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Powdered activated carbons as effective phases for bar adsorptive micro-extraction (BAμE) to monitor levels of triazinic herbicides in environmental water matrices

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ABSTRACT

Bar adsorptive micro-extraction using three powdered activated carbons (ACs) as adsorbent phases followed by liquid desorption and high performance liquid chromatography with diode array detection (BAμE(ACs)-LD/HPLC-DAD), was developed to monitor triazinic herbicides (atrazine, simazine and terbutylazine) in environmental water matrices. ACs used present apparent surface areas around 1000 $m^2\ g^{-1}$ with an important mesoporous volume and distinct surface chemistry characteristics (pH_{PZC} ranging from 6.5 to 10.4). The textural and surface chemistry properties of the ACs adsorbent phases were correlated with the analytical data for a better understanding of the overall enrichment process. Assays performed on 10 mL water samples spiked at the 10.0 $\mu g\ L^{-1}$ levels under optimized experimental conditions yielded recoveries around 100% for the three herbicides under study. The analytical performance showed good precision (RSD < 15.0%), convenient detection limits (≈0.1 $\mu g\ L^{-1}$) and suitable linearity (1.0–12.0 $\mu g\ L^{-1}$) with good correlation coefficients ($r^2 > 0.9914$). By using the standard addition method, the application of the present method on real water matrices, such as surface water and wastewater, allowed very good performances at the trace level. The proposed methodology proved to be a suitable sorptive extraction alternative for the analysis of priority pollutants with polar characteristics, showing to be easy to implement, reliable, sensitive and requiring a low sample volume to monitor triazinic compounds in water matrices.

1. Introduction

Triazines have been used as selective herbicides for the control of weeds in many agricultural crops and their activity is based upon their ability to inhibit photosynthesis in plants. Due to their high toxicity, endocrine disrupting effect, persistence, water solubility, low partition coefficients ($\log K_{O/W}$) and widespread application, it is necessary to develop cheap, simple, rapid and sensitive methods for monitoring trace levels of their residues in the environment [1,2].

The state of the art analytical methodologies for the determination of triazinic herbicides involve several sample enrichment procedures prior to chromatographic or hyphenated techniques. In recent years, modern sample preparation approaches for trace analysis of triazines have been proposed, in which sorptive extraction methodologies have played a very important role to enhance selectivity and sensitivity [3–9]. In the last years, stir bar sorptive extraction (SBSE) has been successfully employed as static technique to monitor trace levels of priority pollutants due to the great sorptive capacity, generally using 24–126 μL of polydimethylsiloxane (PDMS), a polymeric phase that makes this enrichment technique unique for compounds with non-polar characteristics [10]. However, when polar compounds ($\log K_{O/W} < 3$) or solutes with particular chemical characteristics are envisaged (*e.g.*, triazines), SBSE(PDMS) presents enrichment limitations [11] and therefore, other strategies must be implemented such as a derivatization step to decrease polarity [12]. Another possibility could be the use of novel polymeric phases with textural and chemical properties more convenient for the enrichment purposes of the more polar solutes, like triazines or their metabolites, such as polyurethane (PU) foams, as it was recently proposed by our group [13–15], or even the use of other specific materials [16].

Lately, our group have been involved in the development of novel analytical approaches, adsorptive microextraction (AμE) techniques, especially indicated to monitor trace levels of polar compounds in aqueous media and therefore, overcoming the limitations presented by the SBSE(PDMS) methodology [17]. This novel analytical technology uses powdered activated carbons (ACs) and other materials as adsorbent phases, presenting surface characteristics probably more indicated to solutes such as triazine herbicides.

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ACs are amorphous solids, composed essentially by carbon and present high adsorption capacities. These solids can be prepared from carbon-rich raw materials and, depending on the preparation methodology used and the precursor, it is possible to tailor the pore size distribution, *i.e.*, texture and surface chemistry, in order to meet the requirements for a given application [18,19]. The acid/base nature of the ACs surface depends on the content of heteroatoms as, for instance, oxygen, hydrogen and nitrogen, corresponding usually to a small percentage of the total AC composition. These heteroatoms form surface species that strongly influence the adsorptive properties of these materials, which are extensively used as adsorbent both in gas and liquid phase for remediation purposes. To our knowledge only in very few studies a correlation in between the analytical data and the ACs characteristics is made [20,21].

The aim of this work was to characterize and apply three commercial ACs as sorbent phases for bar adsorptive μ-extraction followed by liquid desorption and high performance liquid chromatography with diode array detection (BAμE(ACs)-LD/HPLC-DAD) to monitor trace levels of triazine herbicides, using atrazine, simazine and terbutylazine as model compounds in water matrices. The performance of the ACs was correlated with the textural and surface chemistry properties. The comparison of the data obtained by the present approach with other sorptive extraction techniques is also addressed.

2. Materials and methods

2.1. Chemicals and samples

All reagents and solvents were of analytical grade and used with no further purification. HPLC-grade methanol (MeOH, 99.8%) and acetonitrile (ACN, 99.8%) were purchased from Merck (Germany). Sodium chloride (NaCl, 99.9%) and sodium hydroxide (NaOH, 98.0%) were obtained from AnalaR BDH Chemicals (UK). Atrazine (ATZ, 99.2%), simazine (SIM, 99.9%), and tertbutylazine (TBZ, 99.5%) were purchased from Supelco (USA). Hydrochloric acid (37.0%) and sodium carbonate (99.5%) were purchased from Riedel-de Haën (Germany). The commercial ACs were supplied by Salmon & Cia. (The Netherlands) – N2 and NS – and Riedel-de Haën (Germany) – R. Individual stock methanolic solutions of each herbicide (500 mg L^{-1}) were used to prepare the working and calibrations standard solutions. Ultra-pure water was obtained from Milli-Q water purification systems (USA). Surface water samples were collected in the metropolitan area of Lisbon (Portugal). Wastewater samples were obtained from the urban wastewater treatment plant located in east side of Lisbon (Beirolas, Portugal) and were collected before the primary decantation. All samples were previously filtered (Whatman No. 1 filters) and stored refrigerated at 4 °C until their analysis.

2.2. Experimental set-up

2.2.1. ACs characterization

The ash content of the ACs was estimated by the mass residue left after the combustion of the samples in air, according to the procedure described by Mestre et al. [21]. Briefly, ca. 1 g of dried AC was heated in a horizontal furnace equipped with a Eurotherm 2416 controller, from ambient to 500 °C in 10 min, kept for 30 min and then raised to 815 °C in 15 min and kept for 2 h 30 min. The ash content (mean of three assays) is the amount of sample that remains after this treatment, expressed by dried mass of AC. Mass weights were determined in a Mettler AE 240 analytical balance. The characterization on the surface chemistry was made measuring the pH at the point of zero charge (pH_{PZC}) of the sample by reverse mass titration, following the method proposed by Noh and Schwarz [22]. Slurries of (in %) 1, 2, 6 and 10 were prepared by mixing the AC with ultra-pure water in a glass bottle, bubbled and sealed under N_2 (to eliminate CO_2). The pH of the slurry was measured after shaking for, at least, 24 h at room temperature. The pH_{PZC} value corresponds to the plateau of the curve of equilibrium pH *versus* solid weight fraction. The pH was measured in a Metrohm 744 pH meter (Switzerland). The textural characterization was made by the N_2 adsorption isotherms at −196 °C, determined in a conventional volumetric apparatus equipped with an MKS-Baratron (310BHS-1000) pressure transducer (0–133 kPa). Before the isotherm acquisition the sample (≈50 mg) was outgassed for 2 h at 300 °C, under vacuum better than 10^{-2} Pa.

2.2.2. Recovery assays and method validation

The bar μ-extraction devices were prepared in the laboratory by coating a polyethylene bar with an adhesive film (15 mm length and 0.5 mm thickness) which was recovered with the powdered AC (approximately 1.5 mg), as previously reported [17,19]. The μ-extraction bars were cleaned with ultra-pure water before use. In a typical assay, 10 mL of ultra-pure water spiked with 200 μL of a standard working mixture at a desired concentration and a μ-extraction bar device previously coated with powdered ACs were introduced into glass flasks. The assays were performed in a multipoint agitation plate (Variomag, Germany) at room temperature.

For the optimization of BAμE(ACs) efficiency, parameters such as agitation speed (750 and 1000 rpm), extraction time (1, 2, 3, 4 and 16 h), organic modifier (MeOH; 5, 10 and 15%, v/v) and ionic strength (NaCl; 5, 10 and 15%, w/v) were systematically studied in triplicate. For back-extraction, the μ-extraction bar device was removed from the samples with clean tweezes and placed into a 2 mL vial containing 1.5 mL of the stripping solvent, ensuring their total immersion prior to ultrasonic treatment at room temperature. To evaluate the best back-extraction conditions, several assays using MeOH, ACN and a mixture of both (1:1), with different desorption times (30, 45 and 60 min) were performed in triplicate. After back-extraction, the AC bar was removed by clean tweezes and the stripping solvent was evaporated until dryness under a gentle stream of purified nitrogen (>99.5%), followed by reconstitution with 200 μL of mobile phase. The vial was then sealed and placed on the auto-sampler for HPLC-DAD analysis. For the method validation experiments, 10 mL of ultra-pure water were spiked with 200 μL of the working standard mixture at desired concentrations, and the extraction and back-extraction experiments were performed as described above, under optimized conditions. For real sample assays, 10 mL of water sample were used, in which the standard addition methodology (SAM) was applied, following by the same procedure employed for the validation experiments. Blank assays were also performed using the procedure above described without spiking.

2.3. HPLC-DAD settings

Analyses were carried out on an Agilent 1100 Series LC system (Agilent Technologies, Germany), constituted by the following modules: vacuum degasser (G1322A), quaternary pump (G1311A), autosampler (G1313A), thermostated column compartment (G1316A) and the diode array detector (G1315B). The data acquisition and instrumental control were performed by the software LC3D ChemStation (version Rev.A. 10.02[1757], Agilent Technologies). Analyses were performed on a Tracer excel 120 ODS-A column, 150 mm × 4.0 mm, 5 μm particle size (Teknokroma, Spain). The mobile phase consists on a mixture of MeOH and water with ratio of 58/42% (25 °C) and a flow of 0.8 mL min^{-1}. The injection volume was 20 μL with a draw speed of 200 μL min^{-1}. The detector was set at 226 nm. For identification purposes,

Table 1
Nanotextural and chemical characteristics of the commercial ACs.

ACs	A_{BET} ($m^2\ g^{-1}$)	V_{total}[a] ($cm^3\ g^{-1}$)	V_{meso}[b] ($cm^3\ g^{-1}$)	α_s Method			Ash %	pH_{PZC}
				$V_{\alpha\ total}$ ($cm^3\ g^{-1}$)	$V_{\alpha\ ultra}$ ($cm^3\ g^{-1}$)	$V_{\alpha\ super}$ ($cm^3\ g^{-1}$)		
R	937	0.65	0.36	0.29	0.10	0.19	0.7	6.5
N2	896	0.60	0.29	0.31	0.04	0.27	12.0	10.6
NS	1065	0.70	0.30	0.40	0.02	0.38	13.0	8.4

[a] Volume adsorbed at $p/p^0 = 0.95$.
[b] Difference between V_{total} and $V_{\alpha\ total}$.

standard addition was used by spiking the samples with both pure standards, as well as by comparing the retention parameters and peak purity with the UV/vis spectral reference data. For recovery calculations, peak areas obtained from each assay were compared with the peak areas of standard controls used for spiking. For quantification purposes on real matrices, calibration plots using the standard addition methodology were also performed.

3. Results and discussion

3.1. Characterization of the ACs

The nitrogen adsorption isotherms allow characterize the porosity of the activated carbons. According to the IUPAC classification [23] the porosity is divided in micropores (width < 2 nm), mesopores (2 < width < 50 nm) and macropores (width > 50 nm). Micropores can also be subdivided in ultramicropores (width < 0.7 nm) and supermicropores (0.7 < width < 2 nm). The adsorption process occurs essentially in the micropores and the mesopores are transport pores [24]. A quantitative assessement of the microporosity was made applying α_s method, taking as reference the isotherm reported in [25]. With this methodology the values of total micropore, $V_{\alpha\ total}$, ultramicropore, $V_{\alpha\ ultra}$, and supermicropore $V_{\alpha\ super}$, volumes were obtained [26].

The nitrogen adsorption isotherms (data not shown) of the three commercial ACs (R, N2 and NS) exhibit a type I allied with type IV character [27], indicating that we are in the presence of microporous carbons with a very important development of mesoporosity. These samples clearly present an opening of the nitrogen isotherms knee at low relative pressures, suggesting a wide microporous size distribution. The N_2 isotherms also show a H4-type hysteresis loop, characteristic of the slit-shaped pores where the adsorption and desorption branches are parallel. This analysis is in good agreement with the results of the nanotextural characterization quoted in Table 1. All the samples present apparent surface areas near the 1000 $m^2\ g^{-1}$ and the mesoporous volume corresponds to 55%, 48% and 43% of the total porous volume, for samples R, N2 and NS, respectively. The carbons N2 and NS have only a very small volume of ultramicropores (13% and 5% of the total microporosity, respectively) while in the R carbon the $V_{\alpha\ ultra}$ accounts for 34% of the total microporous volume. The surface chemistry of the ACs plays a determinant role in the adsorption process from liquid phase. It was characterized by the determination of pH_{PZC}. When the solution pH is equal to the pH_{PZC} the number of positive and negative surface groups is equal and thus net surface charge becomes zero. When the solution pH is below pH_{PZC} the net charge of the ACs surface is positive and when pH > pH_{PZC} the net surface charge becomes negative. The values of pH_{PZC} revealed that the ACs used have distinct acid–base natures. The carbon R is acidic while the carbons N2 and NS present basic character. From the more acid to the more basic carbon, the pH_{PZC} value has always an increment of around two pH units. The ash content of carbon R is negligible but in carbons N2 and NS the inorganic matter accounts for 12% and 13% in weight, respectively.

3.2. Instrumental conditions

In a first approach, the HPLC-DAD conditions including the UV/vis spectral data, as well as retention characteristics were evaluated, selecting ATZ, SIM and TBZ as model compounds for the present study. The chemical structures are depicted in Fig. 1. In agreement with the UV/vis data obtained (data not shown), the wavelength (λ_{max}) of 226 nm was selected since it maximizes the DAD response for the three target compounds. By combining a conventional reversed phase column with a mobile phase constituted by MeOH and water (58/42%, 25 °C), good response was obtained for all three herbicides by HPLC-DAD, showing suitable resolution within convenient analytical time (<15 min). The instrumental sensitivity was checked through the limits of detection (LODs) and quantification (LOQs) for all three triazinics, obtained by the injection of diluted calibration standards and calculated with a signal-to-noise (S/N) ratio of 3/1 and 10/1, respectively. Values range within 4.3 and 4.8 $\mu g\ L^{-1}$ for LODs, and 14.3 and 16.1 $\mu g\ L^{-1}$ for LOQs were measured. Subsequently, instrumental calibration was performed with six standard solutions having concentrations ranging from 1.0 to 12.0 $\mu g\ L^{-1}$. From the data obtained, good linear dynamic responses were observed for the three herbicides with correlation coefficients (r^2) higher than 0.9964. To evaluate the instrumental precision, repeated injections for each calibration level were carried out, resulting in relative standard deviations (RSDs) below 4.0%. Furthermore, no carry-over was observed by series of replicate injections since the background was always below the LODs achieved.

3.3. Optimization of the BAμE(ACs)-LD assays

In the present work, several parameters affecting the extraction and back-extraction efficiency of the BAμE(ACs)-LD were evaluated. Therefore, systematic assays were performed to optimize

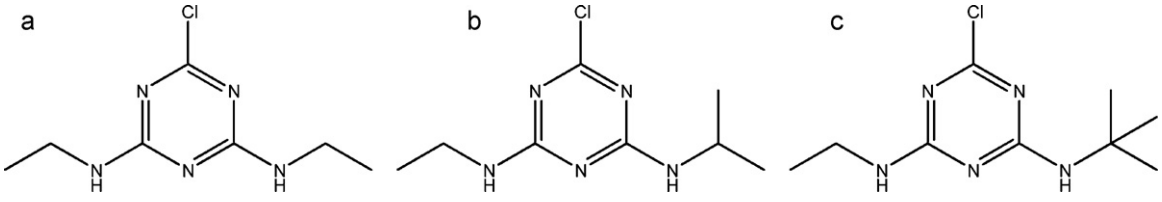

Fig. 1. Chemical structures for the three herbicides under study. SIM (a), ATZ (b) and TBZ (c).

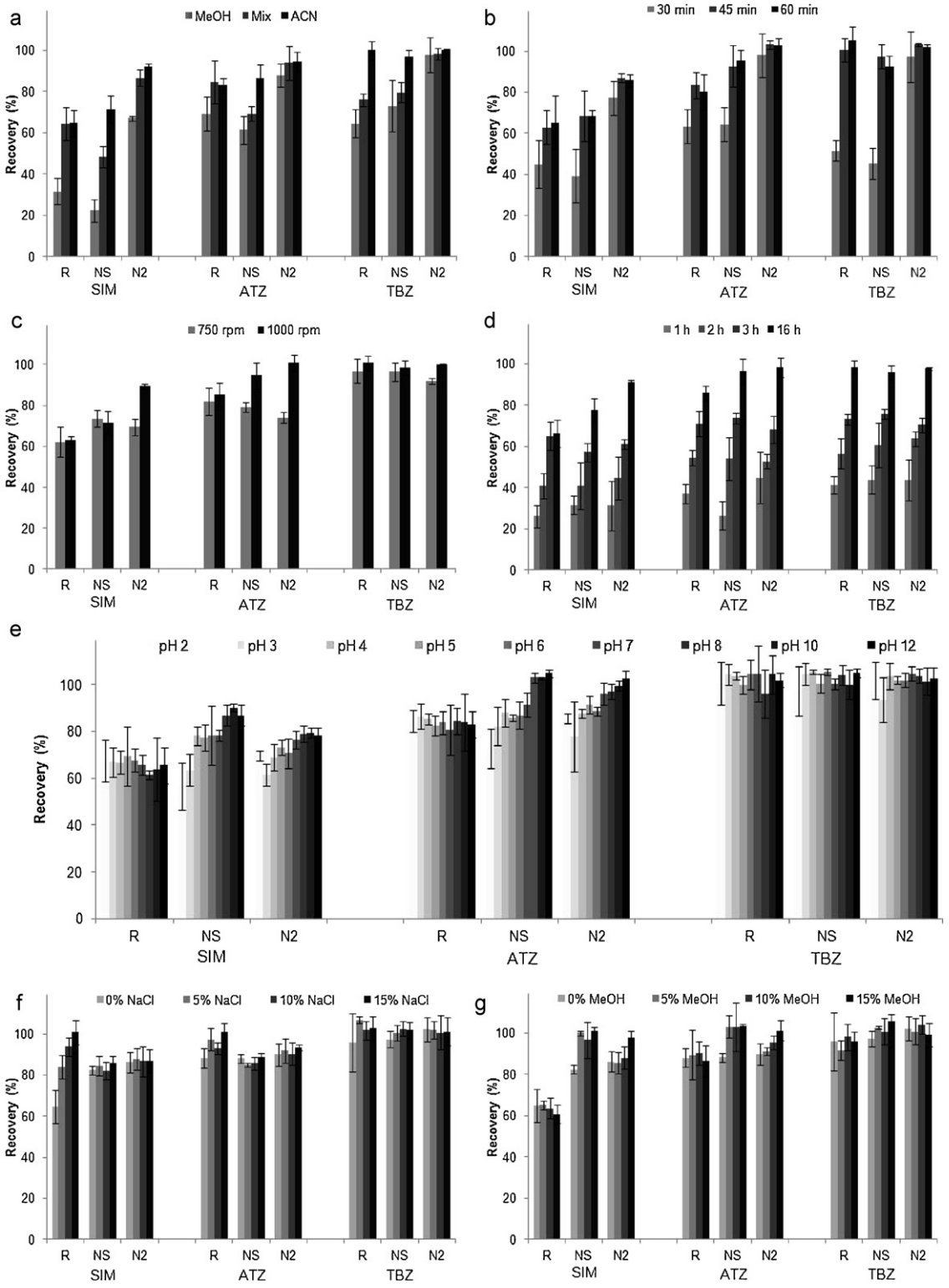

Fig. 2. Effect of desorption solvent (a) and time (b), agitation speed (c), extraction time (d), matrix pH (e), matrix ionic strength (f) and matrix organic modifier (g) on the recovery of ATZ, SIM and TBZ by BAμE(ACs)-LD/HPLC-DAD, using different carbon phases (R, N2 and NS).

parameters that are known to influence this analytical process, such as extraction time, agitation speed, matrix characteristics (pH, organic modifier and ionic strength) and LD conditions. In a first approach, the LD conditions that ensure complete back-extraction for the three herbicides from the bars μ-extraction devices were optimized. Solvents such as MeOH, ACN and a mixture of both (1:1) were assayed to survey the LD performance. Fig. 2a depicts the data obtained using standard conditions (extraction time: 16 h (1000 rpm) and desorption time: 45 min), in which ACN was selected as back-extraction solvent, since it presents the highest ability to desorbs all the herbicides from three AC phases. After the selection of the most effective solvent for back-

extraction, desorption times of 30, 45 and 60 min were also assayed. A great increment on the back-extraction efficiency was observed for 45 min and no advantages were obtained for longer periods, as depicted in Fig. 2b. For the particular case of TBZ, the difference of back-extraction yields was up to 50% for carbons R and NS and, as a consequence, 45 min was established for the back-extraction process.

The evaporation step is essential for solvent switch, so it was necessary to carefully check for possible analyte losses in this process. According to a previous work [14], negligible losses of triazinic herbicides occur during the evaporation step since we are dealing with semi-volatile compounds. Furthermore, no carry-over was observed by series of replicate desorptions, in which the background was always below the LODs achieved. According to literature [10,11], extraction time and agitation speed are extremely important parameters to be optimized for better extraction conditions. Concerning the stirring rate, it can have great influence in the mass transfer process of the herbicides towards the ACs during the adsorption process. Therefore, these two parameters have been evaluated through BAμE(ACs). Fig. 2c depicts the data from two stirring levels (750 and 1000 rpm), where a slight increment on the efficiency of the three herbicides was observed for carbon R with higher stirring speed. In the case of carbon N2 the recovery yields of SIM and ATZ were improved around 20% with 1000 rpm stirring speed and, as a consequence, the latter agitation speed was established for further experiments. Subsequently, the extraction time was evaluated by carrying out experiments within 1, 2, 3 and 16 h, as illustrated in Fig. 2d, where the recovery yields increase until 16 h of extraction, except for SIM using carbon R, for which the efficiency reaches the maximum after 3 h. Thereby, the extraction time was set at 16 h for further assays.

Since we are working at trace level we consider that all the analyte is adsorbed onto the ACs and the experimental results reflect the influence of the parameters evaluated in the desorption process. These results are most likely the consequence of the different porous structures of the three ACs. Carbon R having the highest volume of ultramicropores must be the one where the adsorption process is expected to be stronger. Consequently, the recovery of the analyte is hindered and the overall process results in lower recovery yields. The molecules shape (Fig. 1) also influence the adsorption process since bulky molecules have size exclusion effects leading to lower adsorption affinities. All the above mentioned justifies the results obtained for the recovery of three analytes with carbon R; higher the stereo chemical hindrance of the molecule higher the recovery (SIM < ATZ < TBZ), since the desorption process is favored.

The main parameters that affect the extraction process were studied in order to optimize the recovery yields. Concerning the optimization of desorption solvent and time, extraction time and agitation speed, all the ACs presented the same pattern for the three probe molecules under study. However when the effect of matrix pH, ionic strength and organic modifier were evaluated, the ACs presented different behavior, certainly due to their different porous structure and surface chemistry properties. In this work, we will discuss these effects separately, trying to understand the correlation between the analytical data obtained and the ACs characteristics. The results of the pH effect for the three ACs studied are presented in Fig. 2e and, as expected, for the extraction process pH plays an important role on the recovery yields. This behavior is linked with two factors, namely, the ionization of the analyte and the net charge on the carbon surface, at a given pH. In a first approach, pH changes affect the dissociation of the triazinic molecules; for pH $\geq$3 all the probe molecules are neutral while for lower pH we must consider the presence of a considerable amount of protonated molecules with positive net charge [28,29]. One the other hand, as it was previously discussed, pH changes also affect the surface chemistry of the adsorbent due to the dissociation of the surface functional groups. The carbon surface may be either positively or negatively charged depending on the nature of the AC; therefore, at a given pH, the carbon surface and the adsorbate species may coexist in a complex system, in which the same or opposite charges may be present. However, as the three ACs have distinct pH_{PZC} values the influence of the pH on the surface chemistry of each carbon will be different.

Each of the ACs was assayed at different pH values chosen in order to study the overall process at different adsorbate–adsorbent systems, that is, with different charge interactions. The recovery yields of TBZ are not effected in any case by the solution pH what, as previously discussed, can be justified by the lower adsorption strength that can be expected for this molecule. The desorption process is then highly favored. In the case of SIM and ATZ the recoveries of carbon R are not dependent of the pH while for the other carbons higher the pH, higher the recovery yields. The results of carbon R are most likely linked to its porous characteristics that disfavor the desorption process. So, the influence of the surface chemistry is only noticed for carbons NS and N2 when SIM and ATZ are used. The increase in the recoveries suggest that the progressive modification of the ACs surface towards negative leads to weaker adsorption strengths and consequently easier desorption.

The ionic strength and polarity were modified through the addition of NaCl and MeOH (5, 10 and 15%) onto matrix media, respectively. In a first approach, a progressive addition of NaCl increased significantly the recovery yields of SIM and ATZ when carbon R is used, as shown in Fig. 2f. Nevertheless, for carbon NS and N2, the salt addition does not affect the efficiency. According to literature [14,30], the "salting-out" effect consists on decreasing the solubility of the analytes in order to thrush it towards the adsorbent, consequently increasing the recovery. However it depends on the polarity of the analyte. On the other hand, a progressive addition of MeOH increased significantly the recovery yield of SIM and ATZ with carbons NS and N2, but a negligible effect was observed for carbon R, as shown in Fig. 2g. For TBZ, both NaCl and MeOH does not affect at all the recovery yields.

In short, when experimental conditions are fully optimized (extraction time: 16 h (1000 rpm); carbon R: pH 5, 15% NaCl; carbon NS: pH 10, 5% MeOH; carbon N2: pH 10, 15% MeOH; LD: ACN, 45 min), the data obtained for the three ACs under study, allows efficiency yields around 100% for the herbicides under study (Table 2).

Table 2
Recovery yields, correlation coefficients (r^2), LODs and LOQs achieved for three herbicides in ultra-pure water samples by BAμE using three commercial ACs followed by liquid desorption and HPLC-DAD analysis.

Triazines	ACs	Recovery[a] (% ± RSD; n = 3)	r^2[b]	LOD (ng L^{-1})	LOQ (μg L^{-1})
SIM	R	100.9 ± 6.0	0.9922	94	0.31
	NS	100.0 ± 1.3	0.9959	91	0.30
	N2	97.8 ± 3.5	0.9918	107	0.36
ATZ	R	101.3 ± 4.3	0.9930	92	0.31
	NS	103.1 ± 5.3	0.9929	91	0.30
	N2	101.2 ± 5.0	0.9952	92	0.31
TBZ	R	102.7 ± 6.1	0.9945	93	0.31
	NS	102.6 ± 0.6	0.9948	91	0.30
	N2	99.3 ± 5.7	0.9914	94	0.31

[a] Method efficiency after extraction and back-extraction with AC in water sample spiked at the 10.0 μg L^{-1} level under optimized experimental conditions (LD: 45 min with ACN; 16 h of extraction (1000 rpm); R: pH 5, 15% NaCl; NS: pH 10, 5% MeOH; N2: pH 10, 15% MeOH).
[b] Five levels of concentration ranging from 1.0 to 12.0 μg L^{-1}.

3.4. Validation of the BAμE(ACs)-LD/HPLC-DAD method

After the optimization study we proceed to the validation of the proposed methodology. From the data obtained (Table 2), excellent linearity (1.0–12.0 μg L^{-1}) was attained with good correlation coefficients ($r^2 > 0.9914$). It is also noteworthy that the precision achieved for the present methodology, using within- and between-day repeatability assays calculated as RSD on five replicates, gave rise to variations lower than 15.0%. It must be noted that, according to the requirements of Directive 98/83/EC for trace analysis of organic compounds, the proposed methodology may be considered acceptable if an overall precision with a RSD below 25% is reached [31]. Furthermore, the sensitivity of the methodology was also verified through the LOD and LOQ achieved for the three triazinic herbicides and measured with S/N of 3/1 and 10/1, respectively. The values attained depending on the AC involved as adsorbent phase ranging from 91 to 107 ng L^{-1} and 0.30 to 0.36 μg L^{-1} for LODs and LOQs, respectively. According to literature [32], the LODs achieved for the proposed methodology can be considered very acceptable to monitor triazine herbicides in surface water matrices, since the sum of them is much lower than 3 μg L^{-1}. Furthermore, no carry-over was observed by series of replicates, for which the background was always below the LODs achieved. Table 2 summarizes the experimental recovery yields, the correlation coefficients (r^2), LODs and LOQs achieved for the three triazinic compounds in ultra-pure water matrices by BAμE(ACs)-LD/HPLC-DAD using different AC phases (R, N2 and NS). To demonstrate the advantages of the proposed analytical approach by comparing with other sorptive extraction techniques, several assays at the 10.0 μg L^{-1} level were performed by BAμE(ACs) and SBSE(PU), under similar optimized experimental conditions. The latter method was tested since PU foams showed very good properties to monitor triazinic herbicides at trace level as demonstrated by our group before [13–15]. Fig. 3 depicts the comparison of the recovery yields obtained for ATZ and SIM in water matrices between the proposed method and SBSE (PU) followed by LD/HPLC-DAD, where the former present much better recovery performance (≈100%) when compared with the latter (<30%). These results prove the remarkable selectivity and sensitivity attained by BAμE(ACs)-LD/HPLC-DAD to monitor these particular types of triazinic herbicides in aqueous media.

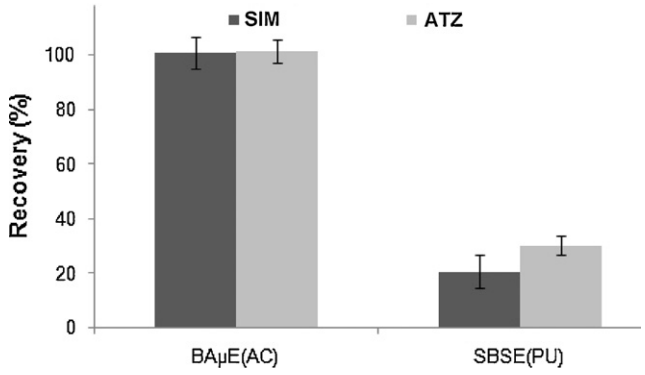

Fig. 3. Comparison of the recovery yields obtained from assays performed on ultra-pure water samples spiked with ATZ and SIM through BAμE(ACs) using carbon R and SBSE(PU) followed by LD/HPLC-DAD, under optimized experimental conditions.

3.5. Application to environmental water matrices

To evaluate the applicability of the proposed methodology, assays on environmental matrices, *i.e.*, surface water and wastewater samples, were performed using the SAM to account for intrinsic contamination and particular pronounced matrix effects. In a first approach, the matrix was fortified with four working standards to produce the corresponding spiking levels (3.0–12.0 μg L^{-1}) for the three herbicides under study. Blank assays ("zero-point") were also performed without spiking to assure maximum control of the analytical methodology. The results obtained from the assays performed by the SAM using this novel methodology, present good linearity ($r^2 > 0.99$). Fig. 4 depicts chromatogram profiles from a surface water and wastewater samples spiked at the 12.0 μg L^{-1}, obtained by the presented methodology, under optimized experimental conditions, where a remarkable selectivity and sensitivity is noticed. Table 3 resumes the level of contamination detected (C_0) for the three herbicides in real matrices, as well as the regression parameters obtained from the assays performed by the SAM using the present methodology. The data obtained in the surface water matrices seems to be consistent, since all the three triazinic

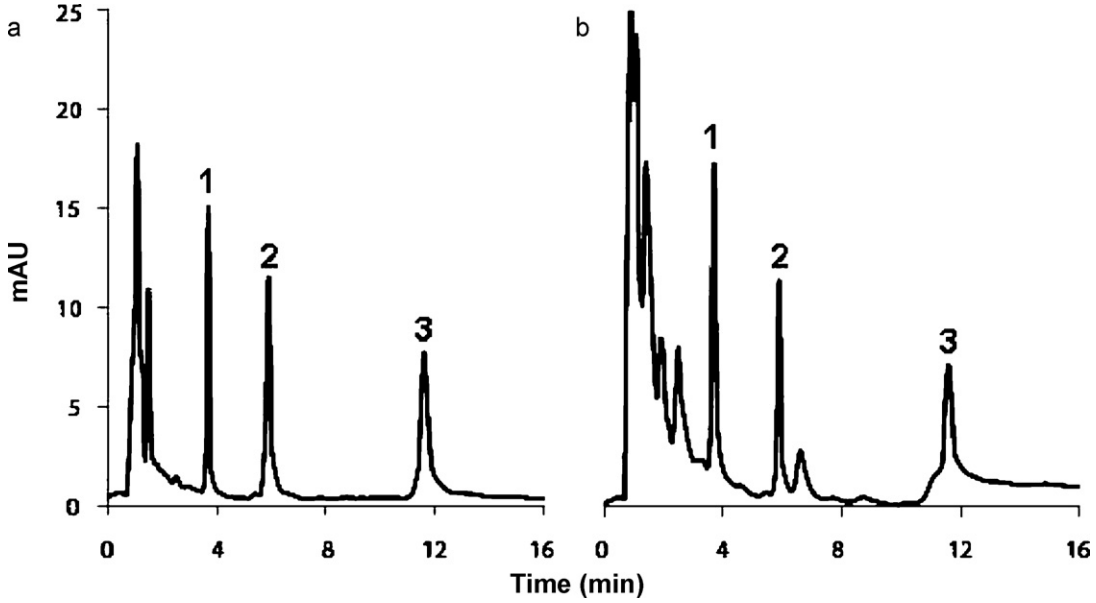

Fig. 4. Chromatogram profiles from surface water (a) and wastewater (b) matrices spiked at 12.0 μg L^{-1}, obtained by BAμE(ACs)-LD/HPLC-DAD, under optimized experimental conditions. 1: SIM, 2: ATZ, 3: TBZ.

Table 3
Content (C_0) and regression parameters obtained from the standard addition method for three triazinic compounds determined in real matrices by BAμE(ACs)-LD/HPLC-DAD, under optimized experimental conditions.

Triazines	ACs	Wastewater C_0 ($\mu g L^{-1}$)	r^2 [a]	Surfacewater C_0 ($\mu g L^{-1}$)	r^2 [a]
SIM	R	3.6 ± 0.4	0.9930		0.9932
	NS	3.7 ± 0.4	0.9945	<LOD	0.9945
	N2	3.7 ± 0.4	0.9915		0.9960
ATZ	R		0.9900	<LOD	0.9962
	NS	<LOD	0.9963		0.9936
	N2		0.9924		0.9924
TBZ	R		0.9955		0.9984
	NS	<LOD	0.9959	<LOD	0.9971
	N2		0.9940		0.9940

[a] Five levels of concentrations.

herbicides were below the LODs achieved for the present methodology in agreement with previous works reported by other authors [33,34]. For wastewater matrices in particular, the data obtained by BAμE(ACs)-LD/HPLC-DAD showed the occurrence of SIM with average concentrations around 3.6 $\mu g L^{-1}$, consistent for the different ACs adsorbents (R, N2 and NS) used.

In short, it must be emphasized that the present methodology, besides easy to work-up and environmentally friendly, exhibits a remarkable range of applicability, since the methodology promotes very high selectivity for triazinic herbicides, avoiding potential interferences and simultaneously a great analytical sensitivity in real water matrices at the trace level.

4. Conclusions

The methodology proposed in the present work (BAμE(ACs)-LD/HPLC-DAD), using three commercial ACs (R, N2 and NS) as adsorbent phases, was successfully applied to determine traces of ATZ, SIM and TBZ in environmental water samples. Under optimized experimental conditions, good accuracy, suitable precision, convenient linear dynamic ranges and convenient detection limits were achieved. The analytical data obtained was correlated with the textural and surface properties of the ACs to a better understanding of the overall enrichment process. The influence of matrix pH on the recovery yields was discussed and correlated with the pH_{PZC} of the ACs and also with the speciation of the three triazinic herbicides. The application of the present methodology to monitor traces of triazinic herbicides in surface water and wastewater matrices provided very good performance through the standard addition methodology. The proposed method also demonstrates to be easy to work-up, selective, sensitive and requires low sample volumes. This new analytical approach has proved to be a suitable alternative to monitor trace levels of priority pollutants, whenever other sorptive micro-extraction techniques, *i.e.*, SPME and SBSE, present limitations.

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