Improved microextraction of selected triazines using polymer monoliths modified with carboxylated multi-walled carbon nanotubes

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Abstract

This article reports on the enhancement of the capacity of an acrylate-based monolithic solid sorbent by anchoring carboxylated multi-walled carbon nanotubes (c-MWCNTs) in its pores and on its surface. Monolithic poly(butyl acrylate-*co*-ethyleneglycol dimethacrylate) [poly(BA-*co*-EGDMA)] was synthetized inside a fused silica capillary via free-radical polymerization, and an ethanolic dispersion of c-MWCNTs was passed through the capillary. The resulting poly(BA-*co*-EGDMA-c-MWCNTs) monolith was characterized by scanning electron microscopy to confirm the presence of the c-MWCNTs. The effect of using three different kinds of carbon nanoparticles and the microextraction step were studied using triazine herbicides as model compunds. The use of c-MWCNTs resulted in best performance in terms of extraction enhancement (compared to carboxylated single-walled carbon nanotubes and oxidized single-walled carbon nanohorns). The use of these carbon nanoparticles improved the extraction of triazines in any case when compared to using a bare poly(BA-*co*-EGDMA) monolith. The triazines were then quantified by gas chromatography with mass spectrometric detection. Detection limits ranged from 0.03 to 0.1 $\mu g \cdot L^{-1}$ (except for simazine; 0.6 $\mu g \cdot L^{-1}$), and the precision (relative standard deviation)

varied between 3.0 and 11.4%. The reproducibility between units is <14.3% (expressed as relative standard deviation) which demonstrates the robustness of the method. The method was applied to analyze an unknown sample of orange juice and gave a value of 0.18 $\mu g \cdot L^{-1}$ for prometryn. Finally, the analysis of spiked samples of water and orange juices yielded recoveries ranging from 81 to 113% and 75 to 125%, respectively.

Keywords: *Monolithic solid, carboxylated multi-walled carbon nanotubes, (micro)solid phase extraction, triazines, water, orange juice.*

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Running title: Poly(BA-*co*-EGDMA-c-MWCNTs) monolith as a microextraction unit

Introduction

Sample preparation has been the focus of intense research in order to improve the isolation and preconcentration steps of the analytical procedures. Current trends in this context involve the simplification and miniaturization of separation techniques in both solid and liquid phase formats. The success of these tendencies depends on the efficiency of the extracting medium [1]. Nanostructured materials can be identified as a turning point on the development of new miniaturized approaches [2], as they are more efficient than silica-based or polymeric sorbents due to their high aspect ratio and chemical nature.

Monoliths are a continuous piece of a highly porous material, allowing solvents to flow through their large pores (>50 nm macropores, 2-50 nm mesopores). The monoliths can be classified in three types: polymer monoliths [3], silica-based monoliths [4] and organic-silica hybrid monoliths [5]. In the chromatographic and electrophoretic context, these materials have some advantages over particle packed columns such as: easy synthesis, mechanical stability and direct linkage of the solid with the inner walls of the support. Besides, they feature tolerance to high flows allowing fast separations of target analytes, much more efficient mass transfer, great diversity in shapes and supports and good synthesis reproducibility. Due to their versatility, sorbent monoliths have been used to improve chromatographic [6-8] and electrophoretic [9, 10] separations. Their potential has also been evaluated in the microextraction context [11-14].

Carbon nanoparticles (CNPs) have been extensively used in microextraction techniques thanks to their outstanding sorbent capacity [15].This property is usually ascribed to the high surface to volume ratio of the nanomaterials. However, a relevant disadvantage of

using CNPs as sorbent, and carbon nanotubes in particular, is their aggregation tendency due to their low solubility in common organic solvents and water. This fact hinders their use in conventional cartridge-SPE formats and also limits their packing in microcolumn inserted in flow configurations because of the high back-pressure generated. Therefore, in order to benefit from their sorbent capacity, CNPs have to be efficiency dispersed or immobilized on a surface/support, such as disk [16], controlled-pore glass [17] or porous-hollow fiber [18] to minimize or avoid the presence of aggregates.

Although there are references dealing with the use of nanoparticles to improve the chromatographic or electrophoretic separations [19-23], the combination of nanoparticles and monolithic solids as extraction phase is scarcely reported [24-26]. In the particular case of multi-walled carbon nanotubes (MWCNTs), they exhibit limited solubility in most of the porogen solvents used for the synthesis of the monolith. Aggregates of MWCNTs are observed even at very low concentrations in the polymerization mixture.

This study evaluates the potential of a poly(butyl acrylate-*co*-ethyleneglycol dimethacrylate) monolithic capillary modified with carboxylated multi-walled carbon nanotubes as a microextraction unit for preconcentration of triazine herbicides (prometon, simazine, atrazine, propazine, terbumeton, secbumeton, simetryn, prometryn and terbutryn) from waters and orange juices. The preparation of the hybrid solid has been deeply studied as well as all the variables affecting the microextraction process. Gas chromatography with mass spectrometric detection was used for analytes identification and quantification.

Experimental section

Reagents, materials and samples

All reagents were of analytical grade or better. Triazines (prometon, simazine, atrazine, propazine, terbumeton, secbumeton, simetryn, prometryn and terbutryn) were purchased from Sigma-Aldrich (Madrid, Spain. http://www.sigmaaldrich.com). Standard solutions of each analyte were prepared in methanol (Sigma-Aldrich) at a concentration of 1 $g \cdot L^{-1}$ and stored at 4 ºC. Working standard solutions were prepared on a daily basis by rigorous dilution of the stocks in ultrapure Milli-Q water. Methanol was also used for triazines elution.

Uncoated fused-silica capillaries (320 µm i.d., Sigma Aldrich) were used for the preparation of the monolithic extraction unit. Ferrules 1/16" ID, PEEK tubing 1/16" and internal union zero volume 1/16" to 1/16" (Sigma-Aldrich) were also employed.

The reagents used for the synthesis of the monolithic phase, butyl acrylate (BA), ethyleneglycol dimethacrylate (EGDMA), lauroyl peroxide (LPO), 2-propanol (2-PrOH), formamide, 3-(trimethoxysilyl)propyl methacrylate, ethanol, sodium hydroxide, hydrochloric acid, acetone and acetic acid were purchased from Sigma-Aldrich. Carboxylated multi-walled carbon nanotubes (c-MWCNTs, < 8 nm o.d., 10-30 µm length, > 95 wt% purity, 3.86 wt% functional content) and carboxylated single-walled carbon nanotubes (c-SWCNTs, 1-2 nm o.d., 5-30 µm length, >90 wt% purity, 2.73 wt% functional content) were obtained from Sigma-Aldrich. Single-walled nanohorns were purchased from Carbonium S.r.l (Padua, Italy. http://www.carbonium.it/public/site/index.php). The production of SWNHs was carried out, according to the information reported by the manufacturer, by direct graphite evaporation in Ar flow and the purity obtained was above 90 wt%. SWNHs form stable dahlia-shaped aggregates with an average diameter of 60-80 nm. Individually, the lengths of these SWNHs are in the range of 40 to 50 nm, and the

111 diameter in the cylindrical structure varies between 4-5 nm. Table S1 presents the
112 schematic structure as well as the TEM micrographs obtained for the three carbon
113 nanoparticles used in this article. A 7% (v/v) aqueous solution of ethylenediamine (Sigma-
114 Aldrich) was used to immobilize the c-MWCNTs on the monolith.

115 The dispersion of the c-MWCNTs was made in ethanol. In brief, 0.5 mg of c-MWCNTs
116 were weighed, added to a glass vial and ultrasonic-assisted dispersed in 50 mL of ethanol
117 for 30 min.

118 Tap and river water samples were selected for the determination of the target compounds
119 using the monolithic microextraction unit. Water samples from the Guadalquivir river were
120 collected in amber glass bottles (Sigma-Aldrich) without headspace and stored at 4 °C until
121 analysis. All the aliquots were filtered using a 0.45 μm disposable Nylon filter (Análisis
122 Vínicos, Córdoba, Spain. http://www.analisisvinicos.com) prior to analysis. The water
123 samples were prepared with the analytes at a concentration of 1 $\mu g \cdot L^{-1}$, and then they were
124 left to stand for 24 h prior to the analysis. The oranges and juice samples were purchased
125 from local markets and stored at 4 °C until their use. The squeezed juice was prepared in
126 the laboratory prior to analysis. 1 mL of both orange juices were diluted with Milli-Q water
127 to 5 mL and filtered through a 0.20 μm disposable Nylon filter prior to the analysis.
128
129 *Apparatus*

130 SP-400 Nanobaume^{TM} System (http://www.chromatography.hplcsupply.com) was used to
131 pump the c-MWCNTs dispersion through the monolithic microextraction unit. For analytes
132 preconcentration and elution, a micro-HPLC pump Jasco 1585 (Jasco Analítica Spain,

Madrid, Spain. http://www.jasco-spain.com) was employed. The poly(BA-*co*-EGDMA-c-MWCNTs) microextraction unit was connected to the pump by means of a stainless steel internal union fitted with a PEEK adapter.

Chromatographic analyses were carried out on a gas chromatograph (Varian CP-3800)-mass spectrometer (Varian 1200 MS/MS) working under single quadrupole mode and with an electron multiplier detector. The gas chromatograph was equipped with a fused silica capillary column VF-5 ms (30 m x 0.25 mm i.d.) coated with 5 % phenyl-95 % dimethylpolysiloxane (film thickness 0.25 μm) (Sigma-Aldrich) to separate the nine analytes. The GC oven was programmed as follows: the initial temperature, 40 °C, was maintained for 2 min, raised up to 170 °C at 10 °C·min^{-1} and then immediately ramped at 2 ºC·min^{-1} up to 200 ºC. The final temperature, 260 °C, was reached with a ramp of 10 °C·min^{-1} and maintained for 2 min. The injector temperature was 280 °C and the splitless mode was selected. The injection volume, 2 μL of methanol, was measured with a 5 μL microsyringe (Hamilton Co., Nevada, USA). The carrier gas used was helium (6.0 grade, Air Liquide, Seville, Spain) at a flow rate of 1.0 mL·min^{-1}, and it was regulated by digital pressure controller. The transfer line and ionization source were maintained at 280 ºC and 250 ºC, respectively.

The ionization mode employed in the mass spectrometer was electron impact (EI) with ionization energy of 70 eV. Mass spectra were acquired using the selected ion monitoring mode (SIM), dividing the analysis time in four temporal windows: the first one with m/z 200, 201, 210 and 214 (from 9 to 12.15 min), the second one selecting the m/z 196 (from 12.15 to 13.72 min), the third one with m/z 213 and 241 (from 12.15 to 15.45) and the fourth temporal window selecting m/z 226 (15.45 to 28.25), all of them at 1 scan/s.

Chromatograms were acquired and processed using MS Workstation on an AMD Sempro™ Processor computer (https://www.bruker.com) which also controlled the whole system.

A JEOL JSM 6300 scanning electron microscopy (Isaza, Alcobendas, Spain) was also used to obtain the micrographs of the monolithic solid with and without carbon nanoparticles. An ultrasonic bath model 3510 from Branson (Connecticut, USA) was also used in different steps of the procedure. In the preparation of the poly(BA-*co*-EGDMA) monolithic capillary, an oven (Binder, Madrid, Spain) was also needed to maintain the temperature at 70 ºC during the polymerization step.

Preparation of monolithic solid

The fused-silica capillary was pretreated to favor the covalent binding of the monolithic phase to the capillary inner wall [19]. For this aim, the capillary (1 m in length) was flushed with acetone (5 min) and Milli-Q water (20 min) at a flow rate of 1 $mL \cdot min^{-1}$. NaOH (0.2 M) was sequentially pumped through the capillary using the micro-HPLC pump for 30 min at a flow rate of 50 $\mu L \cdot min^{-1}$. Then, the capillary was rinsed with Milli-Q water (1 $mL \cdot min^{-1}$, 20 min), and then a 0.2 M HCl stream was passed for 30 min (50 $\mu L \cdot min^{-1}$) to protonate the silanol groups previously formed. Next, the acid was removed with Milli-Q water and ethanol (1 $mL \cdot min^{-1}$, 30 min), followed by a 20% (v/v) solution of 3-(trimethoxysilyl)propyl methacrylate in ethanol (adjusted to pH 5 using acetic acid) at a flow rate of 50 $\mu L \cdot min^{-1}$ (45 min). Finally, the capillary was washed with acetone (1 $mL \cdot min^{-1}$, 20 min) and dried under a nitrogen stream. The whole pretreatment of fused-

177 silica capillary was performed at room temperature. Pieces of 3 cm were then used to
178 synthesize the monolith.

179 The polymerization mixture is composed of 20 wt% monomers (25 wt% BA and 75 wt%
180 EGDMA) and 80 wt% porogens (50 wt% 2-PrOH and 50 wt% formamide). As free-radical
181 initiator, 0.3 wt% of LPO (out of the total weight of monomers) was added to the
182 polymerization mixture. This reaction mixture was sonicated for 20 min and purged with
183 nitrogen for 10 min. A piece of the pretreated fused-silica capillary (3 cm in length) was
184 filled with the reactant solution by means of a syringe and then sealed with a septum at both
185 ends. Next, the capillary was introduced into an oven at 70 ºC for 24 h. After completing
186 the polymerization reaction, poly(BA-*co*-EGDMA) monolith was washed with methanol to
187 remove the unreacted monomers and porogenic solvents.

188 *Immobilization of carboxylated multi-walled carbon nanotubes on the monolith*

189 In order to immobilize the carbon nanoparticles on the monolithic solid, primary amine
190 functional groups were generated on its pores and surface [27]. For this purpose, an
191 ethanolic solution of ethylenediamine (7% (v/v)) was pumped through the capillary for 90
192 min at a flow rate of 50 $\mu L \cdot min^{-1}$. Then, the capillary was washed with water to neutral pH
193 for 30 min at a flow rate 0.3 $mL \cdot min^{-1}$.

194 Next, the poly(BA-*co*-EGDMA) monolith was dried under a nitrogen stream and an
195 ethanolic dispersion of 0.01 $g \cdot L^{-1}$ of the c-MWCNTs was pumped at a flow rate of 0.3
196 $mL \cdot min^{-1}$ for 5 min under continuous stirring using the set-up represented in Fig. 1A.
197 Micrographs of the cross-section of monolithic capillary columns (320 µm i.d.) were
198 obtained for the poly(BA-*co*-EGDMA) monolith (Fig. 2A) and the poly(BA-*co*-EGDMA-
199 c-MWCNTs) monolith (Fig. 2B). The micrographs were obtained using scanning electron

microscopy. The section of the capillaries was coated with gold to increase the conductivity. The presence of the nanoparticles was corroborated by comparing both micrographs.

Microextraction procedure

The poly(BA-*co*-EGDMA-c-MWCNTs) monolith was used for the isolation and preconcentration of triazine herbicides from waters and juices. The microextraction is schematically depicted in Fig.1B and it is as follows. First, 3 mL of aqueous standards or samples containing the nine target analytes at concentrations within the linear range were passed through the microextraction unit at a flow rate of 0.3 $mL \cdot min^{-1}$ for 10 min, followed by Milli-Q water (3 min). Prior to elution, the aqueous phase remaining in the column was removed by means of a nitrogen stream (10 min). After that, the retained analytes were eluted with 200 μL of methanol at flow rate of 0.1 $mL \cdot min^{-1}$. An evaporation–redissolution step was included in order to reduce the final volume to 20 μL, thus increasing the method sensitivity. Finally, 2 μL of the organic phase with the extracted analytes were injected into the gas chromatograph/mass spectrometer for their separation and detection. The chromatographic peak areas were used as analytical signals. Between samples, the poly(BA-*co*-EGDMA-c-MWCNTs) monolith was conditioned with methanol (1.3 mL, 0.1 $mL \cdot min^{-1}$), dried with a nitrogen stream for 10 min and finally rinsed out with Milli-Q water. Following this procedure, the monolithic capillary can be reused for 20 times without efficiency losses. Longer uses reduce the extraction efficiencies in ca. 30%.

Results and discussion

Variables affecting to the preparation of the poly(BA-co-EGDMA-c-MWCNTs) monolith

The polymerization was carried out in one-step procedure using a 3 cm pretreated silica capillary, mixing monomers, porogens and an initiator at 70 ºC for 24 h. The temperature and reaction time were fixed according to the indications of Viklund et al. [28]. The initial experimental conditions were: 20 wt% monomers (50 wt% BA and 50 wt% EGDMA) and 80 wt% porogens (50 wt% 2-PrOH and 50 wt% formamide). A solution of LPO (0.3 wt% out of the total weight of the monomers) was used as an initiator of the reaction. The poly(BA-*co*-EGDMA) monolithic capillary was evaluated using the determination of triazine herbicides as model compounds. For this purpose, 4.8 mL of a working standard solution containing the nine analytes at a concentration of 1 $\mu g \cdot mL^{-1}$ was preconcentrated, using methanol as eluent. Three replicate analyses for each monolithic column to evaluate also the repeatability of the different extraction units.

The first variable studied was the monomers/porogens ratio within the following proportions: 20/80% (w/w), 40/60% (w/w), 60/40% (w/w) and 80/20% (w/w). The high percentage of monomers resulted in the smaller pores and therefore it led to an increased flow resistance. Thus a 20/80% (w/w) ratio was selected for further experiments.

Next, the BA/EGDMA ratio was studied within the following percentages: 75/25% (w/w), 60/40% (w/w), 40/60% (w/w) and 25/75% (w/w). When the ratio was 75/25% (w/w) the resulting pores were too small and the high backpressure generated hindered the flow of solvents through the capillary. However, although monoliths prepared with the other ratios exhibited a favourable permeability to flow the solvents, the extraction efficiency of the bare monolithic solid towards the triazines was very low as it shown in the Fig. 3A.

Therefore, the inclusion of carbon nanoparticles in the microextraction unit was deeply studied, including both the type and their amount. For this purpose, commercially available carboxylated carbon nanotubes (c-SWCNTs, c-MWCNTs) and laboratory-oxidized carbon nanohorns (o-SWNHs) were selected taking into consideration their better dispersibility in organic media [29].

Dispersions of each carbon nanoparticle were prepared at a concentration of 1 $mg \cdot L^{-1}$. A volume of 900 µL was flushed through the monolithic capillary column at a flow rate of 0.3 $mL \cdot min^{-1}$ in order to retain the nanoparticles on the microporous material.

When the proportion was 60/40% (w/w), the monolithic solid was collapsed under pressure during the procedure of the immobilization of the carbon nanoparticles. While for the ratios 40/60% (w/w) and 25/75% (w/w) it was possible to anchor the NPs on the monolithic surfaces, obtaining a greater increase when the percentage of BA decreased as regards that of the cross-linker. We attribute this to the highest adsorption on the larges pores when dispersions of the NPs were passed through the monolithic solid. For this reason, the selected ratio was 25/75% (w/w) of BA/EGDMA. Fig. 3A exemplified this behavior for c-MWCNTs and terbutryn as model NPs and compound, respectively.

Besides, as it is shown in Fig. 3B, the presence of the c-MWCNTs, c-SWCNTs, and o-SWNHs increased the retention of the triazines on the microextraction unit in comparison with the bare monolithic solid. The best results were obtained using c-MWCNTs as modifiers of the bare poly(BA-*co*-EGDMA) monolith. They exhibit the highest sorbent capacity owing to their larger size and number of sheets in comparison with the other carbon nanoparticles (c-SWCNTs and o-SWNHs). Also, the precision of the results (n=3)

267 expressed as standard deviation and reflected in the Fig. 3B as error bars, was better for
268 almost all the analytes. The better performance of o-SWNHs as regards c-SWCNTs can be
269 explained taking into consideration their ability to form stable large aggregates (60-80 nm)
270 which results in higher extraction capacity. From these results, c-MWCNTs were selected.

271 The influence of the amount of c-MWCNTs immobilized on the monolithic solid surface
272 was tested using ethanolic dispersions of the nanoparticles at concentrations of 0.001, 0.01
273 and 0.05 $g \cdot L^{-1}$. Aliquots of 900 μL were passed through the column at a flow rate of 0.3
274 $mL \cdot min^{-1}$. The highest concentration generated a backpressure in the system, probably due
275 to the aggregation of the nanoparticles which resulted in pores blockage. The results
276 obtained for the other two concentrations are shown in Fig. 4. As expected, the higher
277 amount of nanoparticles resulted in higher efficiency and therefore, a concentration of 0.01
278 $g \cdot L^{-1}$ of the c-MWCNTs in ethanol was selected. This dispersion was flushed in an interval
279 from 3 to 25 min at a flow rate of 0.3 $mL \cdot min^{-1}$ (0.9-7.5 mL). The graphic comparison of
280 the results given in Fig. 5, shows that 1.5 mL (5 min) was the best option since higher
281 values resulted in a decrease of the extraction, probably due to bundle formation on the
282 pore and surface of the monolith.

283 *Evaluation of the variables affecting to the microextraction process*

284 The variables directly related with the extraction step were studied using aqueous standards
285 containing the selected triazines at a concentration of 1 $\mu g \cdot mL^{-1}$.

286 The following parameters were optimized: (a) Sample flow rate; (b) sample volume and;
287 (c) elution volume. Respective data and Figures are given in the *Electronic Supporting*
288 *Material*. The following experimental conditions were found to give the best results: (a) a

289 sample flow rate of 0.3 mL·min^{-1}, (b) a sample volume of 3 mL and, (c) an elution volume
290 of 0.2 mL.
291
292 *Analytical figures of merit*

293 Once optimized, the monolithic extraction unit was characterized in terms of sensitivity,
294 linearity, and precision. The corresponding calibration graphs were constructed by using
295 aqueous standards containing the nine analytes at concentrations in the range 0.1-1000
296 μg·L^{-1}. Standards were processed in duplicate using the optimized method, and 2 μL of the
297 organic extract was injected into the GC/MS for analysis. The corresponding equations
298 were obtained by plotting the peak areas of the characteristic m/z fragment ions against the
299 concentration for each target analyte.

300 The limits of detection (LODs) were calculated as the concentrations giving a signal-to-
301 noise ratio (S/N) of 3. As it can be seen in Table 1, they were in the range 0.03-0.6 μg·L^{-1}.
302 The limits of quantification (LOQs) were calculated as the concentration providing
303 chromatographic peak areas ten times higher than the background noise and varied between
304 0.1 and 0.4 μg·L^{-1} for all analytes (simazine excepted, 1 μg·L^{-1}). The precision of the
305 method (intra and inter-day conditions), expressed as relative standard deviation (RSD) was
306 calculated from five individual standards prepared at a concentration of 1 μg·mL^{-1} and it
307 was lower than 11.4 % for all the analytes. Fig. 6 shows a chromatograph with the different
308 m/z fragment ions obtained after the analysis of a standard with the nine triazines (1 μg·L^{-1})
309 following the microextraction procedure. In addition, the reproducibility between extraction
310 units was evaluated. For this purpose, five poly(BA-*co*-EGDMA-c-MWCNTs) monolithic
311 microextraction units were prepared and a standard solution of the nine triazines (1 μg·mL^{-}

312 [1]) was analyzed. The results, expressed as RSD, are also given in Table 1 and they were
313 acceptable in all cases.

314 *Analysis of water and orange juice samples*

315 Prior to the analysis of real samples, the identification of potential interferences from the
316 matrix on the quantification of the analytes is a relevant issue, especially when analyzing
317 unknown samples. Therefore, the accuracy of the proposed method was evaluated through a
318 recovery study. As neither certified reference materials (CRMs) nor quality control (QC)
319 samples were available for this specific analytical problem, different blank water and juice
320 samples were fortified with the nine target analytes (prometon, simazine, atrazine,
321 propazine, terbumeton, secbumeton, simetryn, prometryn and terbutryn) at a concentration
322 of 1 $\mu g \cdot L^{-1}$, and they were left to stand for 24 h prior to analysis. Then, the fortified
323 samples were analyzed using the extraction method, and the concentration for each triazine
324 was calculated by interpolating the peak area obtained in the corresponding calibration
325 graph. The recovery values were calculated dividing the concentration found by the
326 concentration added, and expressed in percentage. Each sample was analyzed by triplicate;
327 the results obtained are listed in Table 2. As it can be seen, they were acceptable in all
328 instances and they are ranged from 75 to 125 %.

329 The extraction method was applied to the determination of the target triazines in two water
330 samples (river and tap waters) and two types of orange juice samples (squeezed and
331 commercial). Aliquots of 3 mL of water and juice samples were passed through the
332 poly(BA-*co*-EGDMA-c-MWCNTs) monolith and processed under the optimum conditions.
333 As a result, none of the analytes were found in waters and squeezed orange juices.

However, as it can be seen in Table 2 a low content of prometryn was detected in commercial orange juices. Herbicide residues may be present in the juice made from concentrate due to the great consumption on agrochemical for the protection of crops in agriculture and they can be transferred from orange peels to juices.

Conclusions

The use of monolithic solids in the microextraction context has been recently reviewed [14]. Table 3 summarizes the comparison of the present method with other monolithic packings for the extraction and isolation of triazine herbicides from different samples. Most of these extraction units are based on methacrylate monolithic columns, and LODs ranged from 0.18 to 95.0 $\mu g \cdot L^{-1}$. The extraction of efficiency of these porous materials has been enhanced by the incorporation of nanoparticles, and especifically carbonaceous ones, in the monolith. In this regard, carboxylated single-walled carbon nanotubes, have been used to improve the sorption capacity of poly(MAA-*co*-EDMA) monoliths. In this approach, the nanoparticles are added to the polymerization mixture in such a way that they are finally embedded into the solid. This procedure presents as an advantage the higher stability of the hybrid sorbent as the nanoparticles are included in the polymer. However, only those nanoparticles remaining on the pores are available for interaction. In addition, nanoparticles must be soluble in the polymerization mixture (usually the porogenic solvent) to minimize the aggregation of the material. Moreover, avoiding the sedimentation of the nanomaterial during polymerization also has to be taken into account in order to obtain a homogeneous distribution.

The hybrid monolithic sorbent presented in this article [poly(BA-*co*-EGDMA-c-MWCNTs)] overcomes these two shortcomings as the carbon nanoparticles are immobilized on the monolithic sorbent previously formed. Therefore, LODs reached with the present method were comparable with the poly(MAA-*co*-EDMA-SWNT) monolithic approach. Also aggregation is reduced as they are prepared in an organic medium (ethanol) where they are soluble. Besides we have evaluated the performance of three carbon nanoparticles (c-SWCNTs, o-SWNHs and c-MWCNTs) as component of the monolithic sorbent, showing the multi-walled structures the most favourable features in terms of extraction efficiency.

This study, demonstrates that the immobilization of c-MWNTs onto the pore surface of poly(BA-*co*-EGDMA) monoliths, significantly increases the extraction efficiency for the target triazines. In addition, the microextraction method shows favorable analytical features for the analytical problem selected.

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Figures

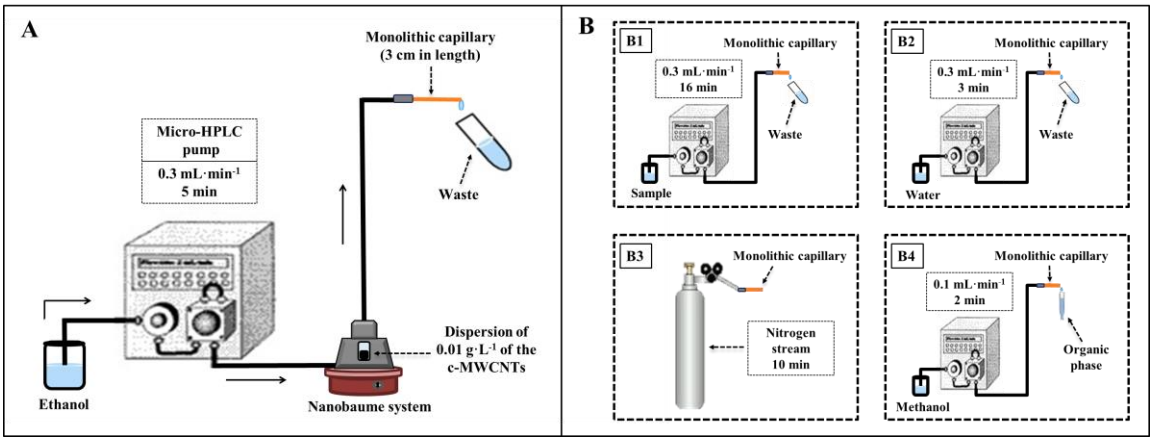

Fig. 1 (A) Instrumental set-up used for the immobilization of c-MWCNTs on the monolithic capillary. (B) Schematic representation of the microextraction procedure for the extraction of the triazine herbicides from waters and orange juice; (B1) sampling, (B2) washing, (B3) drying, and (B4) desorption.

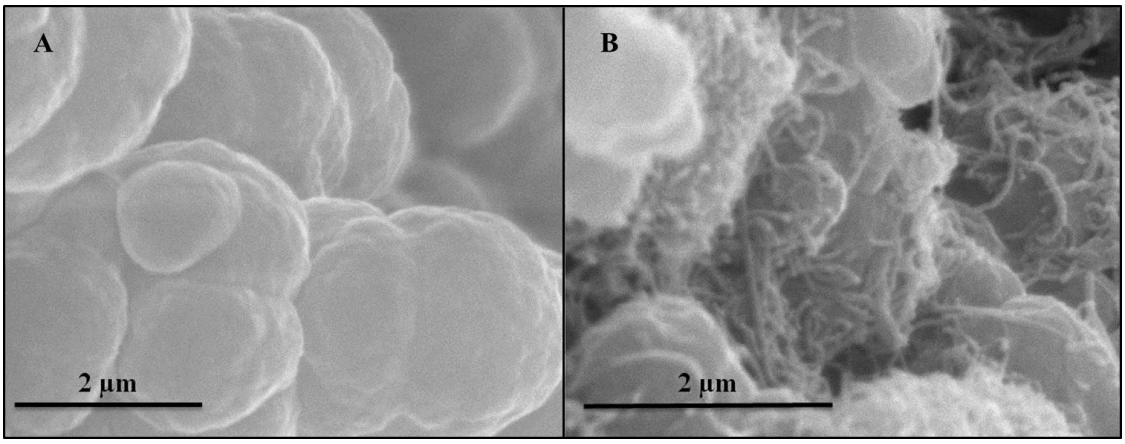

Fig. 2 (A, x15000) Scanning electron microscopy of poly(BA-*co*-EGDMA) and (B, x20000) poly(BA-*co*-EGDMA-c-MWCNTs) monolith.

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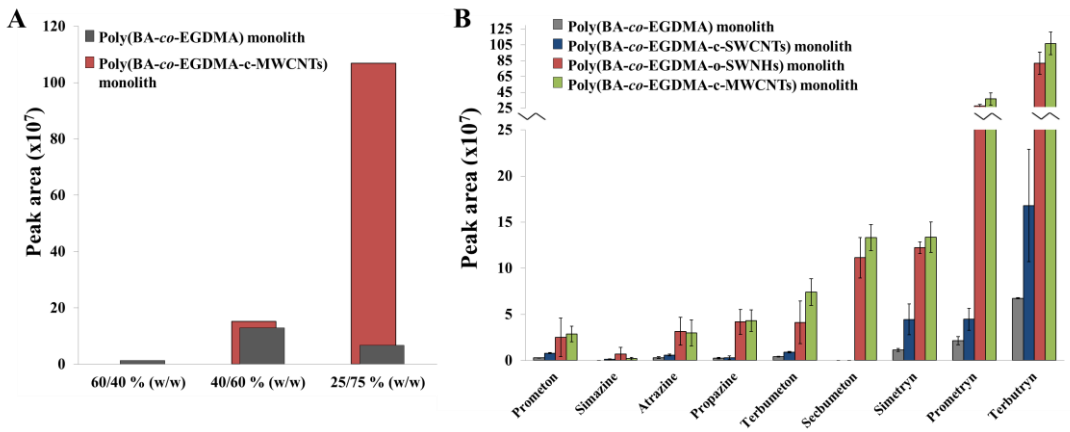

501 Fig. 3 (A) The relative extraction efficiency for terbutryn as model compound, using the
502 bare poly(BA-*co*-EGDMA) monolith and the poly(BA-*co*-EGDMA-c-MWCNTs) monolith
503 as microextraction unit. (B) Comparison of the analytical performance of poly(BA-*co*-
504 EGDMA) monolith without nanoparticles and the monolith with c-MWCNTs, o-SWNHs
505 and c-MWCNTs immobilized on its pores for 20/80 % (w/w) and 25/75% (w/w)
506 proportions of monomers/porogens and monomers/cross-linker ratios, respectively.

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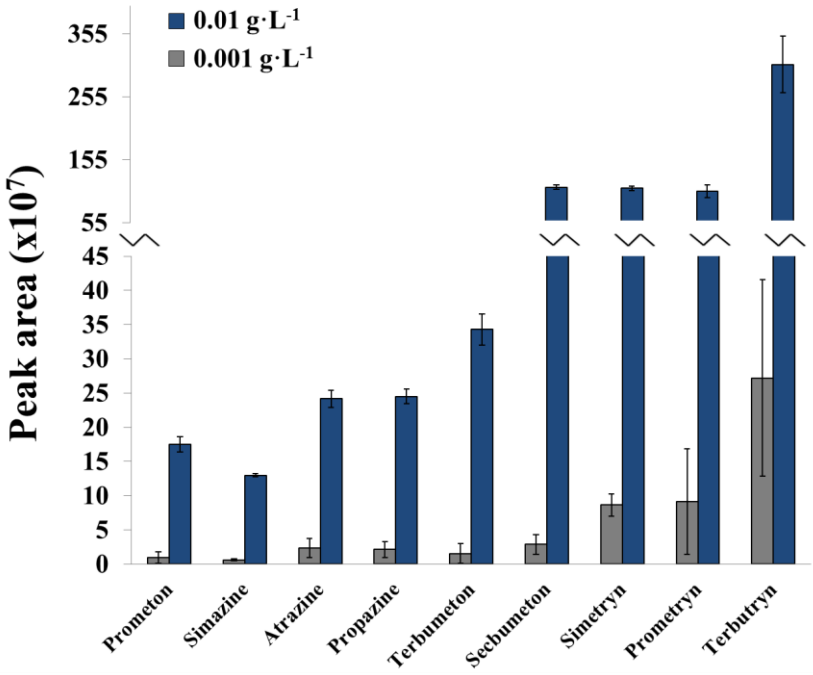

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510 Fig. 4 Influence of the concentration of the c-MWCNTs dispersion on the triazines

511 retention.

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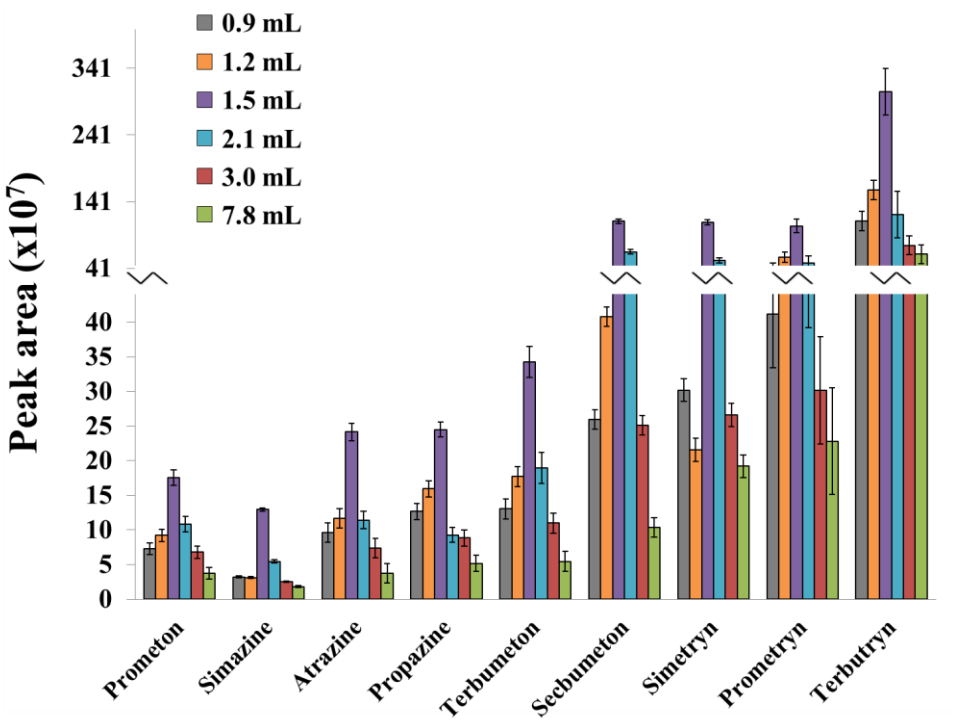
513 

514 Fig. 5 Effect of the volume of the 0.01 g·L^{-1} c-MWCNTs dispersion passed through the

515 poly(BA-*co*-EGDMA) monolith at a flow rate of 0.3 mL·min^{-1}.

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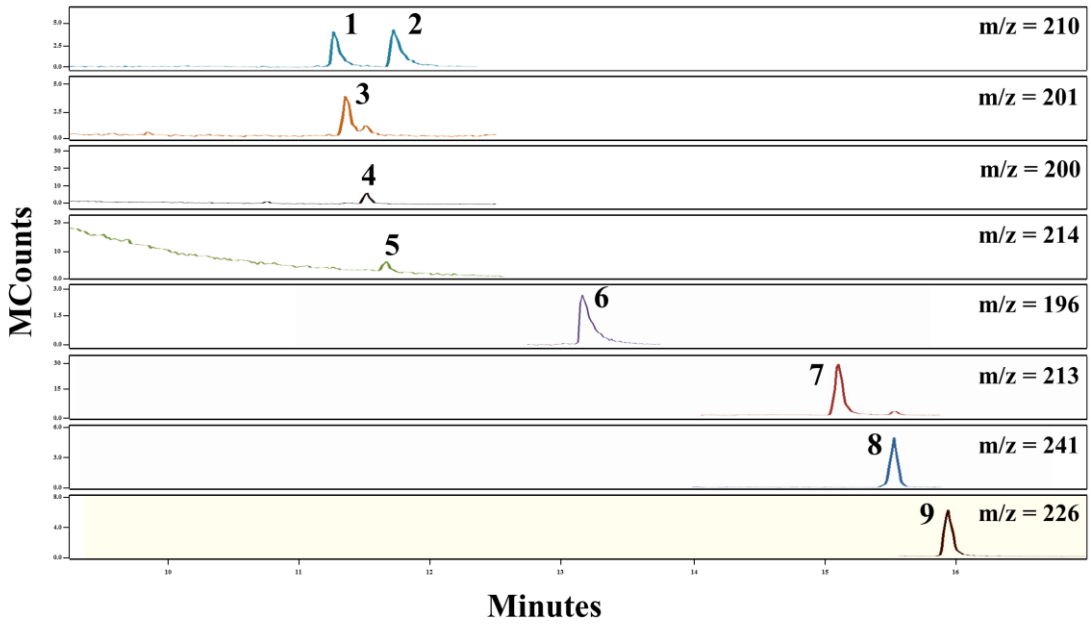

Fig. 6 Chromatogram obtained after monolith microextraction of a standard with the target analytes at a concentration of 1 $\mu g \cdot L^{-1}$. Peaks: (1) Prometon, (2) Terbumeton, (3) Simazine, (4) Atrazine, (5) Propazine, (6) Secbumeton, (7) Simetryn, (8) Prometryn, (9) Terbutryn.

529 Table 1. Analytical figures of merit of poly(BA-*co*-EGDMA-c-MWCNTs) monolithic
530 microextraction unit to the determination of the target triazines.

Analyte	**m/z**	**LOD (µg·L^{-1})**	**LOQ (µg·L^{-1})**	**Precision**		
				Intra-day RSD (%, n=5)	Inter-day RSD (%, n=5)	Inter-units RSD (%, n=5)
Prometon	210	0.10	0.4	9.4	11.4	6.8
Simazine	201	0.60	1	4.2	7.1	7.9
Atrazine	200	0.10	0.4	11.4	9.9	3.9
Propazine	214	0.10	0.4	6.0	5.3	8.2
Terbumeton	210	0.10	0.4	7.2	10.3	8.7
Secbumeton	196	0.03	0.1	3.0	7.4	10.0
Simetryn	213	0.03	0.1	4.1	8.6	9.0
Prometryn	241	0.03	0.1	5.9	8.1	13.8
Terbutryn	226	0.03	0.1	10.5	11.3	14.3

531 *LOD limit of detection, LOQ limit of quantification, RSD relative standard deviation*

532

533

Table 2. Recovery study for prometon, simazine, atrazine, propazine, terbumeton, secbumeton, simetryn, prometryn and terbutryn spiked to water samples and orange juices analyzed following c-MWCNTs monolithic extraction unit.

Analytes	Spiked ($\mu g \cdot L^{-1}$)	Tap water		River water		Commercial orange juice		Squeezed orange juice	
		Detected ($\mu g \cdot L^{-1}$)	Recoveries (%, n=3)	Detected ($\mu g \cdot L^{-1}$)	Recoveries (%, n=3)	Detected ($\mu g \cdot L^{-1}$)	Recoveries (%, n=3)	Detected ($\mu g \cdot L^{-1}$)	Recoveries (%, n=3)
Prometon	0	ND		ND		ND		ND	
	1	1.07	107 ± 11	0.85	85 ± 8	1.06	106 ± 10	0.84	84 ± 11
Simazine	0	ND		ND		ND		ND	
	1	1.11	111 ± 9	0.95	95 ± 7	0.75	75 ± 9	1.25	125 ± 10
Atrazine	0	ND		ND		ND		ND	
	1	0.80	80 ± 7	0.81	81 ± 11	1.03	103 ± 10	1.25	125 ± 11
Propazine	0	ND		ND		ND		ND	
	1	0.87	97 ± 8	0.96	96 ± 3	0.75	75 ± 10	0.94	94 ± 11
Terbumeton	0	ND		ND		ND		ND	
	1	1.13	113 ± 15	0.85	85 ± 9	0.91	91 ± 10	0.76	76 ± 10
Secbumeton	0	ND		ND		ND		ND	
	1	0.89	89 ± 10	0.87	87 ± 16	1.49	121 ± 8	0.76	76 ± 8
Simetryn	0	ND		ND		ND		ND	
	1	0.99	99 ± 5	0.98	98 ± 8	0.98	98 ± 6	1.21	121 ± 8
Prometryn	0	ND		ND		0.18		ND	
	1	0.81	81 ± 14	0.98	98 ± 14	1.18	100 ± 13	0.98	98 ± 12
Terbutryn	0	ND		ND		ND		ND	
	1	0.93	93 ± 5	1.01	101 ± 8	0.99	99 ± 13	1.15	115 ± 14

ND: not detected

Table 3. Comparison of the performance of the poly(BA-*co*-EGDMA-c-MWCNTs) monolith versus other monolithic sorbent described in the literature for the determination of triazine herbicides.

Monolithic sorbent	Selected triazines	Packing	Sample	Limit of detection (LODs)	Precision (RSD, %)	Recovery (%)	Reference
Poly(MAA-*co*-EDMA-SWCNT) monolith	Simazine, atrazine, prometon, ametryn, propazine, and prometryne	Monolithic capillary column	Lake water and orange juice	0.02-0.14 $\mu g \cdot L^{-1}$	3.1-10.9	85.0-106.0	[26]

Poly(MAA-*co*-EGDMA) monolith	Cyanazine, simazine, atrazine, prometon, ametryn, and prometryn	Monolithic capillary column	Cereals	1.1-2.8 $\mu g \cdot kg^{-1}$	1.4-5.5	73.4-107.2	[30]
Poly(MAA-*co*-EDMA) monolith	Atrazine, 2-amino-4-methoxy-6-methyl-1,3,5-triazine, terbutylazine, and ametryn	Monolithic MIP-SPME fiber	Lake water	0.18-0.35 $\mu g \cdot L^{-1}$	5.3-12.0	72.8-113.2	[31]
Poly(MAA-*co*-EGDMA) monolith	Atrazine, simazine, propazine, cyanazine, ametryn, terbutryn, and prometryn	Monolithic MIP-SPME fiber	Tap water, onion and rice	20.0-88.0 $\mu g \cdot L^{-1}$	6.5-11.6	87.8-99.6	[32]
Poly(MAA-*co*-EGDMA) monolith	Atrazine, simazine, cyanazine, ametryn, prometryn and terbutryn	Monolithic MIP-SPME fiber	Grape juice, tap water and groundwater.	2.6-42.0 $\mu g \cdot L^{-1}$	4.4-12.1	82.1-93.5	[33]
Poly(MAA-*co*-EDMA) monolith	Ametryn, prometryn, terbutryn, atrazine, simazine, propazine, and cyanazine	Monolithic MIP-SPME fiber	Tap water, rice, maize and onion	14.0-95.0 $\mu g \cdot L^{-1}$	5.2-11.8	85.1-99.8	[34]
Poly(BA-*co*-EGDMA-c-MWCNTs) monolith	Prometon, terbumeton, simazine, atrazine, propazine, secbumeton, simetryn, prometryn, terbutryn	Monolithic capillary column	Tap and river water, and orange juice	0.03-0.1 $\mu g \cdot L^{-1}$	3.0-11.4	75.0-125.0	Present work

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