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Comparative Study of Different Fabric Phase Sorptive Extraction Sorbents to Determine Emerging Contaminants from Environmental Water Using Liquid Chromatography-Tandem Mass Spectrometry

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ABSTRACT

A new sorptive extraction technique, fabric phase sorptive extraction (FPSE), using different coating chemistries: non-polar sol-gel poly(dimethyldiphenylsiloxane) (PDMDPS), medium polar sol-gel poly(tetrahydrofuran) (PTHF), and polar sol-gel poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPG-PEG triblock) and sol-gel Carbowax 20M were evaluated to extract a group of pharmaceuticals and personal care products (PPCPs) with wide range of polarity from environmental aqueous samples. Different parameters affecting FPSE such as sample pH, stirring speed, addition of salt, extraction time, sample volume, elution solvent and desorption time were optimized for each sorbent coated FPSE media. Under optimum conditions, FPSE media coated with sol-gel Carbowax 20M provided the highest absolute recoveries (77-85%) for majority of the analytes with the exception of the most polar ones. Nevertheless, all four sorbents offered better recovery compared to the commercially available coating for stir-bar sorptive extraction based on Ethylene Glycol/Silicone (EG/Silicone).

The method based on FPSE with sol-gel Carbowax 20M media and liquid chromatography–(electrospray ionization) tandem mass spectrometry (LC-(ESI) MS/MS) was developed and validated for environmental water samples. Good apparent recoveries (41 - 80%), detection limits (1 - 50 ng L⁻¹), repeatability (%RSD<15%, n=5) and reproducibility (%RSD<18%, n=5) were achieved.

1. INTRODUCTION

Effective sample preparation strategy as well as highly sensitive analytical instrument is indispensable to determine low concentrations of contaminants in the environmental samples. Among them, different types of emerging organic contaminants

(EOCs) are found at concentration levels from ng L^{-1} to $\mu\text{g L}^{-1}$ in environmental samples such as waste water and surface water. In addition, these EOCs are grouped in different types of compounds with wide range of physicochemical properties. An example of this is the pharmaceutical and personal care products (PPCPs) group, whose polarities differ broadly from polar to non-polar [1-3].

Several extraction techniques are used to clean-up and pre-concentrate these analytes from a wide variety of sample matrices. Over the last few years, different sorptive extraction techniques such as solid-phase extraction (SPE), solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE) have been commonly used in liquid sample treatment [4-8]. The efficiency of sorption primarily depends upon the characteristics of the sorbent material used as well as the physicochemical properties of the analytes [5,9,10]. Among all the sample preparation technique, SPE is the most commonly used due to the wide variety of extraction phases available [5,11]. SPME, predominantly used in combination with gas chromatography, has also been established due to the availability of different types of fibers [12-14]. However, the main limitation of SPME is the low sample capacity due to the small sorbent loading constrained by the shape and size of the fiber support.

To overcome this limitation, SBSE emerged [4,11]. The main limitation of SBSE is that, till very recently, only one non-polar coating based on poly(dimethylsiloxane) (PDMS) was commercially available, which showed excellent performance for the sorption of non-polar analytes but most of the polar analytes were not retained at all or retained poorly [15-17]. Nevertheless, in the last years, two new SBSE polar coatings have been commercially available and trademarked as Acrylate Twister[®] (based on polyacrylate with proportion of polyethylene glycol) and EG/Silicone Twister[®] (based on polyethylene glycol modified with silicone). Till date, these new coatings have been evaluated for the extraction of PPCPs [18] and benzothiazoles [19] from wastewater samples, and volatile organic compounds (VOCs) in oil, perfume and coffee samples [20] with better extraction performances than those obtained with the PDMS coating [18,20]. Different polar coatings and device formats have also been developed in-house using different synthetic strategies, mainly based on monolithic approaches [21,22] or sol-gel technology [23-25].

Recently, a new sorptive extraction technique, fabric phase sorptive extraction (FPSE), has been introduced [26,27]. FPSE consists of 25 x 20 mm fabric pieces coated with different sorbent chemistries using sol-gel technology. The amount of sorbent material, which is on an average 10 times higher than in the SBSE, is uniformly distributed on the cellulose/polyester/fiber glass fabric substrate. Due to the high primary contact surface area (1000 mm²) of FPSE media, inherently porous sol-gel sorbent coating, high volume of sorbent loading in the form of ultra-thin porous film, and the strong chemical bonding between the substrate and the sorbent, FPSE demonstrates remarkably fast extraction kinetic, extraordinary extraction sensitivity as well as high solvent and chemical stability. FPSE incorporates the advantages of equilibrium based extraction, exploits the benefits of sol-gel coating technology, utilizes the permeability of fabric substrate and increases the primary contact surface area for rapid analyte-sorbent interaction. A large number of sorbent chemistries are available which include: sol-gel poly(dimethylsiloxane), sol-gel poly(dimethyldiphenylsiloxane), sol-gel poly(diphenylsiloxane), sol-gel C₁₈, sol-gel C₈, sol-gel graphene, sol-gel poly(tetrahydrofuran), sol-gel poly(ethylenglycol), sol-gel Carbowax 20M and sol-gel poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) [26].

To date, only a few studies have reported the use of FPSE technique. For example, Kumar et al. [27] demonstrated the suitability of sol-gel poly(tetrahydrofuran)(PTHF) coated FPSE media to extract bisphenol A, 17 β -Estradiol and 17 α -ethynylestradiol from urine and different types of water samples. Samanidou et al. [28] reported the extraction of highly polar amphenicol antibiotics directly from raw milk using sol-gel short-chain poly(ethylene glycol) (PEG) coated FPSE media and demonstrated a substantial simplification in the sample preparation compared to matrix solid-phase dispersion. Racamonde et al. [29] also used sol-gel PEG coated FPSE media to determine non-steroidal anti-inflammatory drugs in different type of environmental water samples. Roldán-Pijuán et al. [30] used the same FPSE technique with integrated magnetic stirring mechanism known as stir FPSE to determine triazines herbicides in environmental water samples. However, none of the FPSE studies have dealt with contaminants with wide

polarity range at trace concentration levels present in complex matrices. At present, there is a long-standing demand for a simple, green, and robust sample preparation and analysis technique that can simultaneously handle polar, medium polar, and non-polar analytes at their low level concentrations present in complex samples. The aim of the present study is to compare four FPSE coating chemistries: non-polar PDMDPS, medium polar PTHF, polar PEG-PPG-PEG triblock and polar Carbowax 20M to extract a group of PPCPs (log K_{ow} values range from -0.6 to 6.1) from environmental water samples. The selection of the best sorbent material for the target PPCPs was followed by the development of an analytical method to determine the selected compounds in river and waste waters by FPSE/LC-MS/MS.

2. MATERIALS AND METHODS

2.1. Reagents and chemicals

The reagents used in the preparation of FPSE media were of analytical grade. Sol-gel active polymers poly(tetrahydrofuran) (PTHF) and poly(ethylene glycol) (Carbowax 20M), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) were purchased from Sigma-Aldrich (Saint Louis, MO, USA); poly(dimethyldiphenylsiloxane) (PDMDPS) was purchased from Gelest (Morrisville, PA, USA). Acetone, methylene chloride (CH_2Cl_2), methyltrimethoxysilane (MTMOS), 3-cyanopropyltriethoxysilane (3-CPTEOS) and trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Thermo Fisher Scientific (Milwaukee, WI, USA). Substrates for fabric phase sorptive extraction media were obtained from Jo-Ann Fabric (Miami, FL, USA).

Unlike other material synthesis, sol-gel synthesis of extraction sorbents does not require a lot of sophisticated equipment. An Eppendorf Microcentrifuge Model 5415 R (Eppendorf North America Inc., Hauppauge, NY, USA) was used to centrifuge different sol solutions in order to obtain particle free sol solutions. A Fisher Scientific Digital Vortex Mixture (Fisher Scientific, Pittsburg, PA, USA) was employed for thorough mixing of different solutions. Bubble-free sol solutions were obtained using a 2510 BRANSON Ultrasonic Cleaner (Branson Ultrasonics, Danbury, USA). A Barnstead Nanopure Diamond (Model D11911) deionized water unit (Dubuque, IA, USA) was used to obtain ultra-pure deionized water (18.2 MV cm^{-1}) for sol-gel synthesis and substrate treatment in the USA lab.

The representative PPCPs: paracetamol (PARA), caffeine (CAFF), antipyrine (APy), propranolol hydrochloride (PROP), methylparaben (MPB), carbamazepine (CBZ), propylparaben (PrPB), 2,4-dihydroxybenzophenone (DHB), benzylparaben (BzPB), 2,2-dihydroxy-4-4-methoxybenzophenone (DHMB), diclofenac (DICLO), 3-benzophenone (BP-3), triclocarban (TCC), triclosan (TCS) were purchased from Sigma-Aldrich (Steinheim, Germany). Table 1 shows the relevant physicochemical properties of the selected PPCPs. All PPCPs standards were high purity grade (>98%). Stock solutions of individual standards were prepared in methanol (MeOH) at concentration of 1000 mg L^{-1} . A mixture of standards of all compounds at 50 mg L^{-1} was prepared in methanol. Working standard solution prepared weekly by diluting with mixture of ultra-pure water pH 3 and acetonitrile (ACN) (80:20). These solutions were stored at 4°C . HPLC grade MeOH, and ACN was supplied from Scharlab (Barcelona, Spain), and formic acid (HCOOH) 95% and sodium chloride (NaCl) were from Sigma-Aldrich (Steinheim, Germany). Ultra-pure water was obtained from a water purification system (Veolia Waters, Barcelona, Spain).

2.2. Preparation of sol-gel poly(dimethyldiphenylsiloxane) (sol-gel PDMDPS), sol-gel poly(tetrahydrofuran) (sol-gel PTHF), sol-gel poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (sol-gel PEG-PPG-PEG) and sol-gel Carbowax 20M coated fabric phase sorptive extraction media

Preparation of fabric phase sorptive extraction media coated with any sol-gel derived sorbent involves a number of sequential steps including: (a) selecting and pretreating the substrate; (b) design and preparation of sol solution for coating; (c) sol-gel coating on the treated substrate; (d) conditioning and aging of the sol-gel coated FPSE media; (e) post-coating cleaning of the sol-gel coated FPSE media.

2.2.1. Selecting and pretreating the substrate for sol-gel coating

The substrate selection for sol-gel coating is primarily dependent on: (a) the hydrophilicity or hydrophobicity of the analyte(s) of interest; (b) the strategy used in analyte back-extraction after preconcentrating onto the FPSE media. If solvent mediated back-extraction is used, fabric substrates such as cellulose, polyester are preferred. On the other hand, if thermal desorption is used, glass fiber based fabric is the best option. Once the substrate selection is made, a chemical clean-up procedure needs to be applied in order to remove external dirt, particulates, and the residues of fabric finishing chemicals such as starch, dye, fillers, etc. and to activate surface hydroxide groups before administering the sol-gel coating process. This fabric treatment regimen is a modified form of a standard industrial process known as “mercerization” [31]. A detailed account of the fabric treatment process is described elsewhere [27]

2.2.2. Design and preparation of the sol solutions for substrate coating

The design of the sol solution primarily depends on the physicochemical properties of the target analytes and includes selection of: (a) organic polymer; (b) inorganic or organically modified inorganic polymer; (c) solvent/solvent system; (d) catalyst; (e) water content; and (f) relative molar ratio of the ingredients. Considering the wide polarity range of the selected PPCPs, a nonpolar PDMDPS, a medium polar PTHF, a relatively polar PEG-PPG-PEG copolymer, and a highly polar Carbowax 20M were selected as potential organic polymer candidates for the sol solution. PDMDPS possesses 14-18% diphenyl containing blocks in the polymer back-bone which should offer π - π interactions, in addition to other intermolecular interactions, towards the target analytes during extraction. PTHF is a hydroxyl-terminated polar polymer frequently used in synthesizing inorganic-organic hybrid materials. Due to the presence of less number of C-O-C linkages into the polymer chain compared to PEG, PTHF is a medium polarity polymer. PEG-PPG-PEG is an amphiphilic block terminal copolymers containing sol-gel active functional groups in both the ends. The selectivity of the block copolymer originates from the hydrophilic segment of PEG and hydrophobic segment of PPG. Carbowax 20M is a polar polymer with diversified applications in foods, cosmetics, pharmaceuticals, biomedicines, etc. Due to the high polarity of PEG, a number of polar microextraction sorbents as well as gas chromatographic stationary phase have been developed.

Another major decision in sol solution design is choosing the appropriate inorganic/organically modified inorganic precursor. The integrity of the hybrid organic-inorganic sorbents largely depends on the sol-gel precursor and/or the sol-gel reaction and processing conditions. Although tetraalkoxysilanes are commonly used as the sol-gel precursors, Malik and co-workers introduced methyltrimethoxysilane (MTMS) in the sol-gel coating technology [32] in order to minimize cracking and shrinking of sol-gel coating. Since then, hundreds of new sol-gel sorbents have been developed using this precursor [33]. The presence of a nonpolar methyl group in MTMS reduces the overall polarity of the hybrid sorbent, regardless of the polarity of the organic polymer employed. As such, it is counter-intuitive to use MTMS as a precursor when enhancing polarity of the composite material is the goal. Herein, we

used 3-cyanopropyltriethoxysilane (3-CPTEOS) as the precursor to increase the polarity of sol-gel Carbowax 20M. A number of research groups have used this precursor along with nonpolar polymers to increase the polarity of the composite material [32,34]. The relative molar ratio of sol solution ingredients were designed based on a previously described formulation [35]. However, due the fact that different polymers have different average molar mass, molar ratio of polymers to other sol solution ingredients varied significantly. Also, in order to have a homogenous sol solution, on one hand, CH₂Cl₂ was used for sol-gel PDMDPS and sol-gel PTHF. On the other hand, an equimolar mixture of CH₂Cl₂ and acetone was used for sol-gel PEG-PPG-PEG and sol-gel Carbowax 20M. The molar ration between precursor: solvent: catalyst: water (1: 3.90: 1.31: 0.30) were kept constant in all the sol solutions. The molar ratio between the precursor and PDMDPS, PTHF, PEG-PPG-PEG, and Carbowax 20M were 1:0.1, 1:0.4, 1:0.05, and 1:0.02, respectively. Exact sol solution composition for individual coating can be found elsewhere [27].

2.2.3. Sol-gel coating process

Preparation of a sol solution for a specific sol-gel coating is followed by the sol-gel coating on the treated substrate. The sol-gel coatings on the substrates were carried out for a duration of 4 hours. The sol-gel coating process, conditioning and aging of the sol-gel coated FPSE media and the final cleaning of the sol-gel coated FPSE media are described in previous reports [27].

2.3. Fabric phase sorptive extraction

The FPSE conditions were optimized for each fabric media. Before using it for extraction, the FPSE media was conditioned and equilibrated by immersing in MeOH for 5 min and then dried by air. For the extraction, the FPSE media was immersed into a 12 mL glass vial having 10 mL of sample adjusted to pH 3 and containing 10% of NaCl (w/v). The sample was stirred for 4 h at room

temperature. After extraction, the FPSE media was removed from the sample and dried with lint-free tissue. For liquid desorption (LD), the FPSE media was introduced into a 5 mL glass vial containing 1 mL of MeOH and placed in an ultrasonic bath for 5 min. The extract was evaporated to dryness under gentle stream of nitrogen. The residue obtained was re-dissolved in 1 mL of solution of ultra-pure water at pH 3 and ACN (80:20, v/v). Then, the extract was injected to LC-(ESI)MS/MS. After every use, the FPSE media was cleaned three times with 2 mL MeOH in the ultrasonic bath for 5 min, then dried and stored in the air tight glass vial till the next experiment.

2.4. Liquid chromatography-tandem mass spectrometry (LC-(ESI)MS/MS) analysis

The chromatographic determination was performed with a 1200 Agilent liquid chromatograph, equipped with an automatic injector, a degasser, a quaternary pump, a column oven, and a 6410 series triple quadrupole mass spectrometer using electrospray ionization (ESI) (Agilent Technologies, Waldron, Germany).

The chromatographic column was a Kromasil 100 C₁₈ (150 mm × 4.6 mm i.d., 5 μm) from Teknokroma (Barcelona, Spain). ACN and ultra-pure water adjusted to pH 3 with HCOOH were used as the mobile phase. The gradient started at 20% ACN, which was increased to 80% ACN in 15 min, then to 100% ACN in 8 min and kept constant for 1 min. Finally, it returned to the initial conditions in 2 min. The chromatographic separation was achieved in less than 20 min. The temperature of the chromatographic column was maintained at 40°C and the flow-rate was 0.6 mL min⁻¹, and 50 μL were injected to LC-(ESI)MS/MS.

The LC-MS/MS parameters were based on a previous study [18] and optimized by injecting each compound at 1 μg L⁻¹ in mixture of ultra-pure water pH 3 and ACN (80:20, v/v) individually in flow injection analysis (FIA). Depending on the acidic or basic properties of compounds, positive [M+H]⁺ or negative [M-H]⁻ ESI mode were used. PARA, CAFF, APy, PROP, CBZ and BP-3 were

acquired in positive ionization mode and MPB, PrPB, DHB, BzPB, DHMB, DICLO, TCC and TCS were in negative ionization mode. The optimal conditions for analytes were as follows: nebulizer pressure of 45 psi, drying gas (N₂) flow-rate of 12 L min⁻¹, source temperature of 350°C and a capillary potential of 4000 V. Ionization mode, cone voltage and collision energies were optimized for each analyte in order to obtain two multiple reaction monitoring (MRM) transitions. The optimized parameters are summarized in Table 1.

All selected compounds showed good linearity ($R^2 \geq 0.999$) by direct injection with a linear range of 0.1 - 50 µg L⁻¹, except for TCS which were of 2 - 50 µg L⁻¹. The instrumental limit of detection (LODs), calculated as signal-to-noise ratio (S/N) of 3 ranged from 0.01 - 0.5 µg L⁻¹. The instrumental limits of quantification (LOQs) were calculated as the concentration of the lowest point of the calibration curve.

2.5. Sampling

River water samples were collected from the Ebre River in Spain. Influent and effluent waste waters were collected from the domestic wastewater treatment plant (WWTP) from Tarragona (Spain). All water samples were filtered using Magna, nylon supported 0.45 µm membrane (Fisher brand, Loughborough, UK), acidified to pH 3 with HCl and stored at 4°C until analysis.

3. RESULTS AND DISCUSSION

3.1. Chemistry of the FPSE substrates and the sol-gel coatings

A large number of commercially available natural and synthetic fabrics can be used as the potential candidates as substrate for FPSE which includes cellulose, polyester, nylon, fiber glass and polyamide. All these fabrics either contain readily available sol-gel active functional groups or may have the capability to contain sol-gel active functional groups *via* surface modification. However, polyester and cellulose fabrics inherently possess sol-gel active functional groups and therefore both fabrics were selected as the substrates for sol-gel coating. Cellulose fabric is known to be hydrophilic and polyester fabric hydrophobic [27]. Since both the substrate and the sol-gel coating contribute to the final selectivity and polarity of the resulting extraction media, a relatively non-polar organic polymer PDMDPS was used as the organic polymer to coat hydrophobic polyester substrate in order to create a non-polar extraction media. PolyTHF is medium polar, whereas, PEG-PPG-PEG triblock and Carbowax 20M polymers are considered as highly polar polymers. As such, they were used to coat hydrophilic cellulose substrate in order to develop extraction media with medium and high polarities.

The chemical reactions involving the sol-gel coating process are well studied and widely reported [34]. The creation of sol-gel hybrid organic-inorganic coating on the substrate involves: (1) controlled catalytic hydrolysis of the sol-gel precursor; (2) polycondensation of hydrolyzed precursor, leading to a growing three-dimensional sol-gel network; (3) random incorporation of sol-gel active polymers into the evolving sol-gel network; (4) chemical immobilization of the growing sol-gel network to the flexible cellulose and polyester substrates *via* condensation. A general reaction scheme for creating sol-gel hybrid organic-inorganic coating on the substrate is shown in Figure 1.

During the polycondensation, the growing sol-gel network reacts with available surface hydroxyl groups of cellulose or polyester microfibrils, resulting in a covalently bonded sol-gel hybrid coating uniformly distributed throughout the substrate matrix with chemical stability as well as highly accessible active sites for efficient and fast analyte extraction. A schematic representation of sol-gel Carbowax 20M coated FPSE media is demonstrated in Figure 2.

3.2. Optimization of FPSE procedure

As the selected analytes possess wide range of polarity, four different FPSE media that covers different polarity (i.e. non-polar with PDMDPS, mid-polar with PTHF, and more polar with PEG-PPG-PEG triblock and Carbowax 20M) were studied and compared. Firstly, different parameters affecting FPSE were optimized for each FPSE media in order to obtain the maximum extraction efficiency with each fabric coating. The extraction parameters optimized were pH, addition of salt, stirring speed, extraction time and volume of sample. After extraction, desorption of analytes is also a crucial step in FPSE; in this case, LD was used since the material can be folded so that the volume required is low. In LD, parameters such as mode of desorption, solvent and desorption time were also optimized.

These parameters were optimized under following initial experimental conditions: 10 mL of ultrapure water adjusted at pH 3 with HCOOH, spiked at $0.2 \mu\text{g L}^{-1}$ for all the compounds and $1 \mu\text{g L}^{-1}$ for triclosan with the mixture of analytes stirring at 900 rpm for 1 h at room temperature and the LD was performed by soaking the fabric sorbent in 1 mL of MeOH for 10 minutes. These conditions were selected from previous experience in SBSE [18], where the same compounds were extracted. The optimization experiments were carried out with all four FPSE media: sol-gel PDMDPS, sol-gel PTHF, sol-gel PEG-PPG-PEG triblock copolymer and Carbowax 20M. Thus, in the next section, we discuss in general the results of each fabric sorbent and in more detail the ones from the Carbowax 20M sorbent because this sorbent provided the best results.

3.2.1. Liquid desorption conditions

LD consisted of immersing the FPSE media in suitable organic solvent to release the extracted analyte from the extraction media. The extracted aliquots were evaporated to dryness and the residue redissolved in 1 mL of ultra-pure water at pH 3 and ACN (80:20, v/v). No significant losses of the analytes during the evaporation step were observed (1-3%).

Two desorption volumes (5 mL and 1 mL) were tested, and when 5 mL were used no improvement in the results were observed. It should be highlighted that only 1 mL of desorption solvent was necessary to completely cover the fabric sorbent. This small volume contributed to enhance the sensitivity of the method as well as required less time during the evaporation step, and therefore, 1 mL was selected as desorption volume.

The modes to desorb the analytes from FPSE were first tested by soaking the fabric sorbent in desorption solvent with and without sonication. As expected, we observed an increase in recovery of 12-15% when sonication was applied.

To ensure the complete desorption of the analytes, different solvents were tested: MeOH, ACN and a mixture of MeOH/ACN (50:50, v/v). When 1 mL of these desorption solvent was evaluated, it was observed that MeOH showed better recoveries (increase of ~ 5%) compared with ACN and MeOH/ACN (50:50, v/v) for all of the compounds. Therefore, sonication with 1 mL of MeOH was chosen as the desorption conditions. Desorption time was also investigated between 5 and 15 min, and sonication for 5 min was enough to desorb all the analytes from the sol-gel PDMDPS, sol-gel PTHF, sol-gel Carbowax 20M sorbents. However, sol-gel PEG-PPG-PEG triblock sorbent needed 15 min to desorb all analytes from fabric sorbent. Therefore, 5 min was selected as the optimal desorption time for three fabric sorbent, except for PEG-PPG-PEG triblock which was 15 min.

3.2.2. Extraction conditions

Once desorption conditions had been optimized, parameters affecting the extraction process such as sample pH, salt addition, agitation speed and extraction time were evaluated.

The sample pH is necessary to be controlled to promote the non-ionic form of analyte with acidic or basic functionalities, and, therefore, to increase retention towards the FPSE sorbent. The extraction was investigated at different pH values (3, 5, 7 and 9)

since the studied analytes possess different pK_a values (Table 1). Figure 3 shows the extraction recovery attained for a group of selected analytes when sol-gel Carbowax 20M sorbent was used with the samples adjusted at the different pHs. As can be seen, the recoveries at all different pHs are similar for all the selected compounds, with the exception of DICLO and TCC, whose recoveries decrease at pH 9 and pH 7, respectively. Similar trends were observed with the other three FPSE sorbents (sol-gel PDMDPS, sol-gel PTHF and sol-gel PEG-PPG-PEG triblock). Overall, sample adjusted at pH 3 showed the best recoveries during the extraction of the analytes for all four FPSE sorbents.

The effect of ionic strength in the recovery of compounds was performed by adding NaCl from 0% to 20% (w/v) to the aqueous solution. For the sol-gel Carbowax 20M sorbent, it was observed that the recoveries decreased (~ 10% on average) with 5% NaCl addition and then increased (~ 30% on average) to the maximum with 10% NaCl addition. This effect may be attributed to the salting-out effect and the electrostatic interaction between polar molecules and salt ions in the solution [36]. With addition of higher percentage (15% and 20% of NaCl), the recoveries started to decrease. The similar behavior was observed with the sol-gel PTHF sorbent. However, in the case of sol-gel PDMDPS and for the most non-polar analytes (BzPB, DHMB, DICLO, BP-3, TCC and TCS) the best recoveries were achieved when 15% of NaCl was added to the sample instead of 10% of NaCl. For the sol-gel PEG-PPG-PEG triblock sorbent the recovery remains the same as the percentage of salt addition increases. Therefore, for sol-gel Carbowax 20M and sol-gel PTHF sorbent 10% of salt was added to the sample, for sol-gel PDMDPS sorbent 15% salt was added whereas for sol-gel PEG-PPG-PEG triblock sorbent no salt was added.

Three agitation rates (300, 600 and 900 rpm) were tested to optimize the stirring speed. The results obtained with an agitation rate of 900 rpm were better (increase of 5-20%) than those obtained at lower rpm for all fabric sorbents. Experiments at higher level of stirring were not feasible since the agitation was not uniform.

Sample volume usually affects both the extraction time and extraction efficiency. In order to select the optimum sample volume, different sample volumes (10, 20 and 30 mL) of standard solution of the analytes were tested. When 20 and 30 mL of a standard solution were extracted, the recoveries decreased significantly (between 10-30%) for all FPSE sorbents. For this reason, 10 mL of sample was selected for further analysis.

The extraction time is also an important parameter in order to determine the time required to reach extraction equilibrium. It was tested from 1 to 8 hours for all four fabric sorbents. Figure 4 shows the extraction time profile for a representative group of analytes when sol-gel Carbowax 20M sorbent was tested. As can be seen in this Figure, from 1 to 3 hours there is an increase in recovery for most of the compounds; at 4 hours, a significant increase in recovery of TCC, BzPB and PrPB was observed; at time higher than 4 hours MPB and CBZ increased their recoveries. However, as a compromise, 4 hours were selected as optimum time in order to not make longer the time of analysis. Although it may seem a long extraction time compared to other techniques, the possibility of doing several extractions simultaneously reduces the whole time of analysis for a set of samples.

The optimal extraction conditions for the different sorbents tested were as follows: 10 mL of sample adjusted at pH 3, containing 10% of NaCl (15% for sol-gel PDMDPS and without salt for sol-gel PEG-PPG-PEG triblock sorbent), extracted at room temperature by stirring at 900 rpm for 4 h extraction time; and for the LD the fabric sorbent was sonicated in 1 mL of MeOH for 5 min (15 min for sol-gel PEG-PPG-PEG triblock sorbent). The extract was evaporated to dryness under gentle nitrogen stream. The residue obtained was re-dissolved in 1 mL of mixture of ultra-pure water at pH3 and ACN (80:20, v/v).

3.3. Comparison of FPSE sorbent chemistries

As mentioned, all parameters were optimized for each FPSE sorbent in ultra-pure water and the extraction recoveries (%) under optimal conditions are detailed in Table 2. From the results, it can be observed that the less polar compounds have better recoveries than the most polar ones for all four sorbents.

Comparing the results for the different sorbent, it can be seen that sol-gel PDMDPS coating achieved recoveries from 25% to 75% for slightly mid-polar to non-polar analytes such as BzPB, DHMB, DICLO, BP-3, TCC and TCS, whereas sol-gel PTHF coated FPSE media showed better recoveries for these compounds and also for PrPB and DHB. A similar trend was observed for sol-gel PEG-PPG-PEG triblock coated media. In any case, the best results were obtained for sol-gel Carbowax 20M FPSE media, with acceptable recoveries (between 24 and 85%) for all compounds with the only exception of the most polar ones (PARA, CAFF, APy and PROP). It should be taken into account that FPSE is not an exhaustive extraction technique but an equilibrium one.

When the results obtained by the novel technique of FPSE are compared with those obtained in a previous study [18] where SBSE with EG/Silicone was evaluated for the same compounds (results included in Table 2), it can be concluded that FPSE provided better recoveries. In particular, when comparing sol-gel Carbowax 20M coating results a very significant increase in recoveries for most of the compounds are observed. In principle, both EG/Silicone and Carbowax 20M own the same functional groups as both are based on ethylene glycol structure. Nevertheless, the better recoveries achieved with the FPSE with sol-gel Carbowax 20M media can be explained by the higher primary contact area in FPSE media, advanced material properties of sol-gel derived material, complementary hydrophilic affinity by the fabric substrate and increased analyte diffusion due to the permeable FPSE media.

Once the different FPSE sorbents had been evaluated for the extraction of the PPCPs from ultra-pure water, the four FPSE media were evaluated for the extraction of these compounds from more complex samples, such as effluent wastewater. Extraction recoveries for the four FPSE media were similar to those obtained with ultra-pure water. For instance, the FPSE extraction

recoveries for sol-gel Carbowax 20M were between 30 and 90% for all compounds with the only exception of the most polar ones (PARA, CAFF, APy and PROP), and therefore, sol-gel Carbowax 20M was selected for the method development and validation because of the higher recoveries obtained. At this point, it should be mentioned that the four most polar compounds (namely PARA, CAFF, APy and PROP) were not included in the following method development since these compounds were hardly recovered.

3.4. Method Validation

A common drawback when quantifying using LC–MS/MS with an ESI source is the matrix effect (ME) expressed as percentage decrease (ion suppression) or increase (enhancement) arising from compounds present in the matrix sample. It was calculated as:

$$\text{ME (\%)} = - [100 - (c_b/c_a \times 100)]$$

Where, c_b is the concentration measured in the post-extraction spiked sample and c_a is the concentration of the standard. If the $\text{ME (\%)} = 0$ no matrix effect is present, if $\text{ME (\%)} < 0$ there is ion suppression and if $\text{ME (\%)} > 0$ there is ion enhancement..

The apparent recovery ($\%R_{\text{app}}$) is referred to the recovery in the whole analytical process, including extraction recovery and ME. It was calculated as:

$$\%R_{\text{app}} = (c_b/c_a) \times 100$$

Where, c_b , and c_a are the concentration measured in the pre-extraction spiked sample, and the concentration of the standard, respectively.

Both values were evaluated for river, influent and effluent waste water samples spiked at both $0.2 \mu\text{g L}^{-1}$ ($1 \mu\text{g L}^{-1}$ for triclosan) and $5 \mu\text{g L}^{-1}$, and similar results were obtained at both levels. To do this, first a blank sample was analyzed in order to subtract the possible signal of analytes present in the samples. Ion suppression was observed in all cases, with the exception of BP-3 and CBZ, that presented ion enhancement in river samples. Table 3 shows the results for each sample spiked at $0.2 \mu\text{g L}^{-1}$ and, even for the influent sample, which is more complex, the ME was acceptable. In order to better quantify the samples, the matrix-matched calibration was applied.

In an analogous trend, $\% R_{\text{app}}$ (Table 3) for each compound is similar for the three samples analyzed, and they are slightly lower to the extraction recoveries, which is mainly attributed to the ME.

Table 4 includes the validation parameters for the effluent wastewater sample and good linearity was observed for the range specified in the table with determination coefficient (R^2) values greater than 0.998. The method LODs (MDLs) of different analytes calculated by $S/N \geq 3$ ranged from $1 - 10 \text{ ng L}^{-1}$, except for TCS (50 ng L^{-1}), the method LOQs (MQLs) were calculated the lowest point of the calibration curve and ranged between $10 - 50 \text{ ng L}^{-1}$ for all the compounds, with the exception of TCS which was 200 ng L^{-1} . In most of the compounds, these MDLs were lower than those obtained in the previous study [18] using SBSE and the same LC-MS/MS instrument, where MDLs of $5 - 10 \text{ ng L}^{-1}$ were obtained. The repeatability and reproducibility between days of five samples spiked at $0.2 \mu\text{g L}^{-1}$ ($1 \mu\text{g L}^{-1}$ for triclosan), expressed as $\%$ relative standard deviation ($\% \text{ RSD}$), were lower than 15% and 18%, respectively.

The results obtained in the validation process demonstrated the good performance of the FPSE/LC-MS/MS method developed using the Carbowax 20M sorbent.

3.5. Analysis of real samples

In order to demonstrate the application of the new method, different samples from Ebre River, effluent and influent waste water were analyzed. Three different samples from the same location and at different sampling period were analyzed in triplicate. Results for waste water samples are included in Table 5. As can be seen, all analytes were present in the collected samples, although in some cases at concentration below the MQLs and TCS were not detected in any of the effluent samples. Those analytes found at higher concentrations were MPB, CBZ, DICLO, and BP-3 in waste water samples. Their presence was confirmed by retention time and ion ratio between qualification and quantification ions.

As regards the river samples, only BP-3 was quantified between MQLs and 26 ng L^{-1} , and MPB and PrPB were found at concentration below the MQLs in one sample.

These results agree with those obtained in previous studies where the samples from the same WWTP [18,37,38] and river [37,38] were analyzed. As an example, Figure 5 shows the chromatogram of one effluent sample analyzed where all target analytes were found except TCS. When the values in influent and effluent samples were compared, it can be seen that, as expected, concentrations were lower in effluent samples due to the treatment process but the elimination was different for each compound. It should be mentioned that the samples were grab samples and the elimination efficiency cannot be calculated, but the trend for some compounds clearly agree with those described in the literature. For instance, it is known that elimination efficiency for CBZ and DICLO are very low [39] and values are similar in influent and effluent samples.

4. Conclusions

A recently developed extraction technique, FPSE, was evaluated for the extraction of a group of PPCPs of wide range of polarity from environmental waters. Four different FPSE sorbents (sol-gel PDMDPS, sol-gel PTHF, sol-gel PEG-PPG-PEG triblock copolymer and sol-gel Carbowax 20M) for the new sorptive extraction technique were compared. Sol-gel Carbowax 20M provided the best FPSE performance for the extraction of selected PPCPs. The sol-gel Carbowax 20M coated FPSE media substantially improved the extraction efficiencies for the analytes with wide range of polarity compared to those obtained in previously studied SBSE-EG/Silicone coating, mainly due to the advanced material properties of sol-gel derived material, larger primary contact surface area of FPSE media, and synergistic selectivity enhancement by the polar Carbowax 20M polymer, polar 3-CPTEOS precursor and strong hydrophilic property of cellulose fabric substrate.

When Carbowax 20M coated FPSE media was used for the extraction of selected PPCPs from 10 mL of river water, effluent and influent wastewater samples, recoveries of target analytes and ME were acceptable taken into account the complexity of the sample. The combination of FPSE with LC-(ESI)MS/MS provided an efficient, simple and sensitive method for the determination of PPCPs from environmental water samples at low levels and it is an economical and green alternative to the other extraction techniques such as SBSE or SPE.

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References

- [1] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, The effect of signal suppression and mobile phase composition on the simultaneous analysis of multiple classes of acidic/neutral pharmaceuticals and personal care products in surface water by solid-phase extraction and ultra performance liquid chromatography-negative electrospray tandem mass spectrometry, *Talanta* 74 (2008) 1299-1312.
- [2] R. Rodil, J. Benito Quintana, P. López-Mahía, S. Muniategui-Lorenzo, D. Prada-Rodríguez, Multiclass determination of sunscreen chemicals in water samples by liquid chromatography - tandem mass spectrometry, *Anal. Chem.* 80 (2008) 1307-1315.
- [3] M. Gros, S. Rodríguez-Mozaz, D. Barceló, Fast and comprehensive multi-residue analysis of a broad range of human and veterinary pharmaceuticals and some of their metabolites in surface and treated waters by ultra-high-performance liquid chromatography coupled to quadrupole-linear ion trap tandem mass spectrometry, *J. Chromatogr. A* 1248 (2012) 104-121.
- [4] A. Prieto, O. Basauri, R. Rodil, A. Usobiaga, L.A. Fernández, N. Etxebarria, O. Zuloaga, Stir-bar sorptive extraction: A view on method optimisation, novel applications, limitations and potential solutions, *J. Chromatogr. A* 1217 (2010) 2642-2666.
- [5] N. Fontanals, R.M. Marcé, F. Borrull, New materials in sorptive extraction techniques for polar compounds, *J. Chromatogr. A* 1152 (2007) 14-31.
- [6] M. Farré, L. Kantiani, M. Petrovic, S. Pérez, D. Barceló, Achievements and future trends in the analysis of emerging organic contaminants in environmental samples by mass spectrometry and bioanalytical techniques, *J. Chromatogr. A* 1259 (2012) 86-99.
- [7] M. Padrón, C. Afonso-Olivares, Z. Sosa-Ferrera, J. Santana-Rodríguez, Microextraction techniques coupled to liquid chromatography with mass spectrometry for the determination of organic micropollutants in environmental water samples, *Molecules* 19 (2014) 10320-10349.
- [8] K. Wille, H.F. De Brabander, L. Vanhaecke, E. De Wulf, P. Van Caeter, C.R. Janssen, Coupled chromatographic and mass-spectrometric techniques for the analysis of emerging pollutants in the aquatic environment, *TrAC, Trends Anal. Chem.* 35 (2012) 87-108.
- [9] E. Duran Guerrero, R. Natera Marín, R. Castro Mejias, C. García Barroso, Stir bar sorptive extraction of volatile compounds in vinegar: Validation study and comparison with solid phase microextraction, *J. Chromatogr. A* 1167 (2007) 18-26.
- [10] S. Risticjevic, V.H. Niri, D. Vuckovic, J. Pawliszyn, Recent developments in solid-phase microextraction, *Anal. Bioanal. Chem.* 393 (2009) 781-795.
- [11] L. Ramos, Critical overview of selected contemporary sample preparation techniques, *J. Chromatogr. A* 1221 (2012) 84-98.
- [12] S. Ulrich, Solid-phase microextraction in biomedical analysis, *J. Chromatogr. A* 902 (2000) 167-194.

- [13] G.A. Mills, V. Walker, Headspace solid-phase microextraction procedures for gas chromatographic analysis of biological fluids and materials, *J. Chromatogr. A* 902 (2000) 267-287.
- [14] J. Pawliszyn, H.K. Lee, G.A. Mills, Progress in sample extraction, *TrAC, Trends Anal. Chem.* 30 (2011) 1699-1701.
- [15] A. Giordano, M. Fernández-Franzon, M.J. Ruiz, G. Font, Y. Pico, Pesticide residue determination in surface waters by stir bar sorptive extraction and liquid chromatography/tandem mass spectrometry, *Anal. Bioanal. Chem.* 393 (2009) 1733-1743.
- [16] A.R. Chaves, S.M. Silva, R.H. Costa Queiroz, F.M. Lancas, M.E. Costa Queiroz, Stir bar sorptive extraction and liquid chromatography with UV detection for determination of antidepressants in plasma samples, *J. Chromatogr. B* 850 (2007) 295-302.
- [17] P. Serodio, J.M.F. Nogueira, Multi-residue screening of endocrine disruptors chemicals in water samples by stir bar sorptive extraction-liquid desorption-capillary gas chromatography-mass spectrometry detection, *Anal. Chim. Acta* 517 (2004) 21-32.
- [18] N. Gilart, N. Miralles, R. M. Marcé, F. Borrull, N. Fontanals, Novel coatings for stir bar sorptive extraction to determine pharmaceuticals and personal care products in environmental waters by liquid chromatography and tandem mass spectrometry, *Anal. Chim. Acta* 774 (2013) 51-60.
- [19] E. Fries, Determination of benzothiazole in untreated wastewater using polar-phase stir bar sorptive extraction and gas chromatography mass spectrometry, *Anal. Chim. Acta* 689 (2011) 65-68.
- [20] B. Sgorbini, C. Cagliero, C. Cordero, E. Liberto, P. Rubiolo, M.R. Ruosi, C. Bicchi, New medium-to-high polarity twister coatings for liquid and vapour phase sorptive extraction of matrices of vegetable origin, *J. Chromatogr. A* 1265 (2012) 39-45.
- [21] D. Bratkowska, R.M. Marcé, P.A.G. Cormack, F. Borrull, N. Fontanals, Development and application of a polar coating for stir bar sorptive extraction of emerging pollutants from environmental water samples, *Anal. Chim. Acta* 706 (2011) 135-142.
- [22] X. Huang, J. Lin, D. Yuan, R. Hu, Determination of steroid sex hormones in wastewater by stir bar sorptive extraction based on poly(vinylpyridine-ethylene dimethacrylate) monolithic material and liquid chromatographic analysis, *J. Chromatogr. A* 1216 (2009) 3508-3511.
- [23] L.R. Melo, A.M. Nogueira, F.M. Lancas, M.E.C. Queiroz, Polydimethylsiloxane/polypyrrole stir bar sorptive extraction and liquid chromatography (SBSE/LC-UV) analysis of antidepressants in plasma samples, *Anal. Chim. Acta* 633 (2009) 57-64.
- [24] C. Yu, B. Hu, Sol-gel polydimethylsiloxane/poly(vinylalcohol)-coated stir bar sorptive extraction of organophosphorus pesticides in honey and their determination by large volume injection GC, *J. Sep. Sci.* 32 (2009) 147-153.
- [25] N. Gilart, R.M. Marcé, F. Borrull, N. Fontanals, New coatings for stir-bar sorptive extraction of polar emerging organic contaminants, *TrAC, Trends Anal. Chem.* 54 (2014) 11-23.
- [26] A. Kabir, K.G. Furton, Fabric Phase Sorptive Extraction (FPSE), US Patent Applications: 14,216,121, March 17, 2014.

- [27] R. Kumar, Gaurav, Heena, A.K. Malik, A. Kabir, K.G. Furton, Efficient analysis of selected estrogens using fabric phase sorptive extraction and high performance liquid chromatography-fluorescence detection, *J. Chromatogr. A* 1359 (2014) 16-25.
- [28] V. Samanidou, L.-D. Galanopoulos, A. Kabir, K.G. Furton, Fast extraction of amphenicols residues from raw milk using novel fabric phase sorptive extraction followed by high-performance liquid chromatography-diode array detection, *Anal. Chim. Acta* 855 (2015) 41-50.
- [29] I. Racamonde, R. Rodil, J.B. Quintana, B.J. Sieira, A. Kabir, K.G. Furton, R. Cela, Fabric phase sorptive extraction: A new sorptive microextraction technique for the determination of non-steroidal anti-inflammatory drugs from environmental water samples, *Anal. Chim. Acta* 865 (2015) 22-30.
- [30] M. Roldán-Pijuán, R. Lucena, S. Cárdenas, M. Valcárcel, A. Kabir, K.G. Furton, Stir fabric phase sorptive extraction for the determination of triazine herbicides in environmental waters by liquid chromatography, *J. Chromatogr. A* 1376 (2015) 35-45.
- [31] P.J. Wakelyn, N.R. Bertoniere, A.D. French, D.P. Thibodeaux, B.A. Triplett, M.A. Rousselle, W.R. Goynes, J.V. Edwards, L. Hunter, D.D. McAlister, *Cotton Fiber Chemistry and Technology*, CRC Press, Boca Raton, 2006.
- [32] S.L. Chong, D. Wang, J.D. Hayes, B.W. Wilhite, A. Malik, Sol-gel coating technology for the preparation of solid-phase microextraction fibers of enhanced thermal stability, *Anal. Chem.* 69 (1997) 3889-3898.
- [33] A. Kabir, K.G. Furton, A. Malik, Innovations in sol-gel microextraction phases for solvent-free sample preparation in analytical chemistry, *TrAC, Trends Anal. Chem.* 45 (2013) 197-218.
- [34] S. Kulkarni, L. Fang, K. Alhooshani, A. Malik, Sol-gel immobilized cyano-polydimethylsiloxane coating for capillary microextraction of aqueous trace analytes ranging from polycyclic aromatic hydrocarbons to free fatty acids, *J. Chromatogr. A* 1124 (2006) 205-216.
- [35] A. Kabir, C. Hamlet, A. Malik, Parts per quadrillion level ultra-trace determination of polar and nonpolar compounds via solvent-free capillary microextraction on surface-bonded sol-gel polytetrahydrofuran coating and gas chromatography-flame ionization detection, *J. Chromatogr. A* 1047 (2004) 1-13.
- [36] X. Huang, N. Qiu, D. Yuan, Development and validation of stir bar sorptive extraction of polar phenols in water followed by HPLC separation in poly(vinylpyrrolidone-divinylbenzene) monolith, *J. Sep. Sci.* 32 (2009) 1407-1414.
- [37] M. Pedrouzo, F. Borrull, R.M. Marcé, E. Pocurull, Ultra-high-performance liquid chromatography-tandem mass spectrometry for determining the presence of eleven personal care products in surface and wastewaters, *J. Chromatogr. A* 1216 (2009) 6994-7000.
- [38] M. Pedrouzo, S. Reverté, F. Borrull, E. Pocurull, R.M. Marcé, Pharmaceutical determination in surface and wastewaters using high-performance liquid chromatography-(electrospray)-mass spectrometry, *J. Sep. Sci.* 30 (2007) 297-303.

[39] M. Pedrouzo, F. Borrull, E. Pocurull, R.M. Marcé, Presence of pharmaceuticals and hormones in waters from Sewage Treatment Plants, *Water Air Soil Pollut.* 217 (2011) 267-281.

Figure Captions

Figure 1. Chemical reactions involved in the synthesis of sol-gel hybrid inorganic-organic polymeric network.

Figure 2. Schematic representation of sol-gel Carbowax 20M coated FPSE media.

Figure 3. Effect of sample pH on extraction recovery for a representative group of compounds using Carbowax 20M sorbent in FPSE. (% RSD (n=3) were lower than 12%).

Figure 4. Effect of the extraction time on the extraction recovery for a representative group of analytes using Carbowax 20M sorbent in FPSE. (% RSD (n=3) were lower than 10% for % R > 10%).

Figure 5. MRM chromatogram of an effluent WWTP sample analyzed by FPSE/LC-MS/MS. For experimental conditions see the text. * Denotes the peak of DHB.

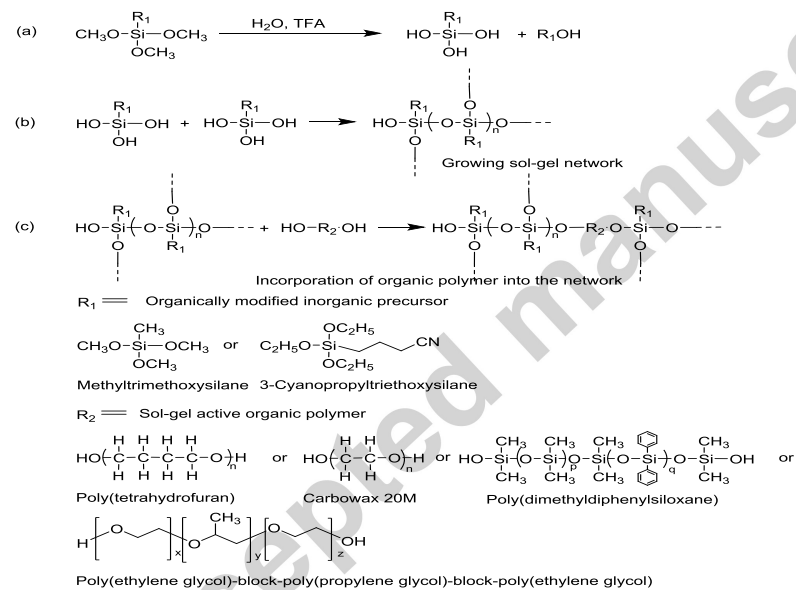


Figure 1

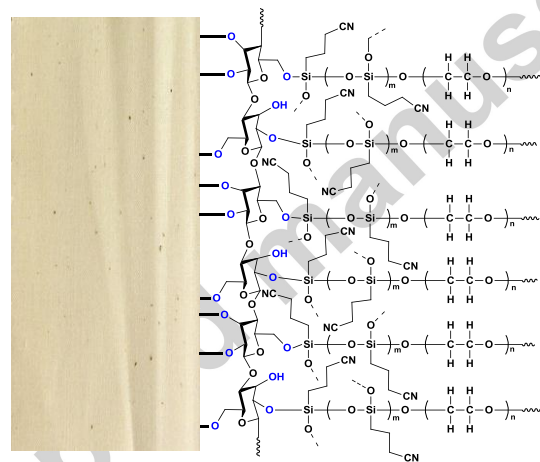


Figure 2

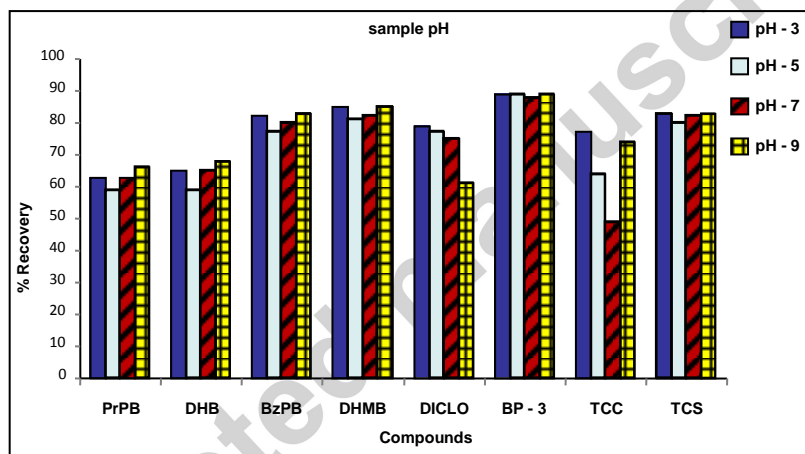


Figure 3

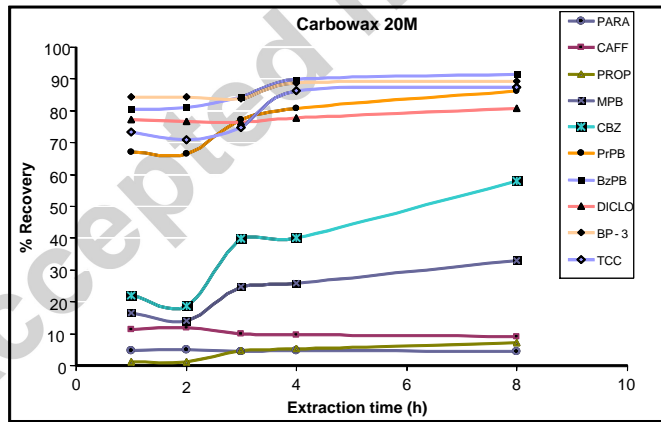


Figure 4

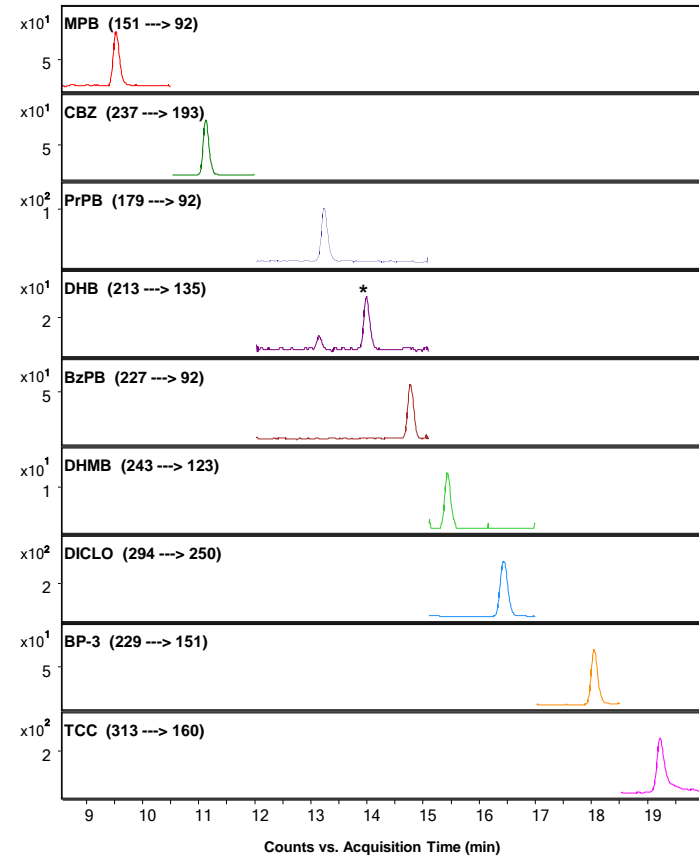


Figure 5

Table1. General parameters of Log K_{ow} , pK_a , and t_R , and LC–(ESI)MS/MS acquisition parameters in MRM mode for each analyte.

Analyte	log K_{ow}	pK_a	t_R (min)	Precursor ion (m/z)	Cone voltage (V)	Product ion (m/z) (Collision energy (eV))	
						Quantification	Confirmation
PA	0.5	9	3.8	152	100	110 (15)	93 (25)
RA		.2	7				
CA	-0.6	1	4.3	195	125	138 (15)	110 (25)
FF		3.4	7				
APy	1.4	1	6.7	189	100	145 (30)	115 (30)
PR		3.3	0				
OP	2.9	9	7.5	260	125	116 (15)	183 (15)
MP		.5	7				
B	1.9	8	9.4	151	80	92 (15)	136 (5)
CB		.3	5				
Z	1.9	1	11.	237	150	193 (35)	179 (35)
PrP		3.7	0				
B	2.9	8	13.	179	100	92 (15)	136 (5)
DH		.2	1				
B	3.2	7	13.	213	130	135 (15)	169 (5)
		.7	9				

BzP	3.6	8	14.	227	100	92 (10)	136 (20)
B	.2	7					
DH	4.3	7	15.	243	80	123 (15)	93 (15)
MB	.1	3					
DIC	4.5	4	16.	294	75	250 (5)	214 (15)
LO	.2	4					
BP-	4.0	7	18.	229	130	151 (15)	105 (15)
3	.6	0					
TC	6.1	1	19.	313	130	160 (5)	126 (15)
C	2.7	2					
TC	5.3	7	19.	287	18	35 (8)	
S	.9	5					
				289	18		35 (8)

* Log K_{ow} calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994–2012 ACD/Labs).

Table 2. Extraction recovery values (%) (n=3) obtained from different FPSE sorbents when 10 mL of ultra-pure water spiked with $0.2 \mu\text{g L}^{-1}$ with analyte mixture were extracted with PDMDPS, PTHF, PEG-PPG-PEG and Carbowax 20M sorbents.

Analyte	Recovery values (%)				
	PDMDPS	PTHF	PEG-PPG-PEG	Carbowax20M	SBSE-EG/Silicone*
PARA	5	5	-	5	-
CAFF	13	12	1	9	-
APy	7	5	2	4	< 1
PROP	2	< 1	2	4	2
MPB	3	6	14	24	1
CBZ	8	2	15	39	< 1
PrPB	4	43	51	77	10
DHB	7	37	58	75	24
BzPB	25	64	59	84	39
DHMB	32	76	58	85	26
DICLO	34	70	55	76	< 1
BP-3	64	86	62	83	45
TCC	75	81	50	74	59
TCS	75	87	53	80	80

%RSD (n=3) were lower than 10% for %R > 10%.

*Recovery values (%) obtained when 50 mL of ultra-pure water spiked with $4 \mu\text{g L}^{-1}$ with analyte mixture were extracted with SBSE-EG/Silicone coating [18].

23 **Table 3.** Matrix effect (%) and apparent recovery (% R_{app}) obtained from different
 24 sample matrices when 10 mL of sample spiked at 0.2 $\mu\text{g L}^{-1}$ with the
 25 analyte mixture were analyzed by FPSE using Carbowax 20M coated
 26 media followed by LC-MS/MS
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Analyte	Effluent water		Influent water		River water	
	ME (%)	R_{app} (%)	ME (%)	R_{app} (%)	ME (%)	R_{app} (%)
MPB	-32	9	-36	14	-21	27
CBZ	-29	20	-17	32	48	92
PrPB	-34	43	-39	41	-22	65
DHB	-24	55	-32	44	-14	74
BzPB	-31	67	-36	45	-28	65
DHMB	-27	74	-26	50	-21	67
DICLO	-37	44	-29	52	-16	73
BP-3	-16	80	-14	59	8	93
TCC	-23	58	-24	57	-19	59
TCS*	-39	47	-38	43	-29	54

28 %RSD (n=3) were lower than 15% for % R_{app} > 20%. * spiked at 1 $\mu\text{g L}^{-1}$
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47 **Table 4.** MDLs, MQLs, linear range, repeatability and reproducibility between days
 48 obtained when 10 mL of effluent wastewater sample spiked at $0.2 \mu\text{g L}^{-1}$ of
 49 each analyte were analyzed by FPSE using Carbowax 20M media followed
 50 by LC-MS/MS.
 51

Analyte	MDLs (ng L^{-1})	MQLs (ng L^{-1})	Linear range (ng L^{-1})	Repeatability (%RSD, n=5)	Reproducibility (%RSD, n=5)
MPB	10	50	50 - 10000	8	9
CBZ	10	50	50 - 10000	7	7
PrPB	2	20	20 - 10000	6	8
DHB	5	50	50 - 10000	6	13
BzPB	1	20	20 - 10000	8	15
DHMB	2	20	20 - 5000	9	15
DICLO	1	20	20 - 5000	10	13
BP-3	2	20	20 - 5000	7	12
TCC	3	10	10 - 1000	8	18
TCS*	50	200*	200 - 10000	15	12

52 * spiked at $1 \mu\text{g L}^{-1}$ under the same conditions
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62 **Table 5.** Concentration range of analytes found in three effluent and influent
 63 wastewater samples by FPSE using Carbowax 20M media followed by LC-
 64 MS/MS.

Analyte	Concentration (ng L ⁻¹)	
	Effluent water	Influent water
MPB	111 - 170	87 - 187
CBZ	189 - 323	289 - 344
PrPB	28 - 49	55 - 227
DHB	<LOQ	129 - 217
BzPB	<LOQ	<LOQ
DHMB	<LOQ	<LOQ
DICLO	57 - 763	205 - 776
BP-3	93 - 168	160 - 356
TCC	21 - 39	<LOQ - 62
TCS	n.d.	<LOQ

65 n.d: not detected
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