

Highlights

- A GO-MIPs materials for DEHP extraction was prepared and characterized
- A GO-MIPs-DSPME method was applied to extract DEHP in water
- DEHP was selectively and effectively extracted and enriched by GO-MIPs-DSPME
- Good recovery and sensitivity were achieved by proposed GO-MIPs-DSPME

1 **Dispersive solid-phase microextraction with graphene oxide based**
2 **molecularly imprinted polymers for determining bis(2-ethylhexyl) phthalate**
3 **in environmental water**

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16
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18 Submitted to *Journal of Chromatography A*

19
20 (Revised)

21 June 12, 2017

24 **Abstract**

25 A novel graphene oxide-molecularly imprinted polymers (GO-MIPs) was prepared and
26 applied for selective extraction and preconcentration of bis(2-ethylhexyl) phthalate (DEHP) in
27 environmental water samples by using the dispersive solid-phase microextraction (DSPME)
28 method. The GO-MIPs was synthesized via precipitation polymerization using GO, DEHP,
29 methacrylic acid, and ethylene dimethacrylate as supporting materials, template molecules,
30 functional monomer, and cross-linker, respectively. The prepared GO-MIPs were characterized
31 by scanning electron microscope and Fourier transform infrared spectroscopy. The GO-MIPs-
32 DSPME conditions including type and volume of elution solvents, adsorbents amount, initial
33 concentration of DEHP, pH and ionic strength of water samples were investigated. Under
34 optimized conditions, the DEHP was selectively and effectively extracted in real water samples
35 and enrichment factors of over 100-fold were achieved. Good linearity was obtained with
36 correlation coefficients (R^2) over 0.999 and the detection limit ($S/N = 3$) was 0.92 ng mL^{-1} . The
37 average recoveries of the spiked samples at three concentration levels of DEHP ranged from
38 82% to 92% with the relative standard deviations less than 6.7%. The results indicated that the
39 proposed GO-MIPs-DSPME extraction protocol combined with HPLC-UV determination could
40 be applied for selective and sensitive analysis of trace DEHP phthalate in environmental water
41 samples.

42

43 **Keywords:** Bis(2-ethylhexyl) phthalate, Graphene oxide-molecularly imprinted polymers,
44 Dispersive solid phase microextraction, Environmental water

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46

47 **1 Introduction**

48 Bis(2-ethylhexyl) phthalate (DEHP), one of the most popular phthalates esters (PAEs)
49 plasticizers, is widely used as plasticizer of common packaging materials such as plastics and
50 rubber to promote their stability and flexibility through weak secondary molecular interactions
51 with polymer chains [1-4]. Because it is physically bound to the polymer chains, it becomes
52 easily released and enters into the environment, and further poses the adverse effects on human
53 health as the suspected endocrine disrupters or mutagens even at low levels [5-8]. Therefore,
54 development of the analytical techniques to efficiently enrich and analyze DEHP in aqueous
55 matrices is essential for extensive surveys on their occurrence and fate in the environment.
56 Conventional sample pretreatment techniques such as liquid–liquid extraction (LLE) and solid
57 phase extraction (SPE) prior to chromatographic determination have been widely used for
58 extraction and preconcentration of the phthalates in environmental samples [9-10]. While reliable,
59 these methods have several shortcomings such as low selectivity and limited enrichment factors.
60 Moreover, the use of large volumes of organic solvents gives rise to large amounts of organic
61 wastes, resulting in environmental and safety concerns.

62 Molecularly imprinted polymers (MIPs) were increasingly developed to meet the need of
63 selective extraction of target analytes from the complicated sample matrix by its molecular
64 recognition properties. This molecular recognition excellence has been very attractive in many
65 different fields, such as sensors, enantiomeric separations, biomedical and analytical applications
66 [11]. A number of papers published in the past decades reported that MIPs had been successfully
67 applied in SPE as sorbents to extract organic pollutants in environmental waters prior to
68 instrumental analysis [12-14, 28-29]. Such approaches usually led to good selectivity and
69 reproducibility. On the other hand, a large number of microextraction methods, such as liquid-

70 phase microextraction (LPME), solid-phase microextraction (SPME), and single drop
71 microextraction (SDME), which are more sensitive, cost-effective and environmentally friendly
72 compared to conventional extraction methods, have been successfully developed for the
73 extraction of trace pollutants from a variety of environmental samples [15-17]. Since these
74 techniques are surface dependent processes, dispersive microextraction techniques including of
75 dispersive liquid-phase microextraction (DLPME) and dispersive solid-phase microextraction
76 (DSPME) were recently proposed by means of dispersion to improve the contact area between
77 sample solution and extractants, and further shorten the extraction time and decrease the
78 extractants consumption [18-20]. The key to those techniques is the use of highly efficient
79 extractants media in order to maintain or even improve the preconcentration of the analytes using
80 only a few milligrams or microliters of extractants. Updated developments in this field are
81 mainly related to the use of new sorbent materials with high surface area as extractants [21].
82 Recently, graphene has received much attention from environmental and analytical scientists
83 ever since their discovery due to its unique mechanical properties and extremely large surface
84 area with two-dimensional structure [22]. Graphene derivatives such as graphene oxide (GO)
85 have been applied to synthesize hydrophilic materials to become water-compatible for various
86 application by modifying with hydrophilic functional groups such as -COOH and -OH [23-25].
87 Theoretically, compared to general MIPs, the prepared MIPs situated at the large surface of GO
88 could provide higher loading capacity, accelerate association/dissociation kinetics and adsorption,
89 improve the accessibility and sensitivity to target species, and effectively avoid the polymers
90 from caking [26]. Moreover, the extraction efficiency could be further dramatically enhanced by
91 employing the DSPME method with GO-MIPs as extractants. However, little information on the
92 application of GO-MIPs-DSPME for the extraction of pollutants in environmental samples is

93 available.

94 In the present study, our aims were: (i) to prepare and characterize the GO-MIPs adsorbents
95 for selective extraction of DEHP in aqueous solution; (ii) to investigate the procedures of the
96 GO-MIPs-DSPME method for preconcentration of the DEHP in aqueous samples; (iii) to
97 optimize the variables involved in the GO-MIPs-DSPME process such as type and volume of
98 desorption solvent, amount of consumed GO-MIPs, pH and ionic strength of sample solution;
99 and (iv) to apply the validated GO-MIPs-DSPME-HPLC-UV method to extract and determine
100 the ultra-trace DEHP in real natural water samples.

101

102 **2 Experiments**

103 **2.1 Materials and Reagents**

104 Bis(2-ethylhexyl) phthalate (DEHP, >98.0%), methacrylic acid (MAA) and ethylene glycol
105 dimethacrylate (EGDMA, 97.0%) were supplied by TCI chemicals (Tokyo, Japan). 2,2'-
106 Azobis(2-methylpropionitrile) (AIBN) and graphite powder (99.95% metals basis, 5000 meshes)
107 were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). HPLC grade methanol were
108 supplied by Tjshield chemicals (Tianjin, China). **Diphosphorus pentoxide (P₂O₅), potassium**
109 **persulfate (K₂S₂O₈), sulfuric acid (H₂SO₄), potassium permanganate (KMnO₄) and acetonitrile**
110 **(ACN, ≥ 99.5%)** was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).
111 Acetone (≥ 99.0%) was purchased from Juhua chemicals (Quzhou, China). The AIBN reagents
112 were refined freshly before used by following procedures: 100 mL methanol were heated at 60
113 °C in a 200 mL beaker until boiling, then added 10 g of original AIBN into the beaker and stirred
114 the solution to make AIBN quickly dissolved. After filtration, the collected solution was recycled
115 in a beaker followed by cooling crystallization in refrigerator overnight. The refined AIBN

116 crystal was dried in vacuum after filtration and showed uniform crystal shape. All other reagents
117 were analytical grade and were used as received. De-ionized water was used throughout the
118 experiments.

119 **2.2 HPLC analysis**

120 The DEHP in standards and water samples were determined by WUFENG LC-100 high-
121 performance liquid chromatograph (Shanghai, China) equipped with a double pump and
122 ultraviolet detector. The chromatographic separations were carried out on a Waters Symmetry
123 C₁₈ column (3.9 × 150 mm, 5 μm) at 30 °C by using an isocratic elution program of mobile phase
124 (methanol) at a flow rate of 1.0 mL min⁻¹. Aliquots of 20 μL were injected into the HPLC system,
125 and the detection wavelength was set at 235 nm. All quantification was performed by the
126 external calibration method based on peak areas. Calibration curve was constructed by linear
127 regression of the peak area of standard versus the concentration.

128

129 **2.3 Preparation and characterization of GO-MIPs adsorbents**

130 **2.3.1 Preparation of graphene oxides (GO)**

131 Graphene oxides were prepared by Hummers' method [26] with some modification as
132 following: 60 mL of concentrated H₂SO₄, 1.2 g of K₂S₂O₈ and 2.5 g of P₂O₅ were added into a
133 150 mL three-necked flask and mixed with the aid of magnetic stirring bar. Then 3 g of graphite
134 was slowly added and dispersed into the reaction solution and the mixture kept for 6 h at 80 °C.
135 Afterwards, the mixture solution was immediately poured into 800 mL of purified ice-water and
136 placed on the lab batch overnight at room temperature. After removal of the supernatant, the
137 graphite oxide precipitates were washed with deionized water until the pH of eluted water
138 became neutral and then dried in vacuum freezing drier. The dried graphite oxide was

139 subsequently mixed with 60 mL of concentrated H₂SO₄ in a 150 mL three-necked flask with
140 mechanical stirring in ice-water bath. And 4.0 g of KMnO₄ was slowly added into the mixture
141 solution and kept at 60 °C for 10 h. Then the mixture solution was poured into 800 mL of
142 purified ice-water, and the residual KMnO₄ and MnO₂ were removed by adding 30% H₂O₂ and
143 1.0 M HCl solutions, respectively. Finally, the graphene oxide liquid crystals were washed with
144 deionized water until the pH of eluted solution became neutral.

145 ***2.3.2 Preparation of GO-MIPs adsorbents***

146 Prior to preparation of GO-MIPs, GO water mixture was centrifuged at 12000 rpm for 10
147 mins and the water supernatant was decanted, and then GO solids were washed with ACN
148 solvents twice to make GO completely dispersed into ACN solvents. The GO-MIPs was
149 prepared by precipitation polymerization as follows: GO-ACN mixture solution (4.0 mL), ACN
150 (100 mL) and methanol (20.0 mL) were mixed in a 250 mL of three-necked flask, and DEHP (1
151 mmol) and MAA (4 mmol) were added into the mixture solutions with the stirring by magnetic
152 bar and kept for 2 h. After removal of the dissolved-oxygen by high purity nitrogen gas blowing,
153 the cross-linking agent EGDMA (20 mmol) and the initiation reagents AIBN (50 mg) were
154 added into the solution and sonicated for 10 min to fully dissolve. The polymerization was
155 performed at 65 °C for 6 h in oil bath. Postsynthesis, the polymeric particulates were freed from
156 template and residual monomers via Soxhlet extraction by using methanol, and then the products
157 were dried to constant mass under vacuum at -50 °C in a freeze vacuum drier. To verify that the
158 affinity to analytes was due to molecular recognition but not just to nonspecific binding, and that
159 the adsorption capability of analytes to adsorbents was enhanced by combining GO with MIPs,
160 GO-NIPs (GO non-imprinted polymers), MIPs, NIPs were synthesized as the same procedure in
161 the absence of the template molecule DEHP, GO, and none of them, respectively.

162 **2.3.3 Characterization of GO-MIPs**

163 The morphology of the prepared polymers were examined by scanning electron microscope
164 (FEI, Nova NanoSEM 200, USA) and the FT-IR spectra were obtained on a Fourier transform
165 infrared spectroscopy (Perkinelmer, Frontier, USA).

166 Adsorption capacity of prepared GO-MIPs and MIPs was investigated and compared prior to
167 optimization of extraction procedure. Twenty milligrams of prepared GO-MIPs adsorbents was
168 dispersed into 10.0 mL spiked DEHP water samples with different concentrations at 0.1, 0.5, 1.0,
169 2.0, 5.0, 10 $\mu\text{g mL}^{-1}$. After adsorption process, the concentration of DEHP in water samples were
170 determined by HPLC. The adsorption capacity of the GO-MIPs was calculated by following
171 equation:

$$172 \quad Q_t = \frac{(C_0 - C_t) \times V_s}{m_{\text{adsorbent}}}$$

173

174 Q_t - Adsorption capacity ($\mu\text{g mg}^{-1}$)

175 C_0 - Initial concentration of DEHP in sample ($\mu\text{g mL}^{-1}$)

176 C_t - Concentration of the DEHP after adsorption ($\mu\text{g mL}^{-1}$)

177 V_s - Volume of spiked DEHP water sample (mL)

178 m - Amount of the GO-MIPs adsorbents (mg)

179 **2.4 GO-MIPs-DSPME procedure**

180 The effects of the type of desorption solvent on GO-MIPs-DSPME procedures were
181 investigated firstly by using the DEHP standard solution. In detail, 20 mg of pretreated GO-MIPs
182 was added into a glass flask containing 600 mL of 20 ng mL^{-1} DEHP aqueous solution, and the
183 GO-MIPs in solution were dispersed in an ultrasonic bath until no GO-MIPs aggregates were
184 observed. After agitation at 600 rpm for 0.5 h using an IKA mixing shaker, the GO-MIPs-DEHP
185 mixtures were transferred into a centrifugation tube. Then the mixtures were centrifugated at

186 12000 rpm for 10 mins, decanted the supernatants, and dried at -50 °C in vacuum. To ensure the
187 DEHP completely adsorbed by GO-MIPs, the DEHP has been analyzed in supernatants after
188 adsorption process and there was no residue DEHP found. The dried GO-MIPs-DEHP particles
189 were transferred into a 5 mL centrifugation tube and 2.5 mL of organic desorption solvents was
190 added. Then, the tube containing GO-MIPs-DEHP-desorption solvent was sealed and vortexed
191 for 1 min, and placed into an ultrasonic bath for 5 min. After centrifugation at 15000 rpm for 10
192 min, the supernatant solutions were pipetted into another tube and the desorption process was
193 repeated once. Finally, the mixture of supernatants was filtered using a 0.22 µm membrane and
194 injected into a HPLC for analysis. Two organic desorption solvents including methanol and
195 acetone were studied in this work. After selection of the desorption solvent, several other key
196 parameters, such as the volume of desorption solvent, consumed amount of GO-MIPs adsorbents,
197 pH and ionic strength of sample solution were investigated and optimized to obtain the best
198 extraction efficiency for GO-MIPs-DSPME procedures.

199 **2.5 Environmental water samples collection and analysis**

200 Rain samples were collected with a Teflon container on the top of the Xinzhou Building in
201 the Wenzhou University campus. River water samples were collected from the surface water of
202 Wen-Rui-Tang River. Lake samples were obtained from the Swan Lake in the Wenzhou
203 University campus. All sites of sample collection are located in the city of Wenzhou, Zhejiang
204 province, China. After sampling, all samples were stored at 4 °C in the dark until use. Prior to the
205 extraction, the water samples were centrifuged and filtered through 0.45 µm membrane filters to
206 remove the impurities. The DEHP phthalate ester in real water samples were extracted by
207 following the optimized GO-MIPs-DSPME method and determined by HPLC. All sample
208 containers, glassware and filtration devices were thoroughly cleaned with 0.1 M HCl solution

209 and then finally rinsed with doubly distilled-deionized water.

210 **3 Results and discussion**

211 **3.1 Characterization of prepared GO-MIPs**

212 The morphology of the prepared GO sheets, spherical MIPs, and GO-MIPs were
213 characterized by scanning electron microscope (SEM) and their images are presented in Fig. 1.
214 The areas of GO sheets were ranged from 5 to 10 μm^2 and the particle sizes of MIPs were
215 estimated through sieving and ranged from 0.2 to 1.0 μm , as shown in Fig. 1a and 1b,
216 respectively. Obviously, Fig. 1c showed that granular MIPs were coated on the surface of the GO
217 with layered structure compared with Fig. 1a and the prepared GO-MIPs were dispersed into the
218 sample solution.

219 The prepared GO-NIPs and GO-MIPs were characterized by using FT-IR analyses to
220 determine the functional group present in polymer matrices. As is shown in Fig. 2, the FTIR
221 spectra of GO-MIPs (b) and GO-NIPs (a) were found to be almost similar, which may be due to
222 their same chemical nature. Characterization of a broad band of NH stretching in 3200 - 3500
223 cm^{-1} region proves the presence of hydrogen bonding and hence confirms the synthesis of
224 polymer. The bands at 1635 cm^{-1} and 1720 cm^{-1} were assigned to C=C and C=O bendings of
225 functional monomer methacrylic acid (MAA) and cross-linker ethylene glycol dimethacrylate
226 (EGDMA). It demonstrates that the prepared polymer is a co-polymer of MAA and EGDMA.
227 The bands in the region of 1600 and 1650 cm^{-1} were assigned to the C=C of GO sheets, while it
228 was weakened due to the effect of the initiator (AIBN). The peaks at 1455 cm^{-1} and 1254 cm^{-1}
229 were characteristic of CH_2 bending vibration and C-C stretching vibration, respectively. In
230 addition, the stretching vibration of C-O at 1148 cm^{-1} (1142 cm^{-1} in GO-NIPs spectrum due to
231 the red shift) revealed the bond formation between GO and MIPs. The results confirmed that the

232 GO-MIPs composite was constructed successfully.

233 The adsorption capacity of prepared GO-MIPs adsorbents was calculated following the
234 procedures and calculation in Part 2.3.3. The results indicated that the adsorbed quantity of
235 DEHP with 20 mg of GO-MIPs increased with the increase of the DEHP concentration in sample
236 solution. However, the adsorbed quantity of DEHP kept stable when the DEHP concentration
237 was higher than $2.0 \mu\text{g mL}^{-1}$. It suggested that the maximum adsorption capacity of prepared GO-
238 MIPs was around $1.0 \mu\text{g mg}^{-1}$ based on the adsorption capacity calculated equation. Meanwhile,
239 the the maximum adsorption capacity of the MIPs was half of that of GO-MIPs.

240

241 **3.2 Optimization of the GO-MIPs-DSPME procedure**

242 ***3.2.1 Type and volume of the elution solvent***

243 In this study, the effects of type and volume of desorption solvents on desorption of DEHP
244 from GO-MIPs were firstly investigated. As opposed to aqueous solutions, hydrophobic DEHP
245 absorbed on the GO-MIPs are expected to be desorbed into organic solvents, especially under
246 ultrasonic irradiation. Two common organic solvents, methanol and acetone, were evaluated for
247 DEHP desorption. The experiments were followed the procedures as described in Section 2.4.
248 As illustrated in Fig. 3, acetone yields greater desorption efficiency than methanol. The reason
249 for this could be that the solubility of DEHP in acetone is higher than those in the methanol
250 solvents [27]. To minimize the amount of organic solvent consumed, different volumes of
251 acetone including 2.00, 4.00, 6.00, and 8.00 mL were used for desorbing DEHP from GO-MIPs
252 separately. As presented in Fig. 4a, the highest recovery were achieved until the volume of
253 acetone decreased as 6.00 mL. Therefore, 6.00 mL of acetone was selected as the desorption
254 solvent in the following experiments.

255 **3.2.2 Amount of the GO-MIPs adsorbents**

256 The effects of the amount of GO-MIPs on the adsorption of DEHP from aqueous solutions
257 were studied. The experiments were performed by adding different amounts of GO-MIPs
258 adsorbents (10, 15, 20, 30 and 40 mg) in 100 mL of 20 ng mL⁻¹ DEHP aqueous solution and
259 following the procedures as described in Section 2.4. As presented in Fig. 4b, the recovery of
260 spiked DEHP dramatically increased when the amount of the GO-MIPs increased from 10 to 15
261 mg. It is easy to explain that more adsorbents would possess larger surface area and more
262 available active sites for adsorbing DEHP. The recovery of spiked DEHP was stable with the
263 increasing amount of GO-MIPs. Therefore, 15 mg was chosen as the optimum amount for GO-
264 MIPs adsorbents used based on the experimental results. Also, the comparisons of four
265 adsorbents including of GO-MIPs, GO-NIPs, MIPs, and NIPs, as shown in Fig. 4b, demonstrated
266 that the performance of GO-MIPs was superior to the other adsorbents. **It indicated that the**
267 **adsorption of DEHP on GO-MIPs adsorbents is based on the molecular recognition, and**
268 **capability of adsorption of DEHP with GO-MIPs is much larger than those with granular MIPs.**

269 **3.3.3 pH and ionic strength of sample solution**

270 For the investigation of the pH effect, a series of DEHP aqueous solutions with the pH values
271 of 3, 5, 7 and 9 were prepared by adding 0.01 M HCl and NaOH solutions prior to extraction. As
272 presented in Fig. 4c, changing the solution pH from 3 to 9 did not affect the adsorption of DEHP.
273 **The slightly decrease of recovery in acid or base solutions might be resulted from the hydrolysis**
274 **of DEHP.** Therefore, the GO-MIPs-DSPME method can be directly applied for DEHP extraction
275 from environmental water samples without adjusting the pH since the typical pH values of
276 natural waters are located in the range from 5 to 9. Generally, the solubility of the hydrophobic
277 compounds decreases with increasing ionic strength in aqueous solution. This “salting-out”

278 effect may slightly enhance their hydrophobic interactions with GO-MIPs. To examine the
279 impacts of ionic strength, experiments were performed by addition of NaCl salt in water samples
280 at 0, 1, 2, 3, 4, 5 to 6 % prior to extraction since the ionic strength of the natural environmental
281 water is located in the range from 0 to 6 %. As shown in Fig. 4d, an increase of ionic strength
282 had a negligible effect on the adsorption of DEHP by the GO-MIPs, suggesting that within the
283 ionic strength range studied, the contribution of the salting-out effect to DEHP was too weak to
284 exert any change in the adsorption of DEHP on the GO-MIPs. Thus, the ionic strength of natural
285 water samples is not expected to exert a significant effect on the adsorption of DEHP by GO-
286 MIPs.

287

288 **3.3 Validation of the GO-MIPs-DSPME-HPLC method**

289 The developed GO-MIPs-DSPME-HPLC-UV method was validated by evaluation of
290 following validation parameters: linearity, sensitivity, precision, selectivity, accuracy and
291 detection and quantification limits. **This study was performed on the rain water samples spiked
292 with DEHP to provide samples containing concentration range of 0.003 - 2.00 $\mu\text{g mL}^{-1}$. The
293 linearity and sensitivity were established through the calibration graph obtained by triplicate
294 analysis of DEHP spiked rain water samples. Linearity was demonstrated calculating the
295 regression line by the least squares method and expressed by correlation coefficients (R^2) over
296 0.996. Selectivity of the method was evaluated by the comparison of chromatograms obtained
297 from spiked rain water with 20 ng mL^{-1} of DEHP, its metabolite mono-(2-ethylhexyl)-
298 phthalate (MEHP) and other phthalates i.e. dimethyl phthalate (DMP), diethyl phthalate (DEP)
299 and dibutyl phthalate (DBP). As presented in Fig. 5, the results verified that there was no
300 significant interference by those phthalates that could compromise the determination of DEHP.**

301 Intra-assay and inter-assay precision data were determined using low, medium, and high
302 concentrations (0.02, 0.10, 2.00 $\mu\text{g mL}^{-1}$, respectively). Intra-assay precision was assessed using
303 six replicates of each concentration in the same day. Inter-assay precision was evaluated for three
304 replicates analyzed on separate days ($n = 5$). The results expressed as percent relative standard
305 deviation (RSDs) were less than 6.7 %. The enrichment factor was 100 based on the ratio of the
306 volume of sample over the desorption solvent and the adsorption/desorption efficiencies.
307 Increasing the volume of the natural water samples could further increase the enrichment factor.
308 The accuracy of the described method was tested in real environmental water matrices with
309 known amounts of DEHP standards added, and the spiked 5.0, 50, 500 ng mL^{-1} of DEHP water
310 samples were subjected to the entire analytical procedures from the sample pre-treatment to the
311 chromatographic analysis. The recoveries, expressed as the mean percentage ratio between the
312 amounts found and those added, were found to be 82 - 92 % in different water samples, and
313 followed the order of rain > Swan Lake > Wen-Rui-Tang River. The possible reason is that the
314 water pollution of Wen-Rui-Tang River is much worse than that of Swan Lake and the rain is the
315 cleanest one in three natural water samples, and the soluble organic compounds in samples could
316 slightly affect the adsorption of DEHP by GO-MIPs due to the direct site competition and pore
317 blockage. The limit of detection and limit of quantification measured as three and ten times the
318 background noise for the developed GO-MIPs-DSPME-HPLC-UV method were 0.92 and 2.82
319 ng mL^{-1} , respectively.

320

321 **3.4 Determination of DEHP in real water samples**

322 The GO-MIPs-DSPME-HPLC-UV method has been successfully applied to the selective
323 determination of DEHP in environmental water samples, including of rain, lake, and river waters,

324 which were collected in Wenzhou, Zhejiang province, China. The typical chromatograms of lake
325 water with and without GO-MIPs-DSPME pretreatment are presented in Fig. 6. Obviously, the
326 sample matrix interference was significantly eliminated and the DEHP in samples was
327 selectively extracted and enriched after GO-MIPs-DSPME pretreatment. The concentrations of
328 the DEHP were $1.56 \pm 0.32 \text{ mg L}^{-1}$ in River and $0.32 \pm 0.08 \text{ mg L}^{-1}$ in lake water samples,
329 respectively, and below the detection limit in rain water. The relatively high concentration of
330 DEHP in the Wen-Rui-Tang River water could come from the direct discharge of domestic
331 sewage by local residents.

332 **4 Conclusions**

333 In this paper, we provided a new method which involved in graphene oxide-based
334 molecularly imprinted polymers coupled with dispersed solid phase extraction (GO-MIPs-
335 DSPME) for the selectively and effectively preconcentration of DEHP in environmental water
336 samples. The prepared GO-MIPs showed higher capacity and affinity than those of traditional
337 spherical MIPs under optimized DSPME conditions in aqueous solution. Thus, proposed GO-
338 MIPs-DSPME extraction protocol combined with HPLC-UV determination could be applied for
339 selective and sensitive analysis of trace DEHP phthalate in water samples.

340

341 **Acknowledgements**

342 The research project was jointly supported by the National Natural Science Foundation of
343 China (21477088), Natural Science Foundation of Zhejiang Province (LY17B070001), and the
344 Zhejiang Scientific and Technological Innovation Fund & Xinmiao Talents Projects
345 (2016R426060).

346

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Figure Captions

Figure 1. Scanning electron microscope (SEM) images of (a) GO sheets, (b) spherical MIPs, (c) GO-MIPs adsorbents

Figure 2. FTIR spectra of (a) GO-NIPs and (b) GO-MIPs

Figure 3. Recoveries of spiked DEHP with different types of elution solvents

Figure 4. Recoveries of spiked DEHP with different (a) volume of elution solvent; (b) amounts of adsorbents; (c) pH values of sample solution; and (d) ionic strength of sample solution

Figure 5. Chromatograms for spiked DEHP, MEHP, DMP, DEP, and DBP (20 ng mL⁻¹) in rain water with and without GO-MIPs-DSPME extraction (Mobile phase: methanol; Flow rate: 1.0 mL min⁻¹; Column temperature: 30 °C; Detection wavelength: 235 nm)

Figure 6. Chromatograms for DEHP in lake water samples with and without GO-MIPs-DSPME extraction (Mobile phase: methanol; Flow rate: 1.0 mL min⁻¹; Column temperature: 30 °C; Detection wavelength: 235 nm)

Figure 1
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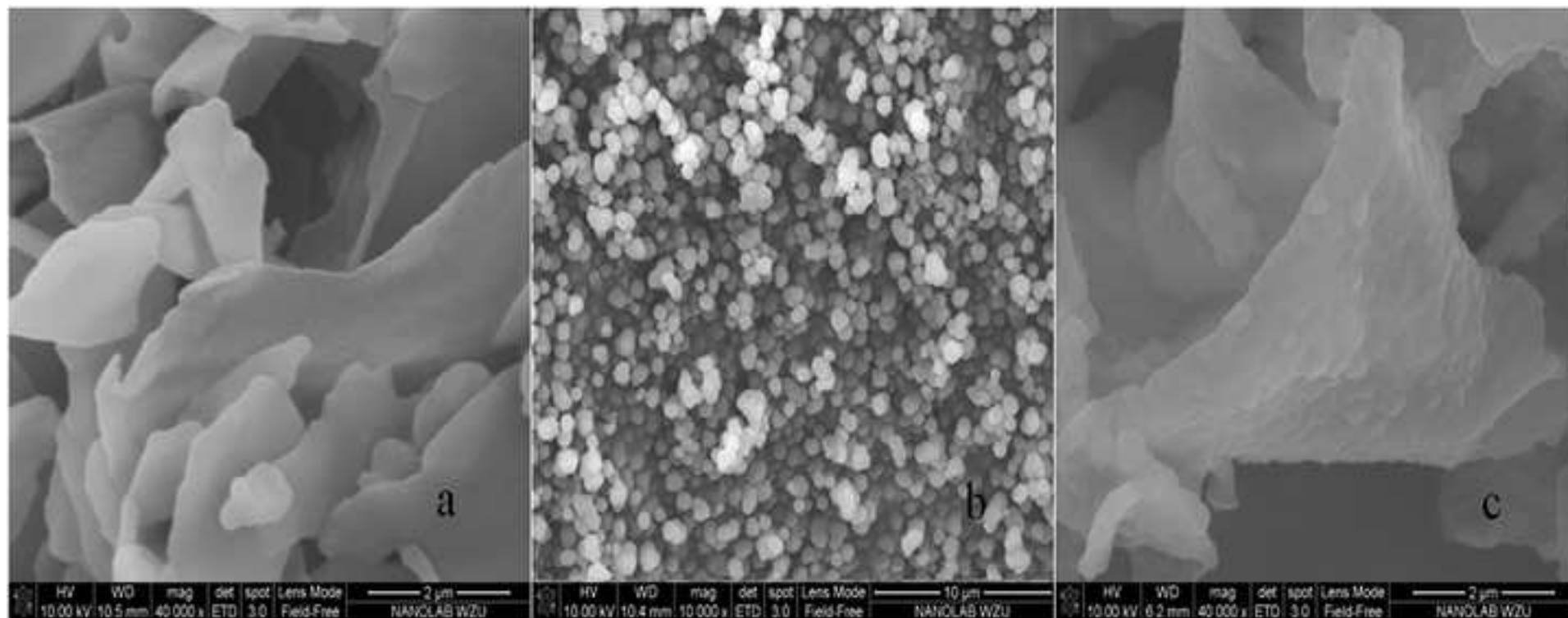


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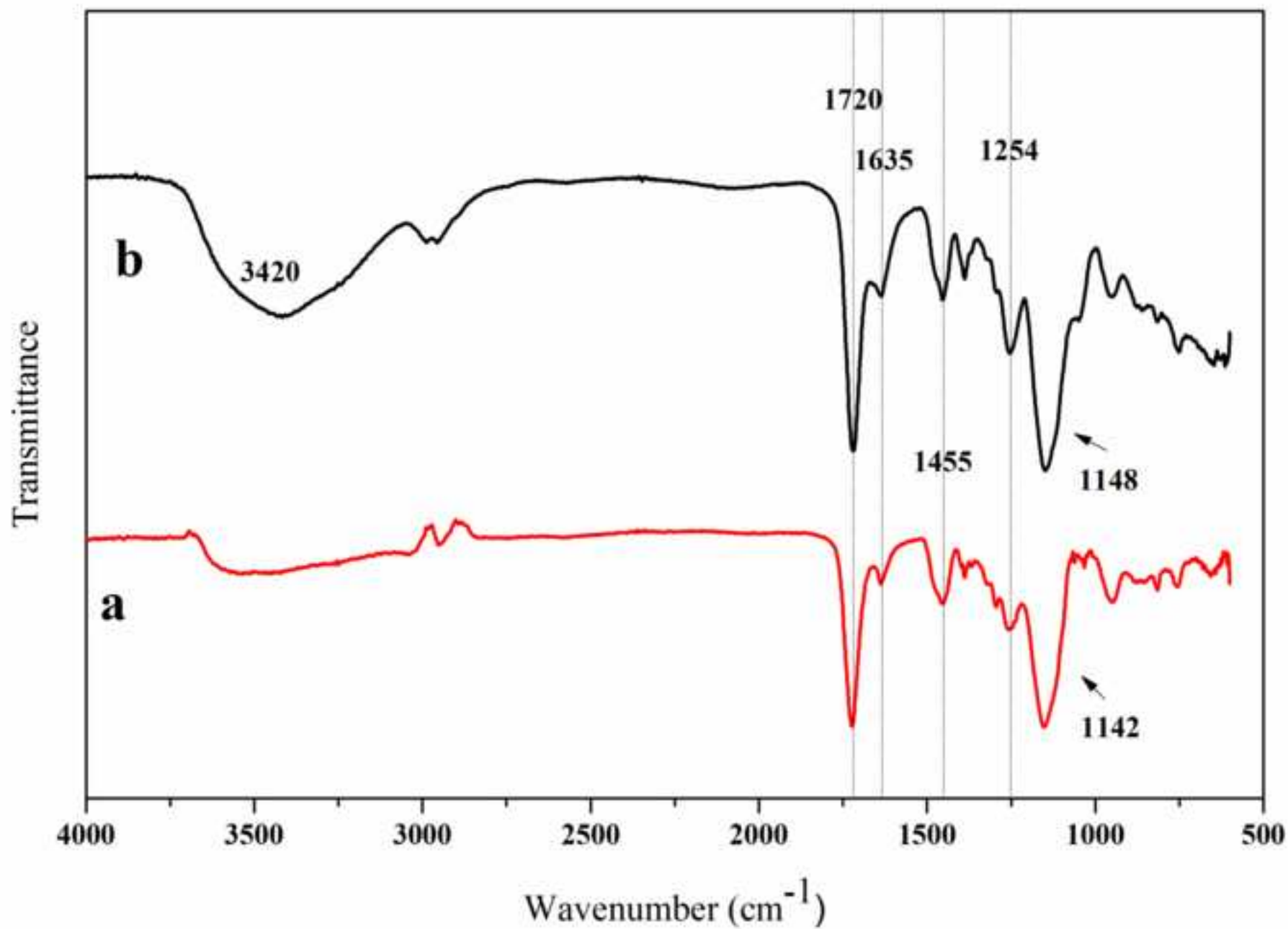


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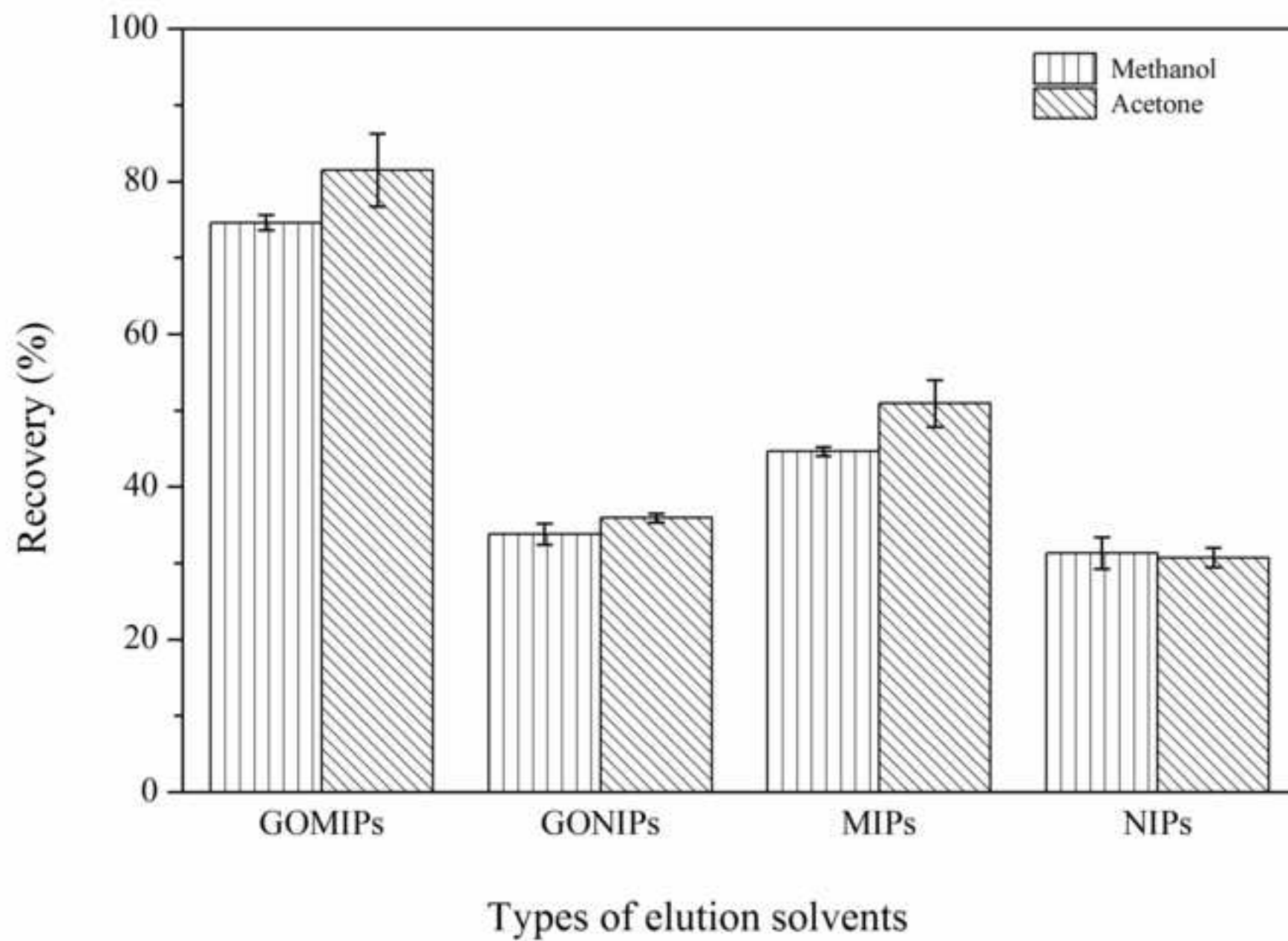


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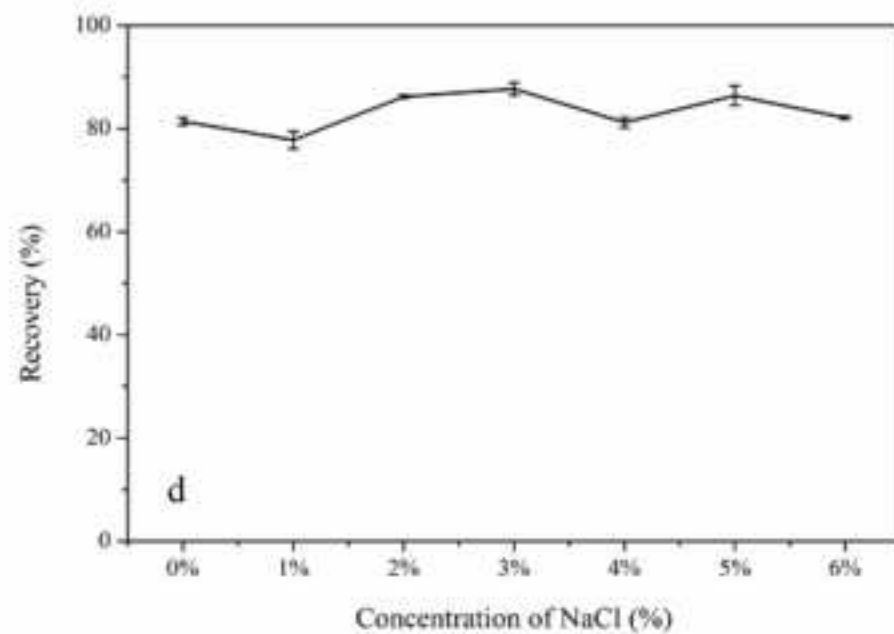
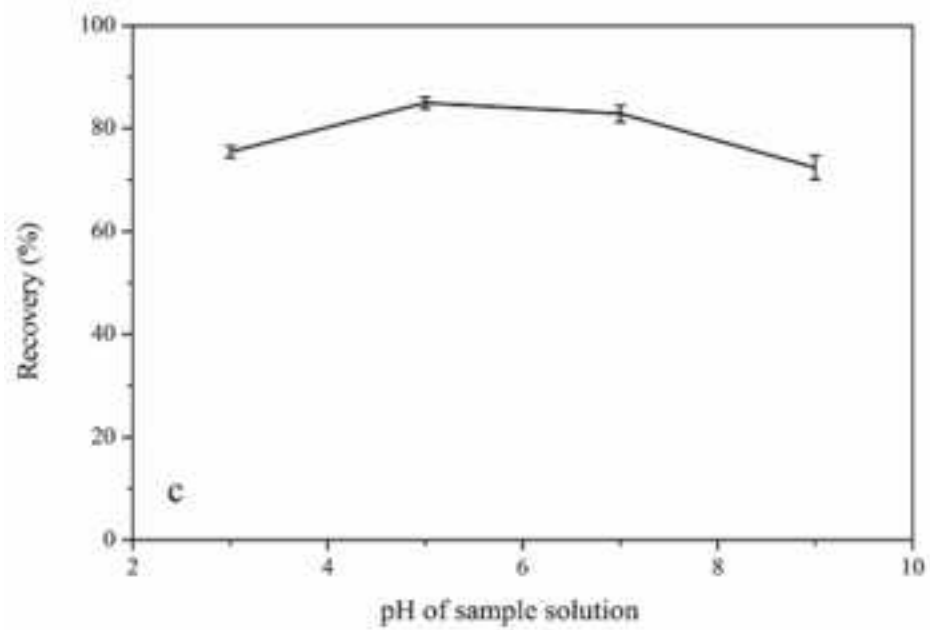
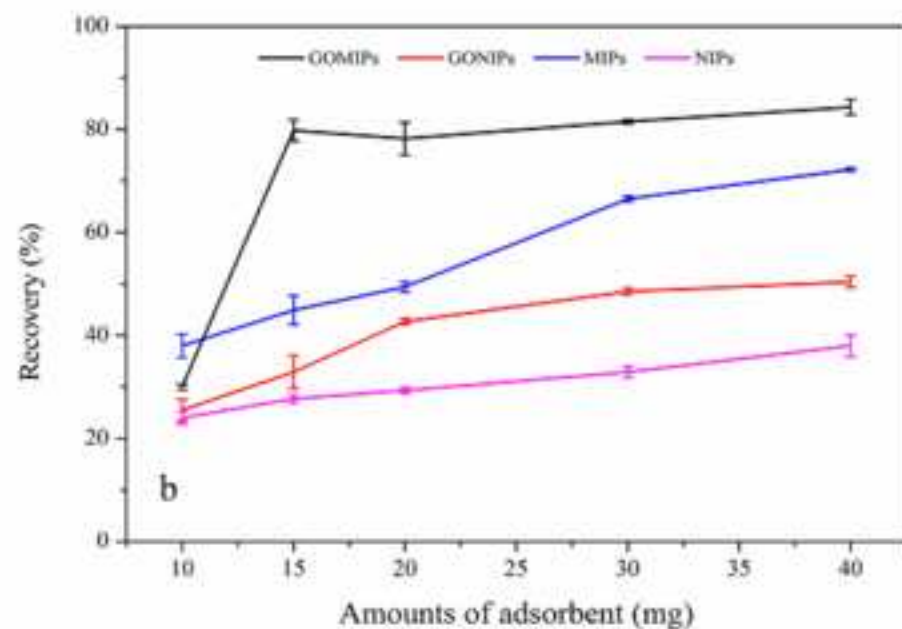
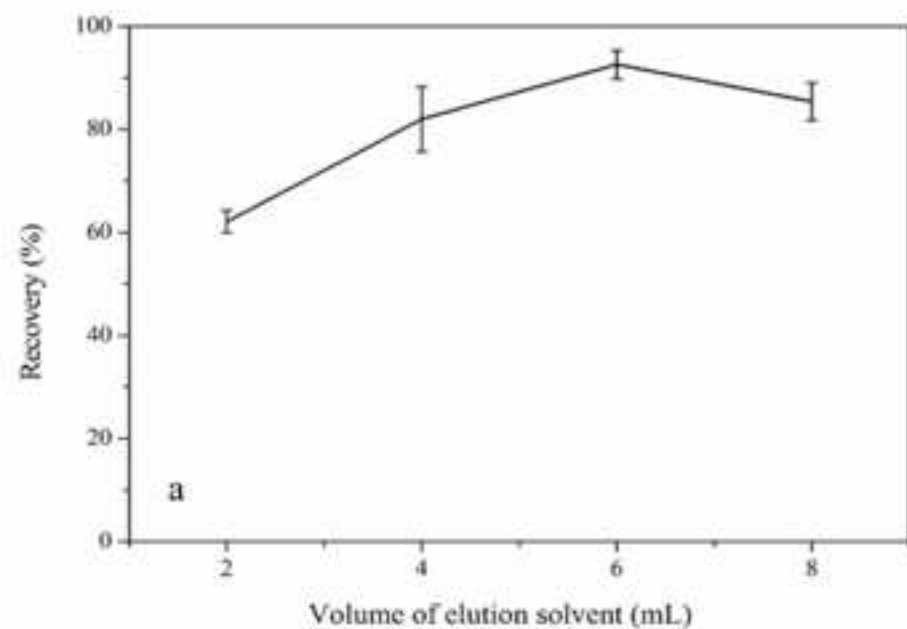


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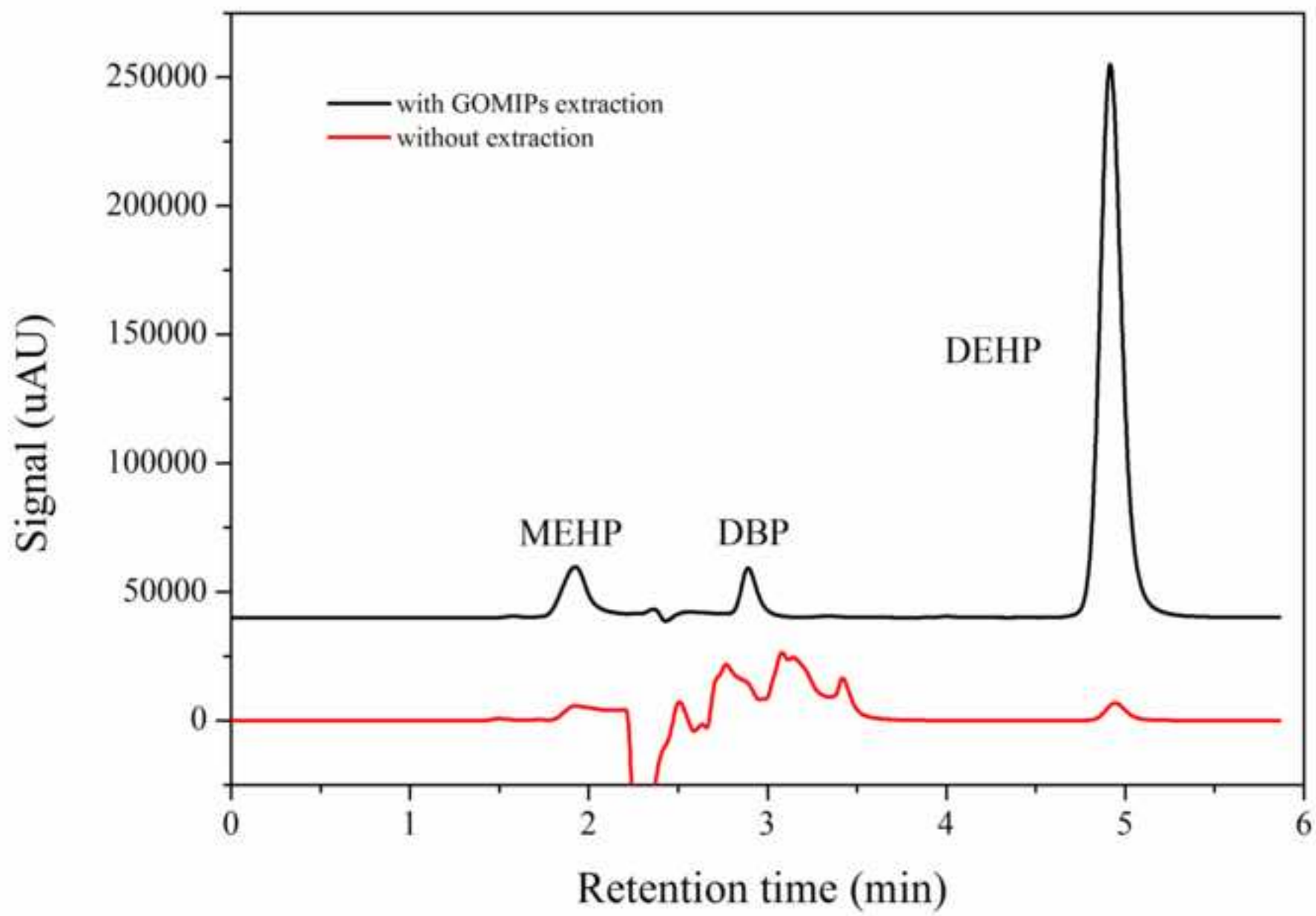


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