Talanta 116 (2013) 695–703

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Comparison between magnetic and non magnetic multi-walled carbon nanotubes-dispersive solid-phase extraction combined with ultra-high performance liquid chromatography for the determination of sulfonamide antibiotics in water samples

Antonio V. Herrera-Herrera [a,1], Javier Hernández-Borges [a,2], María M. Afonso [b,3], J. Antonio Palenzuela [b,3], Miguel Ángel Rodríguez-Delgado [a,*]

[a] Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Química, Universidad de La Laguna (ULL), Avenida Astrofísico Francisco Sánchez, s/n. 38206 La Laguna, Tenerife, Spain
[b] Departamento de Química Orgánica, Instituto Universitario de Bio-Orgánica Antonio González, Universidad de La Laguna (ULL), Avenida Astrofísico Francisco Sánchez, s/n. 38206 La Laguna, Tenerife, Spain

ARTICLE INFO

Article history:
Received 26 April 2013
Received in revised form
10 July 2013
Accepted 24 July 2013
Available online 31 July 2013

Keywords:
Sulfonamides
Dispersive solid-phase extraction
Ultra-high performance liquid chromatography
Antibiotics
Magnetic carbon nanotubes
Water

ABSTRACT

In this manuscript, a new method based on the use of off-line dispersive solid-phase extraction (dSPE) combined with ultra-high performance liquid chromatography with diode-array detection was developed to determine 11 sulfonamide antibiotics (sulfanilamide, sulfacetamide, sulfadiazine, sulfathiazole, sulfamerazine, sulfadimidin, sulfamethoxypyridazine, sulfadoxine, sulfamethoxazole, sulfisoxazole and sulfadimethoxine) in mineral waters with different mineral content. For this purpose, pristine multi-walled carbon nanotubes (MWCNTs) and magnetic-MWCNTs (m-MWCNTs) were used as sorbents. Magnetic nanoparticles were synthesized by means of a solvothermal process, assembled onto CNTs through an "aggregation wrap" mechanism and characterized by scanning electron microscopy. Parameters affecting the extraction such as volume and pH of the sample, amount of sorbent and type and volume of eluent were optimized. Once optimum extraction conditions (250 mL of water at pH 6.0 and elution with 25 mL of MeOH) were obtained, the extraction efficiency of the different carbon nanomaterials was compared. Results demonstrated the higher extraction capacity of pristine MWCNTs with recoveries between 61 and 110% (except for sulfacetamide which ranged between 40 and 53%) and between 22 and 77% for m-MWCNTs. Limits of detection lower than 32 ng/L were achieved for all of the analyzed samples.

1. Introduction

Sulfonamides (SAs, synthetic derivatives of sulfanilamide (SAD)) represent one of the most important families of antibiotics used worldwide to treat both human and animal diseases. Such antibacterial compounds, which difficult the synthesis of bacterial folic acid, are widely used in developing countries especially to treat urinary infections as well as ear infections, bronchitis, bacterial meningitis and other diseases [1]. In veterinary medicine they are commonly administered in feed at sub-therapeutic doses during growth to prevent diseases, to promote growth, to increase weigth gain and to reduce the amount of feed per animal [1,2]. The presence of sulfonamide residues can produce several undesirable effects like the development of microorganism resistance and, as a result, the possible harmful effects on the treatment of bacterial infections [2]. These compounds are continuously introduced in the aquatic environment by means of the waste treatment plants, which are considered the main discharge sources of

Abbreviations: ACN, acetonitrile; CNTs, carbon nanotubes; DAD, diode array detector; DCM, dichloromethane; DMF, dimethylformamide; dSPE, dispersive solid-phase extraction; m-CNTs, magnetic carbon nanotubes; MeOH, methanol; m-NPs, magnetic nanoparticles; MWCNTs, multi-walled carbon nanotubes; m-MWCNTs, magnetic multi-walled carbon nanotubes; PTFE, polytetrafluoroethylene; SAD, sulfanilamide; SAM, sulfacetamide; SAs, sulfonamides; SDD, sulfadimidin; SDM, sulfadimethoxine; SDX, sulfadoxine; SDZ, sulfadiazine; SEM, scanning electron microcopy; SMP, sulfamethoxypyridazine; SMR, sulfamerazine; SMX, sulfamethoxazole; S/N, signal-to-noise ratio; SPD, sulfapyridine; SPE, solid-phase extraction; SPME, solid phase microextraction; SSZ, sulfisoxazole; STZ, sulfathiazole; SWCNTs, single-walled carbon nanotubes; UHPLC, ultra-high performance liquid chromatography

* Corresponding author. Tel.: +349 223 180 46; fax: +349 223 180 03.
E-mail addresses: avherrer@ull.es (A.V. Herrera-Herrera), jhborges@ull.edu.es (J. Hernández-Borges), mmafonso@ull.es (M.M. Afonso), jpalenz@ull.es (J.A. Palenzuela), mrguez@ull.es (M.Á. Rodríguez-Delgado).
[1] Tel.: +34 922318593.
[2] Tel.: +34 922318990.
[3] Tel.: +34 922317421.

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.07.060

pharmaceutical residues [3]. Since sulfonamide agents are very polar and soluble in water, they are easily transferred to surface and ground waters. As a result, it is fundamental to develop adequate analytical methods for their determination in water samples.

The use of carbon nanotubes (CNTs) as solid-phase extraction (SPE) and solid phase microextraction (SPME) sorbents has gained importance in Analytical Science over the last years [4–7]. The popularity of these materials lies in their unique properties that allow the selective extraction of inorganic and organic compounds including non-polar substances (mainly extracted with non-functionalized CNTs) as well as polar molecules (extracted with functionalized CNTs). Moreover, some of them are relatively cheap materials with a broad range in length, diameters and number of walls which could be functionalized to improve their properties in particular applications.

The combination of CNTs with magnetic nanoparticles (m-NPs) represents an interesting modification quite recently introduced [8,9] which facilitates their use as sorbents in dispersive SPE (dSPE), since an easier manipulation of CNTs can be achieved with an external magnetic field provided by a permanent magnet (made with Nd, Fe and B) with a high energy product. In this way, magnetic CNTs (m-CNTs) are mixed with the spiked sample and then the matrix is separated from the sorbent with the analytes using the magnet. Afterwards, m-CNTs are dispersed in the elution solvent which is subsequently collected to be analyzed. Regarding water samples analysis, this kind of CNTs has been successfully used, though not in many occasions, to extract organic analytes like nerve agents [10], phthalate acid esters [11], atrazine [12], fluoroquinolones [13] as well as linear alkyl benzene sulfonates [14]. Among the mentioned manuscripts, only in the work of Tang et al. [12] the extraction efficiency of m-CNTs was compared with the one obtained for pristine CNTs. Results demonstrated that pristine CNTs had a slightly higher removal efficiency for atrazine extraction, probably due the relatively higher superficial area of these materials. It is worth mentioning that Tang et al. [12] and Zhang et al. [15] studied the possible application of m-CNTs for the removal of contaminants from waters. For this purpose, they carried out batch adsorption experiments and obtained the corresponding sorption isotherms.

The assembling of m-NPs onto CNTs can be made via chemical modifications by the formation of covalent bonds in the CNTs surface and/or physical phenomena. The principal drawback for the first type is the possible alteration of the chemical properties of CNTs surface and therefore the disturbance of the adsorption capacity. For this reason soft physical procedures have been used in most manuscripts [10–20]. One of them is carried out by the solvothermal precipitation of the m-NPs which are then dispersed with the CNTs using sonication [10–18] and aggregated by the so called "aggregation wrap" mechanism [18]. In this methodology m-NPs are synthetized by mixing a solution of $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ with NH_4OH, heating for a determined period of time and letting to cool at room temperature. The addition of NH_4OH is fundamental because pH control results essential [10]. A similar procedure was used by Zhao et al. [20] with $FeCl_3 \cdot 6H_2O$, ethylene glycol and ammonium acetate as reactives. Alternatively, the fabrication of m-CNTs can be made by the simultaneous solvothermal precipitation of the m-NPs and the aggregation with the CNTs. For this purpose the reagents ($FeCl_3 \cdot 6H_2O$, ethylene glycol and ammonium acetate) and CNTs are simultaneously mixed in a round-bottom flask [14–19].

Regarding SAs extraction, CNTs have been used as sorbents in SPE only in two occasions [21,22]. Fang et al. [22] used multi-walled CNTs (MWCNTs) with an average diameter between 60 and 100 nm and 5–15 μm of length to extract ten SAs (i.e. sulfadiazine (SDZ), sulfamerazine (SMR), sulfadimidin (SDD), sulfathiazole (STZ), sulfamoxol, sulfametizole, sulfamethoxypyridazine (SMP), sulfachloropyridazine, sulfadoxine (SDX) and sulfisoxazole (SSZ)) from eggs and pig tissues by on-line SPE combined with HPLC-UV. Samples were initially extracted with an aqueous solution of $K_3Fe(CN)_6$ and $ZnSO_4$ at 75 °C and then with acetonitrile (ACN). The efficiency of CNTs as sorbents was compared with that of C_{18} cartridges which provided worse results in terms of LODs, precision and enrichment factors. It is also worth mentioning that recoveries, though high, did not reach 100% and were in the range between 66 and 86%. Niu et al. [21] compared the adsorption potential of single-walled CNTs (SWCNTs, outer diameter, o.d., between 30 and 60 nm) and MWCNTs (o.d. between 0.5 and 1.6 nm) to extract six phenolic compounds, four cephalosporins and four SAs (STZ, SDZ, SDD and sulfapyridine (SPD)) from river, well and tap waters. Determination was carried out by HPLC-diode array detector (DAD). In this case, a conventional SPE approach was used. Regarding SAs, the higher recoveries (55–102%) were obtained using an eluent composed by mixtures 30:70 (v/v) 0.3 M ammonium acetate:methanol (MeOH). Among the selected CNTs the best results, not only for SAs but also for the rest of the studied antibiotics (cephalosporins), were obtained with the MWCNTs. Finally, the extraction efficiency of these materials was compared with that of graphitized carbon black and C_{18}, which provided worse recoveries.

Therefore, the aim of this work was to develop a dSPE method using MWCNTs for the analysis of a group of eleven SAs (SAD, sulfacetamide (SAM), SDZ, STZ, SMR, SDD, SMP, SDX, sulfamethoxazole (SMX), SSZ and sulfadimethoxine (SDM)) in water samples using ultra-high performance LC (UHPLC)-DAD as separation technique. The obtained results were also compared with those achieved using m-MWCNTs. The use of dSPE provides several advantages over conventional SPE procedures like a considerable reduction of the extraction time and a simplification of the whole extraction procedure. The combination of dSPE with UHPLC will clearly join the advantages of the first of them with those of UHPLC separations: higher efficiency, speed of analysis and sensitivity as well as improved peak resolution and lower consumption of organic solvents. To the best of our knowledge, this manuscript represents the first published application in which SAs are extracted by dSPE using CNTs. It also represents one of the very few works in the literature in which a comparison between pristine and m-CNTs is developed for the extraction of organic analytes and the work with the highest number of SAs extracted from water samples using CNTs, also with the lowest LODs.

2. Experimental

2.1. Chemicals, samples and materials

All chemicals were at least of analytical reagent grade and were used as received without further purification.

Analytical standards of SAD, SAM, SDZ, STZ, SMR, SDD, SMP, SDX, SMX, SSZ and SDM were provided by Sigma-Aldrich (Madrid, Spain). Standards had purities higher than 95% (Vetranal quality, except SDX which was TLC quality). Individual standard solutions of the antibiotics of approximately 100 mg/L were prepared by dissolving them in MeOH and stored in the darkness at 4 °C. Mixtures of appropriate concentration were prepared by combination and dilution with methanol (MeOH).

Gradient grade ACN, MeOH for LC and hydrochloric acid were purchased from Merck (Darmstadt, Germany). Dichloromethane (DCM) and acetone were provided by Panreac Química S.A. (Barcelona, Spain). Dimethylformamide (DMF), ammonium hydroxide, ethanol, $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ were obtained from Sigma-Aldrich (Madrid, Spain). Formic acid was provided by Panreac Química S.A. (Barcelona, Spain) while sodium hydroxide was from Scharlau (Barcelona, Spain). MWCNTs with an average

diameter of 6–9 nm and 5 μm length were provided by Sigma-Aldrich (Madrid, Spain). Empty glass SPE tubes of 6 mL volume and polytetrafluoroethylene (PTFE) frits (20 μm porosity) were from Supelco (Madrid, Spain). Permanent magnet composed by Nd–Fe–B of 50 × 15 × 15 mm with a weight of 86 g, strength of 33 kg and coated with Ni–Cu–Ni was acquired from Supermagnete (Gottmadingen, Germany).

Milli-Q water (pH 5.0, conductivity of 4.06 μS/cm at 25 °C) was deionized by using a Milli-Q gradient system *A*10 (Millipore, Bedford, MA, USA). Low mineral content (pH 8.5, conductivity of 320 μS/cm at 25 °C) and very low mineral content (pH 7.3, conductivity of 41.0 μS/cm at 25 °C) water samples were purchased from local supermarkets of Tenerife (Canary Islands, Spain). Water samples were spiked with the selected antibiotics at several concentrations in order to identify and quantify the analytes in the real samples.

2.2. UHPLC-DAD

UHPLC analyses were carried out using an Accela liquid chromatograph (Thermo Scientific, San Jose, CA) equipped with a DAD and an autosampler. Column compartment was thermostated at 25 °C while the temperature of autosampler compartment was 20 °C. Separation was carried out using a Hypersil Gold C_{18} column 100 × 2.1 mm and 1.9 μm of particle diameter (Thermo Scientific) and 0.3% (v/v) formic acid in Milli-Q water as mobile phase A and ACN as mobile phase B. Gradient program was applied as follow: 0.0 min 7.2% B; 2.0 min 18.0% B; 4.0 min 26.0% B; 7.0 min 26.0% B; 9.0 min 92.8% B, 9.1 min 7.2% B. The optimum flow rate was 0.4 mL/min whereas the injection volume was 10 μL. The DAD worked in the two channel mode at 260 and 280 nm. Antibiotics were determined at these wavelengths according to their experimentally obtained maximum of absorption (Table 1). For data storage and evaluation the ChromQuest 5.0 software (Thermo Scientific) and a personal computer were used.

2.3. Synthesis of m-MWCNTs

The fabrication of m-MWCNTs was based on the method previously developed by Luo et al. [11] involving the synthesis of m-NPs and the later assembly with the MWCNTs by sonication. m-NPs were prepared by a solvothermal method carried out dissolving 5.4 g of $FeCl_3 \cdot 6H_2O$ and 2.0 g of $FeCl_2 \cdot 4H_2O$ in 25 mL of HCl 6.0 M. Then, the solution was desgassed with Ar and 30 mL of NH_4OH 29% (v/v) were added. The mixture was heated at 60 °C for 30 min with vigorous stirring under inert atmosphere. After cooling at room temperature for 40 min, the obtained m-NPs were separated using a magnet, profusely washed with water and ethanol, dried at 60 °C for 24 h and ground.

m-MWCNTs were obtained by combination of MWCNTs and m-NPs in proportions 1:1 (w/w), 2:1 (w/w) and 3:1 (w/w). For this purpose 2, 4 or 6 g of MWCNTs were dispersed in 50 mL of DMF by sonication and mixed with 2 g of m-NPs previously dispersed in 50 mL of DMF. After ultrasound agitation for 15 min, 300 mL of water were added to facilitate the separation and the m-MWCNTs formed were collected by filtration of the mixture using a 0.45 μm and 47 mm nylon membrane (Sigma-Aldrich). Finally they were washed with water and dried under vacuum at 90 °C for 24 h.

Both m-NPs and m-MWCNTs were stored under Ar atmosphere to avoid their further oxidation.

2.4. Scanning electron microscopy analysis

The morphology and size analyses of m-NPs and m-MWCNTs were performed by scanning electron microcopy (SEM) using a JSM 6300 microscope (JEOL Ltd.) with a resolution of 3.5 nm equipped with a X-ray microanalyzer which allows the surface observation as well as quantitative studies of the elemental composition.

2.5. dSPE procedure with pristine MWCNTs

It is important to differentiate between the procedure applied using MWCNTs or m-MWCNTs. In the case of MWCNTs, 250 mL of water spiked with the SAs were adjusted to pH 6.0 and introduced in a flask containing 150 mg of sorbent. After intense agitation, the mixture was transferred to a glass column containing two PTFE frits using a Visiprep™-DL SPE vacuum manifold from Supelco (Bellefonte, PA, USA). Then, a new frit was introduced into the glass tube in order to hold the MWCNTs with the retained analytes. Afterwards the SPE glass tube was dried under vacuum of −10 mmHg (1 mmHg = 133.322 Pa) for 20 min and the elution of the retained antibiotics was carried out with 25 mL of MeOH. The eluate was then evaporated to dryness at 40 °C and 200 mbar using a rotavapor R-200 (from Büchi Labortechnik, Flawil, Switzerland) equipped with a vacuum controller V-800 and a vacuum pump V-500 (also from Büchi Labortechnik). The dry residue was redissolved in 500 μL of water and filtrated using 0.20 μm filters (Chromafil® Xtra PET-20/25 from Macherey-Nagel). Then 10 μL of reconstituted sample were injected in the chromatographic system.

Table 1
Detection wavelengths, retention times, intraday and day-to-day precision, standard calibration data and instrumental LODs and LOQs of the selected SAs.

Peak	Antibiotic	DAD detección λ (nm)	t_R (min)	Intraday precision (n=5, RSD %)		Day-to-day precision (n=15, RSD %)		Range of concentration tested (μg/L)	Slope (n=6)	Intercept (n=6)	R^2	$S_{y/x}$	LOD[a] (μg/L)	LOQ[b] (μg/L)
				t_R	Areas	t_R	Areas							
1	SAD	260	1.21	0.4	2.2	1.9	2.7	25–1000	104.99 ± 6.77	(−0.81 ± 3.66) × 10^3	0.997	2.54 × 10^3	4.85	16.2
2	SAM	280	2.30	0.5	2.5	2.4	2.9	25–1000	125.49 ± 8.29	(−1.07 ± 4.49) × 10^3	0.997	3.11 × 10^3	6.87	22.9
3	SDZ	260	2.54	0.4	0.9	2.5	1.9	25–1000	91.99 ± 6.74	(−0.83 ± 3.65) × 10^3	0.996	2.53 × 10^3	3.36	11.2
4	STZ	280	3.02	0.4	1.9	2.0	1.8	25–1000	69.54 ± 4.98	(−0.59 ± 2.69) × 10^3	0.996	1.87 × 10^3	4.48	14.9
5	SMR	260	3.18	0.4	1.7	1.9	1.9	25–1000	83.46 ± 5.92	(−0.80 ± 3.21) × 10^3	0.996	2.22 × 10^3	3.65	12.2
6	SDD	260	3.68	0.4	1.5	1.5	2.1	25–1000	76.79 ± 5.35	(−0.65 ± 2.90) × 10^3	0.996	2.01 × 10^3	3.40	11.3
7	SMP	260	4.08	0.4	1.2	1.2	1.7	25–1000	90.73 ± 6.09	(−0.76 ± 3.30) × 10^3	0.997	2.29 × 10^3	4.25	14.2
8	SDX	260	5.23	0.2	1.7	0.8	1.6	25–1000	96.62 ± 6.87	(−0.75 ± 3.72) × 10^3	0.996	2.58 × 10^3	4.66	15.5
9	SMX	260	5.48	0.2	2.2	0.7	2.6	25–1000	76.36 ± 5.06	(−0.66 ± 2.74) × 10^3	0.997	1.90 × 10^3	6.90	23.0
10	SSZ	280	5.94	0.2	3.7	0.7	2.6	25–1000	79.54 ± 4.85	(−0.48 ± 2.63) × 10^3	0.997	1.82 × 10^3	5.94	19.8
11	SDM	260	7.09	0.3	3.8	0.8	2.3	25–1000	129.43 ± 10.10	(−0.61 ± 5.47) × 10^3	0.995	3.79 × 10^3	5.59	18.6

[a] Calculated for S/N = 3.
[b] Calculated for S/N = 10.

2.6. dSPE procedure with m-MWCNTs

Regarding the extraction with m-MWCNTs, 250 mL of spiked sample at pH 6.0 were introduced in a flask containing 300 mg of m-MWCNTs obtained from the 1:1 combination with pristine MWCNTs, 225 mg of m-MWCNTs 2:1 or 200 mg of m-MWCNTs 3:1 and vigorously shaken. Afterwards the magnet was applied at the bottom of the flask and the sorbent was let to settle for 5 min. The sample was then discarded and SAs were eluted by addition of 25 mL of MeOH. The elution solvent was collected retaining the sorbent in the extraction recipient with the help of the magnet. After evaporation at 40 °C and 200 mbar the residue was redissolved in 500 μL and 10 μL of filtrate sample were injected in the UHPLC-DAD system.

3. Results and discussion

3.1. UHPLC-DAD separation

SAs have two ionizable groups: a basic amine group and an acidic amide group (see Fig. 1). The first of them is capable of gaining a proton at a pH lower than its pKa_1 (1.75–2.5) [23] while the second is able to release a proton at a pH higher than its pKa_2 (5.22–7.65) [23]. Therefore, SAs exist in their cationic, neutral or anionic form under specific pH conditions and, as a result, suitable control of the pH of the mobile phase should be developed for their LC separation. In this sense, it is very frequent to separate them in the reversed phase mode with C_{18} columns [24–29] using acidic mobile phases [25–29].

For this reason, different acidic mobile phases were tested including aqueous solutions containing 0.1–0.3% v/v of formic acid as mobile phase A and MeOH or ACN containing or not formic acid as mobile phase B. The best results in terms of peak shapes and highest signal-to-noise ratios (S/N) were obtained with the use of 0.3% v/v formic acid and ACN. Between the different gradient elution programs tested, the highest separation capacity and the lowest retention times were obtained using the gradient program shown in Section 2.2. Other experimental parameters affecting the separation characteristics were experimentally checked. The temperature of the column and autosampler were varied between 20 and 35 °C. On the one hand, column temperatures higher than 25 °C speeded up analyte elution but deterioration in the separation efficiency and overlapping between adjacent SAs were observed. Similarly, an increase in the temperature of the autosampler resulted in a decrease of separation capacity. On the other hand, column temperatures lower than 25 °C increased the elution time. That is why a column temperature of 25 °C and an autosampler temperature of 20 °C were selected as suitable values for the separation of the 11 selected antibiotics.

Concerning the DAD detection, the detector was initially operated in the scan mode in order to find SAs' characteristic maximum absorption wavelengths in the UV region. Since each individual analyte had a maximum at a particular wavelength around 260 and 280 nm, these values were selected as a compromise between them (see Table 1). Fig. 2 shows an UHPLC-DAD chromatogram of the separation of a standard mixture of the studied sulfonamide antibiotics under the selected conditions. As it can be seen, complete separation of analytes was obtained in less than 7.5 min with an appropriate resolution and relatively high efficiencies as it is usual in UHPLC separations.

3.2. Precision study and standard calibration

Once suitable separation conditions were achieved, instrumental intraday and interday precision were evaluated by means of five consecutive injections ($n=5$) in the same day of a standard mixture of the selected SAs at three levels of concentration (100, 500 and 850 μg/L) in three different days ($n=15$). Table 1 summarizes the results obtained for the lowest concentration level as well as the results of the calibration study of standards carried out by means of three injections of six levels of concentration. As can be seen, RSD values for peak areas were in the range 0.9–3.8% in the same day and between 1.6 and 2.9%, in different days. Similarly, RSD values for retention times were between 0.2 and 0.5% in the same day and in the range 0.7–2.5% in different days. The results obtained for the other concentration levels were very similar. Determination coefficients (R^2) were higher than 0.995 and instrumental LODs (calculated as the concentration that provided a S/N of · 3) were between 3.36 μg/L for SDZ and 6.90 μg/L for SMX while the instrumental LOQs (calculated as the concentration that provided a S/N of · 10) were in the range 11.2–23.0 μg/L for the same antibiotics. These values were experimentally checked. The obtained data demonstrated the suitability of the optimized separation method for the fast and sensitive detection of the studied antibiotics in a single run.

3.3. Synthesis of m-MWCNTs and optimization of the dSPE procedure

The use of MWCNTs as sorbents in dSPE offers an interesting and faster alternative in contrast to traditional SPE, maintaining at the same time its high extraction efficiency. Moreover, as it was previously mentioned, m-CNTs contribute to facilitate the manipulation of CNTs in dSPE, because the sample is mixed with the sorbent and once the extraction time has passed a magnet is approximated to the flask and the matrix can be easily eliminated. Finally, the elution solvent is added, CNTs are dispersed once more to transfer the analytes to the solvent and this one is collected by approximating the magnet once again. Based on this consideration, MWCNTs with an

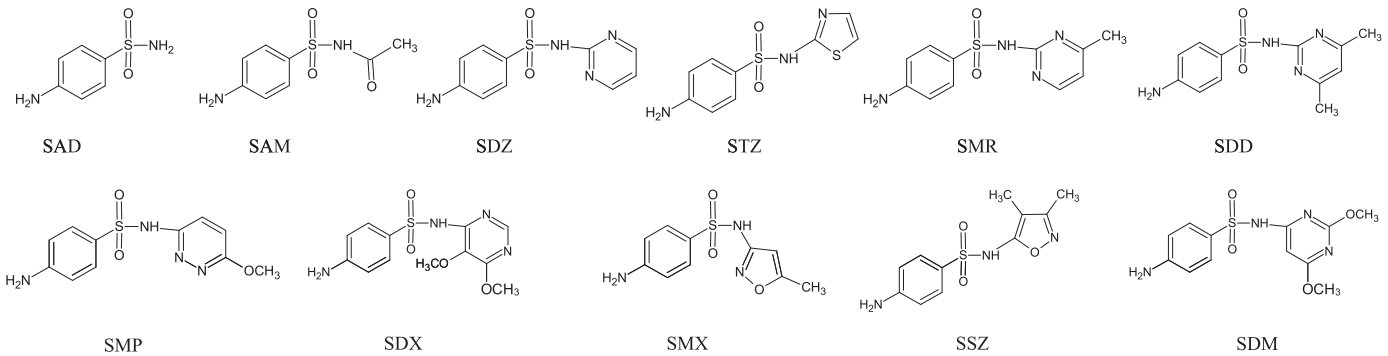

Fig. 1. Structures and acronyms of the studied SAs.

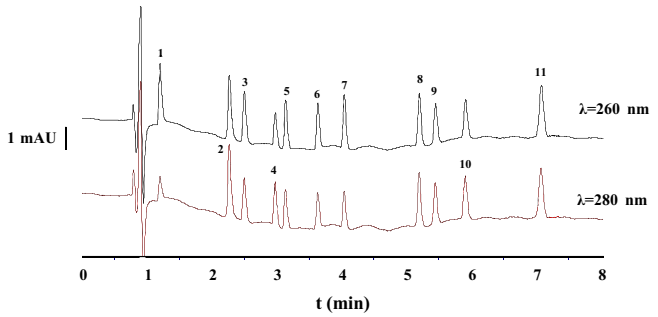

Fig. 2. UHPLC-DAD chromatograms of a standard mixture of the 11 target SAs at their selected detection wavelengths. Flow rate: 0.4 mL/min; injection volume: 10 μL; analyte concentration: 100 μg/L. Mobile phase: 0.3% (v/v) formic acid in Milli-Q water and ACN (for details of gradient elution program and other separation conditions see Section 2.2). Peak identification: 1, SAD; 2, SAM; 3, SDZ; 4, STZ; 5, SMR; 6, SDD; 7, SMP; 8, SDX; 9, SMX; 10, SSZ; 11, SDM.

average diameter of 6–9 nm and 5 μm lengths in their free and magnetized forms were selected. The obtention of m-MWCNTs was adapted from a previously developed procedure [11] as described in Section 2.3. The obtained m-NPs and m-MWCNTs were characterized by SEM (see supplementary material 1). As it can be seen from the photographs, the m-NPs (supplementary material 1A) had a spherical morphology and were aggregated together very closely. Meanwhile, m-MWCNTs (supplementary material 1B) have a tubular structure decorated with spherical m-NPs which appeared in the photography as bright spots.

It is worth mentioning that in the first experiences with CNTs as sorbents, even with Milli-Q water, chromatographic interferences that difficult the correct identification and quantification of SAs appeared. After washing the CNTs with several solvents, evaporation to dryness, reconstitution in mobile phase, and injection in the UHPLC-DAD, it could be observed that impurities came from the industrial synthesis of CNTs. To eliminate them, the sorbent was purified by Soxhlet extraction (3 g) with MeOH (50 mL) for 24 h and dried overnight under vacuum at 60 °C. In this way, although several minor impurities still appeared they did not elute at the analytes retention times.

dSPE conditions affecting the extraction efficiency (i.e. type and volume of the eluent, sample pH, extraction time, sample volume, and amount of CNTs) were investigated in detail following a step by step approach. These experiments were carried out with Milli-Q water with the aim of clearly selecting experimental factors and not to introduce matrix effects. Each experience was carried out in duplicate. Preliminary experiments were developed using pristine MWCNTs because some manuscripts had previously shown that m-MWCNTs had an extraction efficiency at least similar than pristine MWCNTs [10–16].

Initially, 50 mL of water at pH 6.0 spiked at 1.25 μg/L with the SAs were extracted with 100 mg of MWCNTs. Since the polarity of the eluent is an important factor for the complete elution of the analytes, 25 mL of different solvents like MeOH, ACN, acetone and DCM containing 0–1% (w/w) of ammonium acetate or 0–1% (v/v) of NH_4OH were tested. The use of these additives was based on the previous report of Niu et al. [21] in which ammonium acetate was found necessary for the elution of four SAs (STZ, SDZ, SDD and SPD) previously extracted with MWCNTs from water samples. However, in our particular application, and probably due the type of CNTs selected, the inclusion of these additives clearly reduced the recoveries. Among the studied solvents, MeOH provided the highest recoveries (between 37 and 91%), while those obtained with ACN were slightly lower (between 30 and 71%). Among the rest, DCM provided the lowest recoveries (below 20%). Therefore elution with MeOH (25 mL) was used for the following experiments.

Subsequently, the effect of sample pH was investigated in the range between 3 and 9 with the aim of extracting the SAs under their cationic, neutral or anionic form. The highest recoveries were obtained, for most antibiotics, in the range between 5 and 7, in which SAs will be in the neutral form, except for SAM whose recoveries decreased at pH higher than 4 (Fig. 3). Thus, pH 6.0 was selected for the following experiments. It is worth mentioning that at pH higher than 7.0 recoveries decreased drastically as a result of their anionic nature at such pH values. In this sense, it has also been described in literature that CNTs´surface acquire a certain negative charge at pH higher than the so-called "point of zero charge" which could reduce the adsorption of anionic analytes due to electrostatic charge repulsions [4].

Once the sample pH was selected, the extraction time (which was varied between 0 and 15 min) and the volume of elution solvent (varied between 5 and 30 mL) were investigated. Regarding the extraction time, no significant differences in the recovery values were observed for any of the selected SAs. As a result, samples mixed with MWCNTs were transferred to the SPE glass column after a brief and intense agitation. Concerning the volume of MeOH, as can be observed in Fig. 4, the increase of the amount of MeOH produced an increase in the recoveries of the analytes. However, volumes higher than 25 mL reduced the recoveries (below 78%, except for STZ which was 107%). Therefore, 25 mL of MeOH were selected as the suitable volume for the quantitative elution of SAs.

Finally, with the objective of reducing the LODs, sample volumes of 50, 100 and 250 mL were extracted with 100 mg of MWCNTs. Generally, an increase of the sample volume decreased the recoveries (below 86%) and, since a higher sample volume may require a higher sorbent amount, the quantity of MWCNTs was increased till 150 mg (see Fig. 5). Such amount provided the highest recoveries for 250 mL of water and was chosen as adequate.

Therefore, optimum dSPE conditions were the following: 250 mL of spiked water at pH 6.0 extracted with 150 mg of MWCNTs and eluted with 25 mL of MeOH. Under these conditions, mean recovery values were between 63 and 100% except for SAM which were around 40%. This means achieving LODs of the method between 7.00 ng/L and 32.0 ng/L, as it will be later described. Five consecutive extractions of spiked Milli-Q water samples at a concentration of 2 μg/L of each SA (see Table 2), showed that the extraction was repeatable with RSD values below 20%.

3.4. Comparison between pristine and magnetic MWCNTs

Once optimum extraction conditions using pristine MWCNTs were established the dSPE procedure was applied to the analysis of

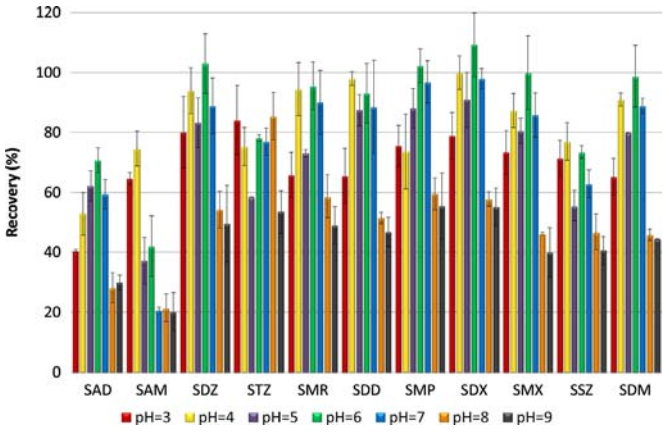

Fig. 3. Effect of the sample pH on the extraction of the eleven SAs from water samples ($n=2$). Extraction conditions: 50 mL of Milli-Q water spiked at 2.5 μg/L of each analyte, 100 mg of MWCNTs and elution with 25 mL of MeOH.

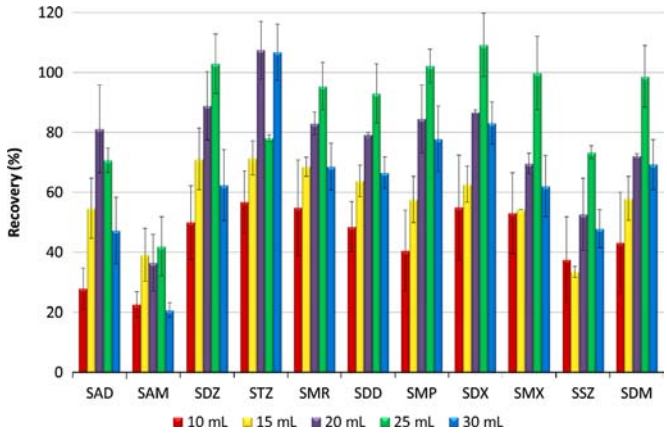

Fig. 4. Effect of the volume of the elution solvent on the extraction of the eleven SAs from water samples ($n=2$). Extraction conditions: 50 mL of Milli-Q water pH 6.0 spiked at 2.5 μg/L of each analyte, 100 mg of MWCNTs and elution with MeOH.

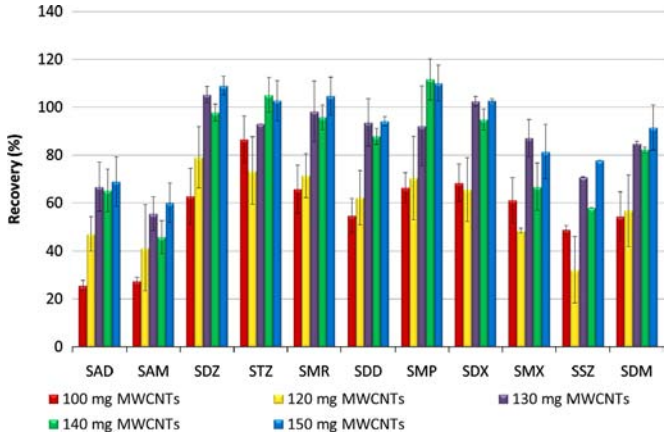

Fig. 5. Effect of the amount of MWCNTs on the extraction of the eleven SAs from water samples ($n=2$). Extraction conditions: 50 mL of Milli-Q water pH 6.0 spiked at 2.5 μg/L of each analyte and elution with 25 mL of MeOH.

Table 2
Average recoveries ($n=5$) and RSD values for the d-SPE-UHPLC-DAD method with the different types of MWCNTs (concentration added = 2 μg/L).

Peak	Antibiotic	MWCNTs Recovery (RSD %)	m-MWCNTs 1:1 Recovery (RSD %)	m-MWCNTs 2:1 Recovery (RSD %)	m-MWCNTs 3:1 Recovery (RSD %)
1	SAD	63 (6)	41 (20)	50 (20)	48 (14)
2	SAM	40 (5)	32 (10)	46 (15)	40 (12)
3	SDZ	90 (18)	52 (18)	76 (12)	62 (15)
4	STZ	83 (17)	46 (11)	62 (14)	47 (18)
5	SMR	91 (18)	53 (18)	77 (13)	61 (16)
6	SDD	95 (14)	55 (18)	75 (13)	59 (16)
7	SMP	85 (17)	36 (18)	43 (19)	22 (10)
8	SDX	100 (16)	53 (20)	62 (9)	47 (10)
9	SMX	86 (11)	51 (18)	69 (7)	59 (16)
10	SSZ	75 (11)	46 (16)	65 (7)	59 (15)
11	SDM	100 (20)	50 (19)	40 (19)	28 (17)

Milli-Q water spiked at 2 μg/L using m-MWCNTs prepared from the ultrasound mixture of MWCNTs and m-NPs in ratios 1:1, 2:1 and 3:1 (w/w).

Subsequent experiments with m-MWCNTs consisted in the extraction of 250 mL of spiked water at pH 6.0 and elution with 25 mL of MeOH. However, before m-MWCNTs were studied, m-NPs were used as sorbents to test if such particles extracted the analytes since in the literature it can also be found some examples in which m-NPs retained, though in a low extent, organic analytes as quinolones (recoveries between 35 and 55%) [16] or linear alkyl benzene sulfonates (37–45%) [14]. In our case, the obtained recoveries were lower than 2% and therefore it was demonstrated that m-NPs do not extract SAs. This was also verified with m-NPs obtained in different batches.

Initially, and with the objective of maintaining the amount of CNTs that provided the highest recovery values (150 mg), 300 mg of m-MWCNTs 1:1, 225 mg of m-MWCNTs 2:1 and 200 mg of m-MWCNTs 3:1 were used. Recoveries obtained with all of them were not satisfactory and varied in the range between 32% for SAM and 55% for SDD using m-MWCNTs 1:1, in the range between 40% for SDM and 77% for SMR with m-MWCNTs 2:1 and between 22% for SMP and 62% for SDZ using m-MWCNTs 3:1. Because the use of m-MWCNTs might alter the retention and the elution steps, several parameters implicated in these stages were slightly modified. In this sense, once the sample was mixed with the nanotubes it was tested to assist the extraction (and also the elution) by sonication. This fact had been previously suggested by other authors [17–20]. Additionally, the amount of each magnetic sorbent and the volume of elution solvent were increased until 400 mg and 35 mL, respectively. However, none of the above mentioned changes improved the extraction. Table 2 provides the results obtained for five consecutive extractions of Milli-Q water samples spiked at 2 μg/L for the three types of magnetic CNTs as well as those obtained for the pristine ones. As it was previously discussed, the 2:1 mixture improved the extraction efficiency if results are compared with those obtained with 1:1 or 3:1 mixtures, but not enough to achieve the recovery values obtained with pristine MWCNTs. These results are also in accordance with those previously obtained by Tang et al. [12] for the analysis of atrazine in water samples. In their work they demonstrated that pristine CNTs also had a slightly higher removal efficiency than m-CNTs

Finally, m-MWCNTs were used to extract the SAs by means of the dSPE procedure developed for the pristine MWCNTs, retaining them in SPE mini columns and drying under vacuum without the use of a magnetic field. This was done in order to fully compare both materials under the same conditions and also to find out if the drying of the material was absolutely necessary. In that case, the use of pristine MWCNTs would be more favorable, since the magnet would not help in the procedure. It could be seen that recoveries increased for the three types of magnetic CNTs being in the ranges between 44% for SAD and SAM and 83% for SDM with the m-MWCNTs 1:1, between 52% for STZ and 119% for SDX with m-MWCNTs 2:1 and between 53% for STZ and 114% for SDD and SMR using m-MWCNTs 3:1. This fact demonstrated that it is necessary to dry the sorbent for the extraction of SAs, what has not been necessary in the applications of m-CNTs previously described in the literature [10–20]. Since the drying step is needed, this would experimentally complicate sample manipulation with the magnet and a dSPE approach like the one developed with pristine MWCNTs (in which no magnet field is applied and the sorbent is retained in a small glass column) is an easier approach. As a result, and since pristine MWCNTs provide slightly higher recovery values it is recommended to carry out the extraction with such materials as previously indicated.

3.5. Matrix-matched calibration

The dSPE method with pristine MWCNTs was then applied to the analysis of Milli-Q and mineral waters. In this last case, samples with low and very low mineral content were selected. The potential matrix effect was studied for each type of sample by comparing the obtained calibration curves of the standards and in each of the three different sample matrices (obtained after the

proposed methodology) at six concentration levels. Each level of concentration was injected in triplicate in the UHPLC-DAD system. Table 3 shows matrix-matched calibration parameters including the regression equation (based on peak areas), R^2 and standard deviation of the residuals ($S_{y/x}$) for the three types of water samples. Determination coefficients higher than 0.990 were obtained in all cases. Statistical comparison (calculation of F and p values using a statistical program–Statgraphics Plus–) of matrix-matched calibration curves with the ones obtained in pure solvent was developed. It could be clearly seen that a matrix effect occurred and statistical differences between slopes, intercepts or both of them were found for all the SAs.

3.6. Recovery study and intraday and interday precision in real samples

Afterwards, an intraday and interday precision study of the method and a recovery study were carried out at two concentration levels (0.12 and 2.0 μg/L) which were extracted five times each ($n=5$) in two days ($n=10$) and injected in triplicate in the UHPLC-DAD system. The results of this recovery study are shown in Table 4. A previous extraction was performed for each blank sample in order to verify the absence of the selected antibiotics. As can be seen, recoveries were in the range 63–108% for Milli-Q water (except for SAM which were around 44%), between 67 and 110% for the water sample with the very low mineral content (except for SAM which were around 44%), and in the range 61–100% for the one with the low mineral content (except, once more, for SAM which were around 53%). It is worth to highlight that recoveries, despite not reaching 100%, were very similar to the ones previously obtained for the extraction of four SAs using several types of CNTs [21,22] but our method clearly provides the extraction of a higher number of SAs. RSD values obtained in the same day were in the range between 2 and 20% for the three types of water. Day-to-day RSD values were in the range between 5 and 20% for milli-Q water, between 3 and 20% for very low mineral content water and between 2 and 20% for low mineral content water.

Table 4 also provides the LODs and LOQs of the whole method. LODs were in the range 7.00–32.0 ng/L, 7.00–31.0 ng/L and 8.00–27.0 ng/L for Milli-Q, very low mineral content and low mineral content water samples, respectively. These LODs were in most cases lower than the ones obtained by Niu et al. [21] for 4 SAs in surface waters (27–38 ng/L) using MWCNTs with a smaller average diameter, although these authors used a larger sample volume (500 mL). Besides, the obtained limits were analogous or even lower than those reached by other authors who used conventional SPE cartridges and more sensitive detection methods [28–30]. For example, Raich-Montiu et al. [28] obtained LODs in the range 1–8 ng/L for 6 SAs extracted from surface water and determined by SPE-HPLC-FD while Ibáñez et al. [30] achieved LODs between 0.05 and 1 μg/L for 4 SAs in water using UHPLC–MS for their later determination. In contrast, the LODs reached were higher than the ones obtained by Chang et al. [25] for 16 SAs extracted by SPE with Oasis HLB cartridges from river and waste waters (8–200 pg/L). However in this last manuscript, the UHPLC was coupled to a MS/MS spectrometer, which provides better LODs. It should be indicated that in most of these works, a reduced number of SAs have been analyzed.

Fig. 6 shows the chromatograms of a spiked and non-spiked low mineral content water sample at 260 nm as detection

Table 3
Matrix matched calibration data of the selected sulfonamides.

Antibiotic	Type of water	Range of concentration tested (μg/L)	Slope ($n=6$)	Intercept ($n=6$)	R^2	$S_{y/x}$	LOD (μg/L)	LOQ (μg/L)
SAD	Milli Q	25–1000	43.51 ± 4.15	$(1.98 \pm 2.62) \times 10^3$	0.995	1.54×10^3	5.64	18.8
	Very low mineral content		59.74 ± 86.31	$(0.42 \pm 38.69) \times 10^2$	0.992	2.52×10^3	3.97	13.2
	Low mineral content		49.02 ± 5.26	$(1.82 \pm 2.47) \times 10^3$	0.994	1.59×10^3	5.49	18.3
SAM	Milli Q	25–1000	42.83 ± 2.13	$(0.13 \pm 1.34) \times 10^3$	0.999	7.86×10^2	7.12	23.7
	Very low mineral content		59.43 ± 3.96	$(-0.60 \pm 2.50) \times 10^3$	0.998	1.46×10^3	7.11	23.71
	Low mineral content		47.21 ± 4.48	$(1.47 \pm 2.11) \times 10^3$	0.995	1.36×10^3	5.92	19.7
SDZ	Milli Q	25–1000	45.17 ± 3.37	$(0.28 \pm 2.13) \times 10^3$	0.997	1.25×10^3	5.72	19.1
	Very low mineral content		63.41 ± 4.40	$(0.06 \pm 27.73) \times 10^2$	0.998	1.63×10^3	4.72	15.7
	Low mineral content		51.20 ± 6.87	$(0.80 \pm 3.23) \times 10^3$	0.991	2.08×10^3	4.84	16.1
STZ	Milli Q	25–1000	46.61 ± 5.05	$(1.30 \pm 3.18) \times 10^3$	0.994	1.87×10^3	5.42	18.1
	Very low mineral content		66.02 ± 7.07	$(-0.23 \pm 4.34) \times 10^3$	0.991	2.83×10^3	5.67	18.9
	Low mineral content		54.32 ± 6.63	$(1.15 \pm 3.12) \times 10^3$	0.992	2.01×10^3	5.21	17.4
SMR	Milli Q	25–1000	31.26 ± 3.03	$(0.38 \pm 1.91) \times 10^3$	0.995	1.12×10^3	7.37	24.6
	Very low mineral content		45.65 ± 3.40	$(-0.44 \pm 2.14) \times 10^3$	0.997	1.26×10^3	7.04	23.5
	Low mineral content		37.84 ± 3.82	$(0.45 \pm 1.79) \times 10^3$	0.995	1.16×10^3	6.89	23.0
SDD	Milli Q	25–1000	39.66 ± 3.38	$(-0.91 \pm 21.32) \times 10^2$	0.996	1.25×10^3	7.88	24.6
	Very low mineral content		56.11 ± 4.58	$(-1.00 \pm 2.89) \times 10^3$	0.997	1.70×10^3	6.35	21.2
	Low mineral content		45.63 ± 6.34	$(0.93 \pm 29.80) \times 10^3$	0.990	1.92×10^3	5.20	17.3
SMP	Milli Q	25–1000	54.23 ± 4.38	$(0.45 \pm 2.76) \times 10^3$	0.997	1.62×10^3	5.37	17.9
	Very low mineral content		90.73 ± 6.09	$(-0.76 \pm 3.30) \cdot 10^3$	0.997	2.29×10^3	3.80	12.7
	Low mineral content		62.41 ± 7.81	$(0.78 \pm 3.67) \times 10^3$	0.992	2.37×10^3	3.53	11.8
SDX	Milli Q	25–1000	51.98 ± 3.82	$(0.29 \pm 2.41) \times 10^3$	0.997	1.41×10^3	6.59	22.0
	Very low mineral content		74.05 ± 4.61	$(-0.68 \pm 2.91) \times 10^3$	0.998	1.71×10^3	6.11	20.4
	Low mineral content		57.14 ± 6.72	$(0.43 \pm 3.16) \times 10^3$	0.993	2.04×10^3	6.47	21.6
SMX	Milli Q	25–1000	33.62 ± 2.50	$(-0.38 \pm 15.78) \times 10^2$	0.997	9.26×10^2	7.44	24.8
	Very low mineral content		47.78 ± 3.22	$(-0.59 \pm 2.03) \cdot 10^3$	0.998	1.19×10^3	7.12	23.8
	Low mineral content		38.79 ± 5.24	$(0.22 \pm 2.46) \times 10^3$	0.991	1.59×10^3	7.84	26.1
SSZ	Milli Q	25–1000	35.22 ± 2.73	$(-0.57 \pm 1.62) \times 10^3$	0.995	1.11×10^3	6.05	20.2
	Very low mineral content		49.21 ± 4.00	$(-1.65 \pm 2.52) \times 10^3$	0.997	1.48×10^3	6.05	20.2
	Low mineral content		40.63 ± 3.99	$(-1.48 \pm 1.88) \times 10^3$	0.995	1.21×10^3	7.45	24.8
SDM	Milli Q	25–1000	40.27 ± 3.54	$(0.53 \pm 22.34) \times 10^2$	0.996	1.31×10^3	7.32	24.3
	Very low mineral content		57.37 ± 3.87	$(-0.61 \pm 2.44) \times 10^3$	0.998	1.43×10^3	7.25	24.2
	Low mineral content		47.03 ± 5.32	$(1.79 \pm 2.50) \times 10^3$	0.993	1.61×10^3	6.55	21.8

[a]Calculated for S/N=3.
[b]Calculated for S/N=10.

Table 4
Results of the recovery study of the MWCNTs–dSPE–UHPLC-DAD method for the selected antibiotics in the three types of water.

Antibiotic	Milli-Q water		LOD method (μg/L)	LOQ method (μg/L)	Very low mineral content water		LOD method (μg/L)	LOQ method (μg/L)	Low mineral content water		LOD method (μg/L)	LOQ method (μg/L)
	Level 1 (0.12 μg/L) Recovery (RSD %)	Level 2 (2 μg/L) Recovery (RSD %)			Level 1 (0.12 μg/L) Recovery (RSD %)	Level 2 (2 μg/L) Recovery (RSD %)			Level 1 (0.12 μg/L) Recovery (RSD %)	Level 2 (2 μg/L) Recovery (RSD %)		
SAD	78 (17)	63 (6)	0.014	0.046	72 (20)	67 (11)	0.014	0.047	83 (8)	100 (15)	0.011	0.035
SAM	47 (12)	40 (5)	0.032	0.106	48 (17)	40 (3)	0.031	0.103	53 (4)	50 (6)	0.027	0.089
SDZ	108 (6)	90 (18)	0.007	0.023	83 (19)	101 (13)	0.007	0.024	83 (11)	85 (16)	0.008	0.027
STZ	84 (15)	83 (17)	0.011	0.036	110 (19)	100 (10)	0.009	0.028	74 (2)	83 (12)	0.011	0.038
SMR	88 (13)	91 (18)	0.008	0.027	86 (12)	105 (12)	0.008	0.026	80 (15)	90 (6)	0.009	0.029
SDD	79 (18)	95 (14)	0.008	0.026	85 (12)	105 (9)	0.007	0.024	75 (18)	90 (5)	0.008	0.028
SMP	81 (20)	85 (17)	0.010	0.034	97 (17)	88 (6)	0.009	0.031	74 (20)	61 (13)	0.013	0.042
SDX	108 (15)	100 (16)	0.009	0.030	75 (17)	105 (11)	0.010	0.034	75 (6)	90 (6)	0.011	0.038
SMX	80 (14)	86 (11)	0.017	0.056	82 (17)	104 (12)	0.015	0.050	86 (6)	80 (11)	0.017	0.055
SSZ	79 (7)	75 (11)	0.015	0.052	83 (16)	94 (11)	0.013	0.045	69 (17)	64 (7)	0.018	0.059
SDM	81 (13)	100 (20)	0.012	0.041	69 (15)	94 (9)	0.014	0.046	83 (13)	87 (11)	0.013	0.044

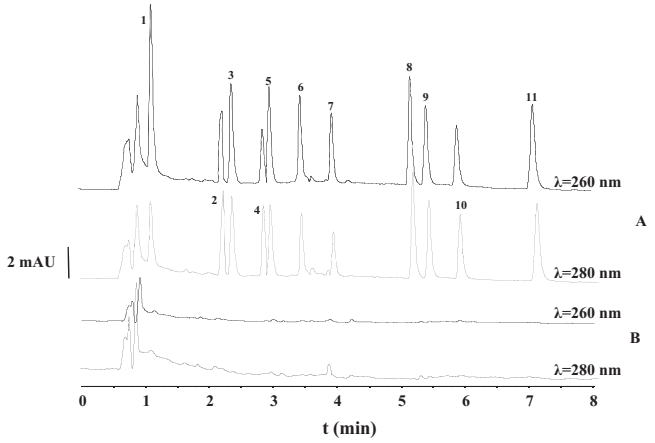

Fig. 6. MWCNTs–dSPE–UHPLC-DAD chromatograms of a mineral water sample with a low mineral content spiked (A) and non-spiked (B) with the SAs at 2 μg/L For other conditions see legend of Fig. 2.

wavelength, after the application of the developed MWCNT–dSPE–UHPLC-DAD method. Similar chromatograms were obtained for the other two types of samples.

4. Conclusions

A new methodology based on the use of dSPE, with MWCNTs as stationay phases, combined with UHPLC-DAD was developed to determine 11 SAs in different water samples. Pristine and m-MWCNTs (synthesized in this work) were compared as sorbents. Results demonstrated that, though m-MWCNTs facilitated the application of the methodology, the highest extraction efficiencies were obtained with the unmodified materials. Besides, in the dSPE with m-MWCNTs it was extremely necessary to dry them before elution which clearly complicates the procedure. The proposed method is simple, selective, repeatable and effective, as demonstrated by the precision, calibration and recovery studies carried out. The optimum extraction conditions allowed the quantitative determination of SAs in the low ng/L range. This work represents the first application in which SAs are extracted by dSPE using MWCNTs as sorbents as well as the first work in which m-MWCNTs are tested as sorbents to extract this family of antibiotics.

Acknowledgments

A.V.H.H. thanks the Spanish Ministry of Education for the FPU grant at the University of La Laguna. J.H.B. thanks the Spanish Ministry of Economy and Competitiveness for the Ramón y Cajal contract at the University of La Laguna. This work has been supported by the Spanish Ministry of Economy and Competitiveness (projects AGL2008-00990/ALI and AGL2009-07884/ALI). Authors would also like to thank Dr. Mario Díaz from the Department of Animal Biology of the University of La Laguna. Authors would also like to thank the Electron Microscopy Service of the "Servicios Generales de Apoyo a la Investigación" (SEGAI) of the University of La Laguna for the SEM analysis.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.07.060.

References

[1] M.J. García-Galán, M.S. Díaz-Cruz, D. Barceló, TrAC—Trends Anal. Chem. 27 (2008) 1008–1022.
[2] K. Hruska, M. Franek, Vet. Med.—Czech 57 (2012) 1–35.
[3] W.W. Buchberger, Anal. Chim. Acta 593 (2007) 129–139.
[4] A.V. Herrera-Herrera, M.A. González-Curbelo, J. Hernández-Borges., M. A. Rodríguez-Delgado, Anal. Chim. Acta 734 (2012) 1–30.
[5] L.M. Ravelo-Pérez, A.V. Herrera-Herrera, J. Hernández-Borges, M.A. Rodríguez-Delgado, J. Chromatogr. A 1217 (2010) 2618–2641.
[6] K. Pyrzynska, Chemosphere 83 (2011) 1407–1413.
[7] K. Scida, P.W. Stege, G. Haby, G.A. Messina, C.D. García, Anal. Chim. Acta 691 (2011) 6–17.
[8] L. Jiang, L. Gao, Chem. Mater. 15 (2003) 2848–2853.
[9] Y. Deng, C. Deng, D. Yang, C. Wang, S. Fu, X. Zhang, Chem. Commun. 44 (2005) 5548–5550.
[10] D. Pardasani, P.K. Kanaujia, A.K. Purohit, A.R. Shrivastava, D.K. Dubey, Talanta 86 (2011) 248–255.
[11] Y.B. Luo, Q.W. Yu, B.F. Yuan, Y.Q. Feng, Talanta 90 (2012) 123–131.
[12] W.W. Tang, G.M. Zeng, J.L. Gong, Y. Liu, X.L. Wang, Y.Y. Liu, Z.F. Liu, L. Chen, X. R. Zhang, D.Z. Tu, Chem. Eng. J. 211–212 (2012) 470–478.
[13] S. Xu, C. Jiang, Y. Lin, L. Jia, Microchim. Acta 179 (2012) 257–264.
[14] B. Chen, S. Wang, Q. Zhang, Y. Huang, Analyst 137 (2012) 1232–1240.
[15] C. Zhang, J. Sui, J. Li, Y. Tang, W. Cai, Chem. Eng. J. 210 (2012) 45–52.
[16] G. Morales-Cid, A. Fekete, B.M. Simonet, R. Lehmann, S. Cárdenas, X. Zhang, M. Valcárcel, P. Schmitt-Kopplin, Anal. Chem. 82 (2010) 2743–2752.
[17] Y. Guan, C. Jiang, C. Hu, L. Jia, Talanta 83 (2010) 337–343.
[18] J. Ding, Q. Gao, L. Xiao-Shui, W. Huang, Z.G. Shi, Y.Q. Feng, J. Sep. Sci. 34 (2011) 2498–2504.

[19] Z. Zhang, X. Yang, X. Chen, M. Zhang, L. Luo, M. Peng, S. Yao, Anal. Bioanal. Chem. 401 (2011) 2855–2863.
[20] Q. Zhao, F. Wei, Y.B. Luo, J. Ding, N. Xiao, Y.Q. Feng, J. Agric. Food Chem. 59 (2011) 12794–12800.
[21] H. Niu, Y. Cai, Y. Shi, F. Wei, J. Liu, S. Mou, G. Jiang, Anal. Chim. Acta 594 (2007) 81–92.
[22] G.Z. Fang, J.X. He, S. Wang, J. Chromatogr. A 1127 (2006) 12–17.
[23] S. Babić, A.J.M. Horvat, D.M. Pavlović, M. Kaštelan-Macan, Trends Anal. Chem. 26 (2007) 1043–1061.
[24] S. Bogialli, A. Di Corcia, Anal. Bioanal. Chem. 395 (2009) 947–966.
[25] H. Chang, J. Hu, M. Asami, S. Kunikane, J. Chromatogr. A 1190 (2008) 390–393.
[26] G. D´Orazio, S. Rocchi, S. Fanali, J. Chromatogr. A 1255 (2012) 277–285.
[27] A. Gentili, D. Perret, S. Marchese, TrAC—Trends Anal. Chem. 24 (2005) 704–733.
[28] J. Raich-Montiu, J. Folch, R. Compañó, M. Granados, M.D. Prat, J. Chromatogr. A 1172 (2007) 186–193.
[29] S. Wang, H.Y. Zhang, L. Wang, Z.J. Duan, I. Kennedy, Food Addit. Contam. 23 (2006) 362–384.
[30] M. Ibáñez, C. Guerrero, J.V. Sancho, F. Hernández, J. Chromatogr. A 1216 (2009) 2529–2539.