} with the

210   investigated pollutants. After vortex-assisted and ultrasonic homogenization, the samples

211   were allowed to stand with the analytes for 2 h. Then, 5 mL of MeOH were added, shaken

212   during 20 min and centrifuged at 6000 rpm for 3 min. The supernatant was collected and

213   the extraction procedure was repeated twice. All methanolic fractions were combined and

214   evaporated at low pressure up to small volume (ca. 100 µL) and reconstituted up to 5 mL

215   with water before application of SPE protocol described below.

216

217 *2.5. Extraction procedure*

218 A SPE protocol using the developed materials as sorbents was applied to the extraction

219 of aromatic benzomercaptans in environmental samples. For the preparation of SPE

220 devices, 20 mg of the metal-organic framework was packed between two frits into 1 mL

221 empty polypropylene cartridges. Prior to loading, the sewage waters were sonicated and

222 centrifuged, and the extraction was carried out following the protocol described above.

223 The material was firstly conditioned with MeOH (500 µL) and water (500 µL), and after

224 that, a known volume of standard solution or sample (5 mL and 25 mL for soil and water

225 samples, respectively) was passed through the cartridge. The sorbent was finally washed

226 with water (500 µL). The retained analytes were later eluted with 250 µL of 50% (v/v)

227 MeOH containing 0.5 mol L^{-1} NaOH. The extraction units were regenerated with water

228 (10 mL) in order to eliminate the NaOH excess. Prior to HPLC injection, the elution

229 fraction was properly neutralized with hydrochloric acid.

230

231 **3. Results and discussion**

232 *3.1. Preliminary considerations*

233 As it was mentioned in the Introduction, the selection of the adequate MOF as SPE

234 sorbent is a key aspect since it strongly influences on the selective retention and the way

235 of interaction with the target analytes. In this sense, ZIF-8 material, due to its pore size

236 and the kind of interactions it can establish with the analytes, has advantageous features

237 making it a good SPE phase candidate. As shown in Fig. S1, the molecular sizes of MBO

238 and MBT are smaller than the pore size of ZIF-8 (3.4 Å) [40, 41]; whereas for NMBT, a

239 partial embedding process may happen into ZIF-8 structure.

240 Regarding the interaction forces involved, there are different possible interaction modes

241 between this MOF and benzomercaptans: i) hydrophobic effects and π-interaction

242 between the imidazole rings of ZIF-8 and the aromatic moieties of these analytes (see

243 structures in Fig. S1); ii) hydrogen bonding between NH groups in ZIF-8, and certain

244 hydrogen-bond accepting groups (*e.g.* ether, organo sulfurs, nitro, among others) present

245 in the analytes (Fig. S1) thus enhancing the hydrophilic binding and improving the

246 selectivity; and iii) electrostatic interaction between ZIF-8 and benzomercaptan

247 molecules. In this sense, the surface charge of ZIF-8 nanocrystals and the ionization

248 degree of benzomercaptans (see Table S1) should be considered (as we discussed below).

249 Additionally, other potential contributions due to the amine moiety such as cation-π

250 interaction between aromatic ring and amino protonated ZIF-8 structure can occur [42],

251 which have been previously reported with other amino functionalized MOFs and

252 compounds with structural similarities [43]. In this regard, the synergetic contribution of

253 BA modulator of the NH_2-ZIF-8-BA in these last interactions can be explained by its

254 presence onto the surface of ZIF-8 crystals as previously demonstrated [36].

255 Indeed, the use of modulators during MOF synthesis has proven to be a promising strategy

256 through which the internal MOF structure (crystal size and morphology), and outer

257 surface functionalities, can be controlled by using monodentate ligands [44]. The

258 modulators then compete with conventional multidentate ligands for coordination to the

259 metal cations [45, 46]. In order to study the influence of BA upon the crystal growth of

260 ZIF-8 and other features, several materials were synthesized varying its molar ratio.

261 Taking into account all these considerations, the ability of these synthesized materials as

262 SPE phases is here evaluated (see Table 1).

263

264 *3.2. Characterization of material*

265 The morphology and crystal size of the prepared materials (ZIF-8 and NH_2-ZIF-8 with

266 different modulators) were investigated by SEM and TEM analysis, respectively. Fig. 1A

267 and B shows the SEM micrograph of the ZIF-8 (without modulator) and NH_2-ZIF-8-BA

268 1 (corresponding to *ca*. 10 mmol of BA) materials, respectively. In both images, a

269 polyhedral shape of the nanocrystals was evidenced, which is in agreement with the

270 typical form of ZIF-8 nanocrystals [40, 41]. Also, SEM images of MOFs prepared at other

271 BA contents were taken (Fig. S2). As it can be seen, the morphology did not change

272 substantially with modulator content. The TEM images of the resulting materials for this

273 set of experiments are summarized in Fig. S2, and the mean sizes of the crystals are given

274 in Table 1. As it can be seen, an increase of the concentration of BA modulator led to the

275 increased mean size of the resulting crystals. The tendency observed for BA-modulated

276 MOFs is consistent with that reported in previous studies focused on the addition of

277 monocarboxylic acid modulators [44, 47]. These results can be explained taking into

278 account that modulating ligands can tailor crystal nucleation and growth via both

279 coordination and deprotonation equilibria [22]. Thus, the addition of a basic ligand (L) as

280 BA (pK_a value in aqueous media is 10.7) can deprotonate the $[Zn(Hmim)_mL_n]$ species,

281 and thus producing an acceleration of rate of ligand exchange reactions, resulting in a

282 higher nucleation rate and therefore in a smaller final crystal size. When a low amount of

283 BA is added a, a large number of nuclei were formed and rapidly grow at the same time

284 affording smaller crystals. However, higher concentration of BA provide a slow

285 nucleation (fewer nuclei) of the MOF giving as result larger crystals. This is due to this

286 additive starts to have a relevant role as a competitive ligand in the complex formation.

287 On the other hand, in absence of modulating ligand (BA), there is not a deprotonation

288 reaction, which led to small concentration of $[Zn(Hmim)_mL_n]$ species decreasing the

289 nucleation rate, and consequently in a large final crystal size.

290 Additionally, energy dispersive X-ray spectroscopy (EDX) of the synthesized materials

291 were performed. As shown in Table 1, nitrogen content increased with increasing BA

292 content, which confirmed not only the presence of BA onto the surface of ZIF-8 crystals

293 but also the possibility of tailoring the loading of surface amine moieties.

294 To determine the surface area, nitrogen adsorption/desorption isotherms of the

295 synthesized materials were performed. They exhibited typical Type I isotherms (a

296 representative example is depicted in Fig. S3), which are indicative of their microporous

297 nature. The specific surface area, calculated using the BET equation, are shown in the

298 Table 1. As it can be observed, high surface areas ($> 1000 \text{ m}^2/\text{g}$) were obtained from BA

299 contents of 10 mmol or higher.

300 Furthermore, X-ray powder diffraction patterns, depicted in Fig. S4, were in good

301 agreement with the simulated one, thus indicating that the current materials were

302 successfully prepared. Also, FT-IR spectra of ZIF-8 materials were taken (Fig. S5). All

303 the spectra display the typical bands of the ZIF-8 MOF [36, 40], corroborating their

304 successful preparation. In addition, a small band close to 2900 cm^{-1} appeared in the NH_2-

305 ZIF-8-BA, which can be assigned to the aliphatic stretching C–H of BA.

306 Next, the synthesized MOFs were evaluated as SPE sorbents in order to study the

307 influence of modulation and choose the phase that provided the highest extraction

308 efficiency. As shown in Table 1, the NH_2-ZIF-8-BA 1 showed high recoveries jointly

309 with exposed surfaces having enough amino moieties for the selective capture of analytes.

310 Additionally, this material was superior to that synthesized without modulator, which

311 clearly demonstrated the important contribution of the amount of attached BA onto ZIF-

312 8 crystals in the extraction efficiency of these pollutants. It is evident from the previous

313 discussion and experimental results that amine group of BA modulator plays a key role

314 in the crystal growth of MOF as well as in his subsequent retention properties. For this

315 purpose, other organic amines (ethyl and hexyl) with similar basicity (pK_a values ranged

316 between 10.6-10.9) were studied as modulators using the same conditions of NH_2-ZIF-8-

317 BA 1. The characterization of the resulting materials gave mean sizes of the crystals

318   similar to those obtained with BA modulated material and surface area values ranged

319   between 1150 and 1324 m2 g^{-1}. Both materials were tested as SPE sorbents, giving

320   recoveries up to 90%. These results suggested that the alkyl chain has not a relevant effect,

321   whereas the introduction of amine in the final framework is an important issue to improve

322   the retention performance. At sight of these results, NH$_2$-ZIF-8-BA 1 was selected for

323   further studies.

324

325   *3.3. Optimization of SPE protocol*

326   In order to obtain the maximal extraction performance, various parameters such as sample

327   pH value, elution solvent composition and volume were investigated. During

328   optimization of SPE conditions, an aqueous solution containing 250 µg L^{-1} of each

329   benzomercaptan was employed as a test mixture.

330   Sample pH is an important variable that influences the extraction performance since it

331   affects the ZIF-8 charge surface as well as the analyte charge state. According to previous

332   reports, ZIF-8 material is charged positively in the pH range of 2-10 due to its imidazole

333   moieties [48, 49]. In any case, zeta potential measurements of the selected material were

334   performed at loading/elution conditions (Fig. S6). Thus, the positive value of this

335   parameter at loading step (pH close to 7.0) implied a positive surface charge of MOF

336   nanoparticles, whereas that it reversed from positive to negative when eluting solution

337   was tested (pH > 12). These results were consistent with the above-mentioned studies.

338   On the other hand, the heterocyclic benzomercaptans may exist as thione and/or thiol

339   forms, and the thiol form can be further ionized in aqueous solutions (see pK$_a$ values in

340   Table S1). In this study, the effect of the sample pH value was evaluated from 5 to 9 (data

341   not shown), by considering aspects such as the structural integrity of this framework (pH

342   > 4) [50] as well as the usual pH range found in surface water systems (6.5 to 8.5).

343   Recoveries in the tested pH range were almost constant for each benzomercaptan. These

344   results can be explained as follows. On the one side, the existence of electrostatic

345   interactions can be present taking into account the surface charge of MOF and the

346   ionization state of benzomercaptans. Particularly, when the solution pH was below 6.0,

347   these compounds are predominantly as neutral (molecular) species, while the surface of

348   ZIF-8 remained positive, which made the electrostatic attraction between them become

349   weak. When solution pH increased from 6.0 to 8.5, the anionic form of benzomercaptans

350   begin to have greater significance due to progressive deprotonation of these molecules

351   (see pK$_a$ values), and the electrostatic attraction between these solutes and ZIF-8 became

352   a main factor in the interaction mechanism. Nevertheless, the recovery values of target

353   compounds on ZIF-8 along the tested pH range remained nearly constant. This fact

354   suggested that the factor controlling the retention of probe compounds was not just

355   electrostatic interaction, and there should be other modes of action that influence on the

356   adsorption process (such as π–stacking and hydrogen bonding interactions). Therefore,

357   no pH adjustment was required in sample solutions.

358   The selection of an appropriate eluting solvent is of major concern for the optimization

359   of the SPE process. To obtain the highest eluting efficiencies, several eluting solvents

360   were investigated (see Fig. 2, left part). Desorption solvents as pure MeOH gave very low

361   recovery values of analytes (< 8%). As can be observed, when MeOH-water mixtures

362   (50/50, v/v) were used, higher recoveries were obtained (up to 29%), which subsequently

363   increased up to around 79% when using mixtures of MeOH-water basified with 0.1 M

364   NaOH. This increment can be explained taking into account the surface charge of MOF

365   and the ionization state of benzomercaptans. As it was mentioned before, the point of zero

366   charge for ZIF-8 is approximately at pH 9.8 [48, 49]. Consequently, at pH above this

367   value, an electrostatic repulsion between the negatively charged ZIF-8 surfaces and the

368   benzomercaptan anions is produced, which favors the desorption of these analytes from

369   the sorbent. Consequently, the content of NaOH (from 0.1 to 0.5 M) in MeOH-water

370   mixtures was optimized. It was found that a content of 0.5 M NaOH gave recoveries

371   ranging between 97 and 108%. So, as in agreement with previous studies [50], the MOF

372   structure was stable at this pH, a 0.5 M NaOH concentration was selected for further

373   studies.

374   The volume of eluent can affect not only the elution efficiency, but also the concentration

375   of the analytes in the eluent. Therefore, the effect of the solvent volume (100-1000 µL)

376   was also investigated (Fig. S7). As can be seen, recoveries of analytes higher than 87.3%

377   (< 6.1% relative standard deviation, RSDs) were obtained for 250 µL, and this value was

378   selected for further experiments.

379   Another essential parameter in a SPE protocol, especially to monitor trace pollutants in

380   environmental analysis, is the breakthrough volume. Thus, the effect of sample volume

381   was evaluated using the NH_2-ZIF-8 as sorbent. Several volumes (in the range 1-100 mL)

382   were loaded by keeping constant the total amount of each pollutant (500 ng) (see Fig. 2,

383   right part). As can be seen, the extraction recoveries of all the benzomercaptans were

384   higher than 80% up to 50 mL, however, higher volumes caused a diminution in the

385   extraction efficiency. Consequently, considering the minimum elution volume found (250

386 µL) and the maximum sample loading volume (25 mL) with average recoveries values

387 *ca.* 100%, a preconcentration factor of 100 was estimated.

388 Finally, the reusability of sorbent was also evaluated, and the obtained results indicated

389 that the MOF could be reused at least 10 times without significant decrease of efficiency

390 extraction (between 87-104% with RSD below to 8%).

391

392 *3.4. Figures of merit and application to real samples*

393 The developed SPE procedure using NH_2-ZIF-8-BA 1 as sorbent, combined with HPLC-

394 UV detection, was validated in terms of linearity, sensitivity and precision under the

395 previously optimized experimental conditions. The obtained results are summarized in

396 Table 2. As can be seen from this table, a good linearity range (r > 0.998) was observed

397 in the chromatographic dynamic range of 7-2500 µg L^{-1} for all analytes. The limits of

398 detection (LOD) and quantification (LOQ) (after applying the extraction protocol) were

399 experimentally obtained as the concentration of the analyte that provided a signal-to-noise

400 ratio (S/N) of 3 and 10, respectively. Thus, the LODs for aqueous samples varied from

401 16 ng L^{-1} to 21 ng L^{-1}, whereas the LOQs were in the range 52 ng L^{-1} and 69 ng L^{-1}. In

402 the case of soil samples, the LOD and LOQ values ranged 0.4-0.5 µg kg^{-1} and 1.3-1.7 µg

403 kg^{-1}, respectively.

404 The precision of the method (intra and inter-units), expressed as relative standard

405 deviation (RSD, %) was also determined from standard solutions at a concentration level

406 of 250 µg L^{-1} of each analyte and subjected to the SPE protocol. RSD values comprised

407 between 2.0 and 7.0% were found.

408 To study the applicability of the developed SPE-HPLC-UV method using NH_2-ZIF-8-BA

409 1 as sorbent, the developed method was applied to monitor the target analytes in

410 environmental complex matrices. The samples were analyzed in order to find any

411 potential presence of the analytes. The results (see Table 3) showed that none of the target

412 benzomercaptan was detected in the nonspiked real samples. Next, validation samples

413 were prepared using these samples fortified with the three target compounds at

414 concentration level of 5-500 µg L^{-1}. As shown in Table 3, the recoveries of analytes were

415 satisfactory, ranging between 74 and 117%. In order to discard matrix effect in sewage

416 water, particularly for that one from Gandía (influent), standard addition calibration

417 curves were done. Several spiked samples at different levels (25-100 µg L^{-1}) were

418 percolated through cartridges and the slopes obtained in the resulting calibration curves

419 were not statistical different from those found with the external calibration method

420 (confidence level of 95%) As representative examples, Fig. 3 (left) shows the

421 chromatograms of a water sample (from influent sewage water) spiked with the analytes

422 without and with SPE pretreatment. On the other hand, the right part of Fig. 3 illustrates

423 the eluted fraction corresponding to a blank soil sample and that spiked with the analytes.

424 As observed, an effective enrichment of analytes of interest in both matrices was

425 evidenced, which demonstrated the performance of the synthesized sorbent to be used as

426 preconcentration purposes in complex samples.

427

428 *3.5. Comparison with other commercial sorbents and extraction methodologies*

429 Next, a comparison in terms of extraction performance with one commercial sorbent

430 (silica gel) commonly used for the extraction of benzomercaptans [51, 52] was made.

431 This generic sorbent gave retention values below 50% (see Fig. S8), which underlines the

432 convenience of using our synthesized sorbent.

433 Finally, the developed material was compared with other extraction sorbents of target

434 analytes in environmental samples (see Table 4). Regarding aqueous samples analysis,

435 the recovery values obtained were quite similar to those found in most reported studies;

436 however, in certain works [23, 28] these values were lower than 65%. Regarding the

437 LODs, our values were better than those described by Parham *et al*. [24], and similar to

438 those reported in refs. [28, 30, 31] using a sophisticated and high-cost MS detector. Other

439 advantage found is the less amount (20 mg) of sorbent required compared with single-use

440 commercial SPE sorbents (commonly up to 150-500 mg) [28, 30, 31]. This amount was

441 also similar to a nanomaterial-based method using CuNPs [23, 24] probably due to

442 surface area-to-volume ratio; however, its reusability was quite lower than that found in

443 the present study.

444 Likewise, in soil monitoring, the present method gave higher recoveries than those

445 described in literature [53, 54]. Concerning LODs, our protocol provided comparable

446 LOD values [53], or higher using MS detection [54]. In any case, this drawback does not

447 reduce the good features of our protocol such as the easy and cheap preparation of the

448 sorbent combined with the accessible equipment required, make this protocol a feasible

449 method to monitor benzomercaptans and their derivatives in environmental samples.

450

451 **4. Conclusions**

452 In this research, n-butylamine modulated ZIF-8 nanocrystals were successfully

453 synthesized, characterized and applied as SPE sorbent to the extraction of

454 benzomercaptans in environmental matrices. Prior to the SPE optimization, the addition
455 of BA (at several molar ratios) as modulator to the reaction mixture was done to evaluate
456 its impact on the crystal growth and adsorption capacity of the resulting MOFs. As a result
457 of this study, NH_2-ZIF-8 containing 10 mmol of BA as modulator was the most
458 appropriate sorbent. Then, several experimental parameters of the SPE protocol (such as
459 sample pH, desorption solvent composition, among others) were investigated in detail
460 using this MOF as SPE phase. The highly selective and efficient retention of
461 benzomercaptans on this MOF take advantages of multiple interactions between these
462 targets and the framework.

463 Moreover, the fruitful combination of NH_2-ZIF-8-BA 1 followed by HPLC-UV analysis
464 led to high extraction recovery values, low LODs, excellent enrichment factors and
465 satisfactory reusability. All these figures of merits prove that the present protocol
466 constitutes a simple, cost-effective, and appropriate methodology for extraction and
467 preconcentration of these pollutants in complex environmental samples. As far as we
468 know, this study reports the first study of influence of modulator content on the
469 morphology and extraction performance of organic pollutants and the subsequent
470 application of the best modulated ZIF-8 for the extraction of benzomercaptans and
471 demonstrate that it could be a promising SPE sorbent for further applications.

472

485

486 **Declaration of competing interest:** None.

15

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655 **Table 1.** Influence on different BA content modulator of textural parameters of
656 synthesized MOFs and their extraction performances.

MOF	Modulator	Particle size (nm)	Surface area ($m^2 g^{-1}$)	N amount (atomic, %)	Recoveries[a] (%)
ZIF-8	None	89 ± 6	1456	45.3	60-63
NH_2-ZIF-8-BA 1	BA, 10 mmol	61 ± 2	1365	52.6	94-102
NH_2-ZIF-8-BA 2	BA, 5 mmol	47 ± 5	856	47.7	64-77
NH_2-ZIF-8-BA 3	BA, 20 mmol	72 ± 7	1213	56.3	99-102

657

658 [a]Extraction conditions: sample concentration, 500 µg L^{-1}; volume, 5 mL; eluting solvent, 0.5 mL of 50:50
659 MeOH:H_2O (v/v) with 0.5 M NaOH.

660

661

662

663 **Table 2.** Figures of merit of the developed material used as SPE sorbent in the extraction
664 and analysis of benzomercaptans.

Analyte	Calibration range (µg L^{-1})	Within-device recovery (%) ± RSD (n=3)	Between-device recovery (%) ± RSD (n=3)	LOD[a] (µg L^{-1})	LOQ[a] (µg L^{-1})
MBO	5 – 2500	109 ± 2	107 ± 2	1.6	5
MBT	7 – 5000	95 ± 7	101 ± 1	2	7
NMBT	7 – 5000	100 ± 7	95 ± 1	2	7

665 [a]Instrumental values (without applying the extraction protocol)

666

667

668

669   **Table 3.** Recovery study of benzomercaptans in spiked environmental samples analyzed

670   following the recommended SPE protocol. Recovery (%) ± SD (n=3)[a].

	Environmental samples											
Analyte	**Gandia sewage water (influent)**		**Paterna sewage water (effluent)**		**Tap water**		**Soil 1 (Sueca)**		**Soil 2 (Burjassot)**		**Soil 3 (Valencia)**	
	Spiked level (µg L^{-1})						Spiked level (µg kg^{-1})					
	-	5	-	5	-	5	-	500	-	500	-	500
MBO	< LOD	76 ± 2	< LOD	94 ± 2	< LOD	117 ± 9	< LOD	109 ± 2	< LOD	100 ± 7	< LOD	102 ± 3
MBT	< LOD	76 ± 5	< LOD	82 ± 2	< LOD	81 ± 4	< LOD	103 ± 1	< LOD	107 ± 1	< LOD	98 ± 6
NMBT	< LOD	74 ± 5	< LOD	75 ± 6	< LOD	74 ± 8	< LOD	93 ± 1	< LOD	84 ± 10	< LOD	82 ± 3

671

672   [a]The recovery values were calculated by dividing the concentration found by the

673   concentration added (calibration curves).

674

675

676 **Table 4.** Comparison with other reported methods for benzomercaptans extraction and
677 analysis.

| Analytes	Material (sorbent amount)	Method	Sample matrix	Recoveries (%)	LOD (ng L^{-1} / ng kg^{-1})	Reusability	EF[a]	Reference
MBT, MBO	Copper oxide nanoparticles (14 mg)	SPE / HPLC-DAD	Industrial water samples	56-93	-	3		[23]
MBT, MBO, MBI	Copper oxide nanoparticles (14 mg)	SPE / HPLC-DAD	Environmental water sample	96-104	1900-2700	3	200	[24]
MBT	Oasis HLB cartridge (200 mg)	SPE / HPLC-MS	Municipal wastewater samples	60-70	16.7	-	7-14	[28]
MBT	Oasis MAX (150 mg)	SPE / HPLC-MS	Environmental water samples	80-118	1-4	-	20-100	[30]
MBT	Oasis HLB (500 mg)	SPE / HPLC-MS	Water samples	70-85	7	-	21-83	[31]
BT, HBT, MTBT, ABT	Strata^{TM}-X cartridges (200 mg)	SPE / HPLC-MS/MS	Dewatered sewage sludge	50-116	40 - 13000	-	-	[51]
MBT, HBT, BT, ABT, MTBT	Poly-Sery HLB cartridge (60 mg)	SPE / UPLC-MS/MS	Road dust / Roadside soil	56-105	20-120	-	-	[52]
MBO, MBT, NMBT	NH$_2$-ZIF-8-BA 1 (20 mg)	SPE / HPLC-UV	Environmental samples	74-117	16-21 / 400-500	10	4[b] ;100[c]	This Work

678

679 [a]The EF from the overall SPE protocol was calculated using the ratio between the final (eluent)

680 extract and the maximum sample volume load (for aqueous samples) or the amount of solid

681 weighed (for soil samples); [b]soil samples; [c]aqueous samples

682

683 EF: enrichment factor. MBT: 2-mercaptobenzothiazole, MBO: 2-mercaptobenzoxazole, MBI: 2-

684 mercaptobenzimidazole, NMBT: 2-mercapto-6-nitrobenzothiazole, HBT: 2-

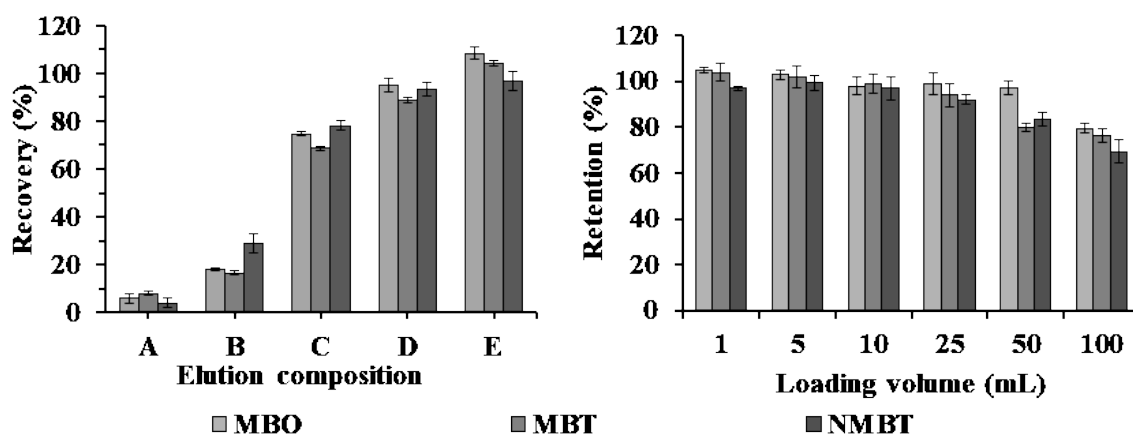685 hidroxybenzothiazole, MTBT: 2-methyl-thiobenzothiazole, ABT: 2-aminobenzothiazole.

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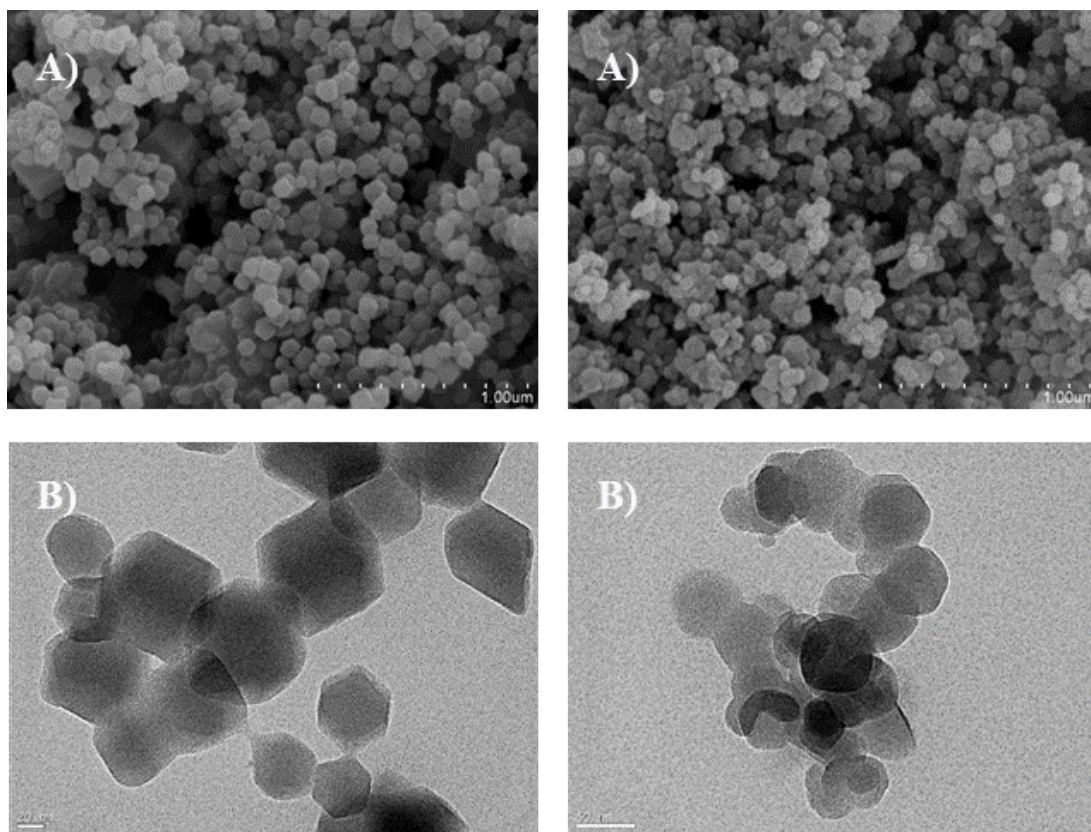
Figure 1. SEM (A) and TEM (B) micrographs of ZIF-8 (left part) and NH$_2$-ZIF-8-BA 1 (right part) materials.

690

691

Figure 2. Effect of elution solvent composition on the recovery values of analytes using NH$_2$-ZIF-8 as SPE sorbent (left part),eluent compositions: A) MeOH, B) 50:50 MeOH:H$_2$O (v/v), C) 50:50 MeOH:H$_2$O (v/v) with 0.1 M NaOH, D) 50:50 MeOH:H$_2$O (v/v) with 0.2 M NaOH and E) 50:50 MeOH:H$_2$O (v/v) with 0.5 M NaOH; effect of loading sample volume on the extraction efficiency of benzomercaptans (right part). Error bar = SD (n = 3).

698

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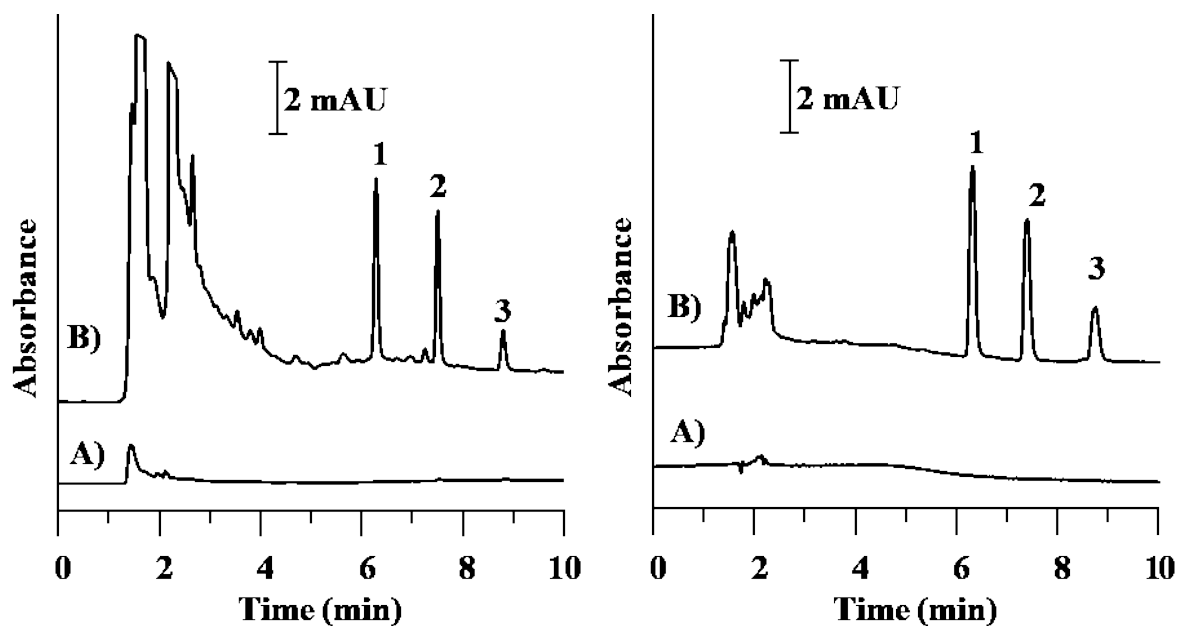
700

701 **Figure 3.** HPLC-UV chromatograms of sewage water (Gandía's plant) (left part) and

702 extracts of soil samples (right part) spiked with 5 µg L^{-1} of each benzomercaptan,

703 respectively, without applying (A) and applying the proposed SPE protocol (B). The right

704 part shows an extract of soil sample without (A) and with spiking of analytes at 500 µg

705 kg^{-1} (B) subjected to the SPE treatment. Chromatographic conditions are given in

706 Experimental Section and Supplementary Information. Peak identification: 1, MBO; 2,

707 MBT; 3, NMBT.

708