Synthesis and characterization of a sulfonic species-based mesoporous sorbent for the pre-concentration of nine personal care products in wastewater and swimming pool water

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ABSTRACT

A mesoporous material functionalized with sulfonic moieties has been synthesized by co-condensation. The functionalized material was characterized and then employed for the solid phase extraction of nine personal care products (UV filters and parabens) in effluent wastewater and swimming pool water. UV filters and parabens were analyzed by liquid chromatography coupled to tandem mass spectrometry. Validation parameters (linearity, matrix effect, limit of quantitation, trueness and precision) were established according to the EURACHEM Guide using a blank effluent wastewater sample. The new sorbent enabled the selective extraction of the target analytes from the rest of matrix components, with low matrix effect (ME ≤ |20 %|) for all analytes, the exception being isopropylparaben with a ME = -27 %. The effect of the co-extracted components from the effluent water sample in the recovery study was evaluated using external calibration curves (using standard solutions) and the standard addition method. Similar results were obtained using both methodologies and, according to the validation guide requirements, slightly better results were obtained using the standard addition methodology (75.0 - 99.6 %) compared to external calibration (66.7 - 115.2 %). The quantitation limits ranged between 0.5 and 5.0 ng·L^{-1} in wastewater. Two types of real samples (effluent wastewater and swimming pool water) were pre-concentrated using the optimized methodology. Four parabens (methylparaben, propylparaben, benzylparaben and butylparaben) and two UV filters (4-hydroxybenzophenone and 4,4´-dihydroxybenzophenone) were found in the effluent water sample at ng·L^{-1} concentration levels. In addition, the same four parabens and 4,4´-dihydroxybenzophenone were detected in the swimming pool water at slightly lower concentrations than those found in wastewater.

 Keywords: Functionalized mesoporous material; Personal care products; Solid phase extraction; UPLC-QqQ-MS/MS; Water analysis

1. Introduction

Personal care products (PCPs) are a group of compounds widely used in everyday products, including disinfectants, ultraviolet filters (UVFs), stabilizers, preservatives, fragrances and insect repellents. These compounds, which are a

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preoccupying group of pollutants due to their toxic effects on the biota, are continually released into the aquatic environment and thus are considered to be pseudo-persistent [1].

UVFs are commonly used due to the increasing preoccupation about the effects of UV radiation [1]. Nowadays, the European Union (EU) regulations authorize the use of 26 UVFs in cosmetics, which enter the environment indirectly via wastewater treatment plants (WWTP) effluents or directly by releasing from the skin surface during aquatic activities. 12 of these 26 UVFs would be considered as "hazardous to the aquatic environment", according to the EU regulation on classification, labeling and packaging (CLP) [2].

The physicochemical properties and massive use of UVFs make them very persistent in the environment [2] and they are well known to bioaccumulate, also showing potential estrogenic activity in aquatic organisms [2,3]. In addition, they can potentially biomagnify in higher trophic levels [3]. Studies on the occurrence of these compounds in the environment showed their presence in rivers, sea, tap and groundwater, as well as in swimming pool water [2,4].

UVFs have been analyzed in waters by liquid chromatography (LC) with ultraviolet (UV) detection [2], liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) [5–7] and ultra-performance liquid chromatography coupled to tandem mass spectrometry (UPLC-MS/MS) [2,8,9], as well as gas chromatography coupled to mass spectrometry (GC-MS) with an additional derivatization step [2,10] and GC-MS/MS [11], due to their improvements in the limits of detection (LODs) in the low ng·L^{-1} level.

Parabens (PBs) are hydroxybenzoate esters with an alkyl or benzyl group, widely used as preservatives in personal care products, among others. Although these compounds are biodegradable under aerobic conditions, they could be considered as "pseudo-persistent" contaminants due to their high consumption and continuous introduction into the environment [12].

These compounds have shown estrogenic activity in addition to potential toxicity for certain aquatic organisms [2,3,13] and have been detected in freshwater and its sediments, drinking water, swimming pool water and marine water, as well as in biota [4,14].

PBs have been determined in environmental water samples by LC-UV and UPLC-UV [15–18], but the technique of choice is LC coupled to triple quadrupole tandem mass spectrometry (QqQ-MS/MS) [7,15,19–21]. Moreover, gas chromatography with flame ionization detector (GC-FID) has also been used [15] and, in recent years, GC-MS or GC-MS/MS have been increasingly applied [15,22–25].

Solid phase extraction (SPE) is the most used technique for the treatment of water samples, with Oasis HLB being the most commonly used SPE sorbent [15]. C18 has been employed for the extraction of two benzophenone UV filters and four PBs in tap water [26], whereas Bond Elut Plexa was used to extract three benzophenone UV filters and four PBs from river water. Oasis HLB has been used to extract the same compounds from effluent and influent wastewater [27], as well as five benzophenone derivatives and four PBs [8]. Additionally, Oasis HLB has also been employed to pre-concentrate four PBs in surface and wastewater [19,28]. Graphitized carbon black was used as sorbent to extract sixteen UV filter (including two benzophenone derivatives) [6] and Oasis HLB was used to extract six 2-hidroxybenzophenone derivatives [29].

New techniques for the treatment of water samples are in continuous development in order to reduce time and solvent consumption as well as to improve their versatility, allowing the simultaneous retention of analytes with very different nature and polarity. In this sense, the interest in the development of new materials has increased significantly in recent years.

Besides the sorbents described above, silica-based mesoporous materials have gained increasing interest because, in addition to their high pore volume and surface area, they offer the possibility of functionalization with hydrophilic, hydrophobic, polar or charged functional moieties, thus expanding their potential use for the extraction of analytes with different nature and properties [30]. Silica-based mesoporous materials, with or without functionalization, have been used in liquid food samples preparation for contaminants analysis [31,32].

Regarding functionalization with sulfonic groups (-SO$_3$H), SBA-15-SO$_3$H has been recently applied to the enrichment of glycopeptides in glycoproteome analysis [33] and SBA-15 bifunctionalized with C8 and -SO$_3^-$ groups (SBA-15-C8-SO$_3^-$) has been used as a mixed-mode sorbent for multi-residue SPE of veterinary drugs in meat samples [30]. MCM-41-SO$_3$H has been widely used as a catalyst [34,35] but, to the best of our knowledge, its suitability in sample preparation has not been studied.

In the present study, MCM-41-SO$_3$H has been synthesized and used in the SPE extraction of several PCPs (three UVFs and six PBs) from a municipal WWTP effluent and swimming pool water. An UPLC-QqQ-MS/MS method was developed

for the simultaneous determination of the target PCPs using both positive ionization (PI) and negative ionization (NI) modes.

2. Experimental

2.1 Chemicals and solvents

Analytical standards (> 98 %) of methylparaben (MePB), ethylparaben (EtPB), isopropylparaben (iPrPB), propylparaben (PrPB), butylparaben (BuPB), benzylparaben (BePB), 4-hydroxybenzophenone (4-HBP), 2-4-dihydroxybenzophenone (2,4-DHBP) and 4,4′-dihydroxybenzophenone (4,4′-DHBP) were purchased from Sigma-Aldrich. **Table S1** in the electronic supplementary material (ESM) contains the structure and physicochemical properties of both types of analytes.

Individual stock solutions of each compound were prepared in acetonitrile with concentrations ranging from 980 to 1550 mg·L^{-1} and stored at -20 °C. These solutions were stable for at least 3 months. Working solution mixtures of the nine PCPs were prepared daily by appropriate dilution of the individual stock solutions in methanol-ultrapure water (20:80, v/v).

Organic solvents (acetonitrile, methanol, ethyl acetate and *n*-hexane) of residue analysis grade, formic acid (95-97 %) and sodium chloride were purchased from Sigma-Aldrich. Ultrapure water was supplied by a Milli-Q water purification system from Millipore (USA).

Tetraethyl orthosilicate (TEOS), 3-mercaptopropyl triethoxy-silane (MPTES, 98 %), cetyltrimethylammonium bromide (CTAB), hydrochloric acid (HCl, 37 %), hydrogen peroxide (H_2O_2, 30 % wt.) and sulfuric acid (H_2SO_4, 98 %) were purchased from Sigma-Aldrich. Ethanol (EtOH, 96 %) was acquired from J.T. Backer.

The SPE cartridges containing MCM-41-SO_3H were prepared in the laboratory using 3 mL polypropylene body syringes and two polyethylene frits, both supplied by Supelco (Spain).

2.2 Water samples

A municipal WWTP effluent and a private swimming pool water were analyzed. Both samples were collected in plastic bottles, filtered through 20–25 μm cellulose membranes and stored at 4 °C prior to their analysis.

One WWTP sample was analyzed using the proposed UPLC-QqQ-MS/MS and the absence of PCPs was confirmed. This sample was used as blank for the optimization and validation studies, according to the EURACHEM Guide [36].

2.3 Synthesis and characterization of MCM-41-SO_3H

The MCM-41 sorbent functionalized with 10 % of –SO_3H groups was synthetized by a co-condensation method based on previous works [37–39] with the following molar composition: 0.0369 TEOS / 0.0041 MPTES / 0.265 H_2O_2 / 0.237 HCl.

First, 2.5 g of CTAB were dissolved in 120 g of an HCl solution (1.9 mol·L^{-1}) with agitation at room temperature and, then, the mixture was stirred (250 rpm) and heated at 40 °C for 10 min. Subsequently, 7.7 g of TEOS and 0.98 g of MPTES (corresponding to 10 % TEOS) were added and the mixture was maintained with agitation at 40 °C for 45 min. Afterwards, 25 g of H_2O_2 (30 % wt.) were added dropwise and the resulting solution was maintained under stirring at 40 °C for 20 h. The mixture was then aged under hydrothermal treatment in a Teflon-lined stainless steel autoclave at 100 °C for 24 h. The obtained white solid was filtered, washed with 100 mL of ultrapure water followed by 100 mL of EtOH and dried at 60 °C in an oven for 24 h.

To remove the surfactant template, the solid material was maintained at reflux with 400 mL of EtOH for 24 h. Next, it was filtered, washed with 100 mL of ultrapure water and 100 mL of EtOH and allowed to dry at 60 °C overnight. Finally, the mesoporous material was suspended in 100 mL of H_2SO_4 (1 mol·L^{-1}) solution for 2 h, filtered, washed with 100 mL of water and 100 mL of EtOH and dried at 60 °C overnight.

The MCM-41-SO_3H was characterized by elemental analysis, Raman spectroscopy, low-angle X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and nitrogen adsorption-desorption isotherms.

The elemental analysis was carried out using an ELEMENTAR Vario Micro CHNS by total combustion of the sample at 1200 °C, separation of the gases produced (C, N, H, S) on a heating column and measurement with a Thermal Conductivity detector (TCD).

The Raman spectrum was obtained using a Bruker Series 126 spectrometer and the XRD patterns were obtained as described elsewhere [40].

The nitrogen adsorption-desorption isotherms were measured as described in a previous work [41]. Prior to the adsorption measurements, the samples were outgassed at 110 °C in a nitrogen flow for 5 h.

The SEM micrographs were obtained as described in a previous paper [40], working at 20 kV and a working distance of 11 mm. The HRTEM images were obtained as indicated in the same paper [40].

2.4 Solid phase-extraction procedure

The SPE cartridges containing 100 mg of MCM-41-SO$_3$H were prepared as described elsewhere [40,41]. The SPE procedure consisted of the conditioning of the sorbent with 5 mL of ultrapure water (pH = 6.5 ± 0.1). Then, 50 mL of water samples (pH = 6.5 ± 0.1) containing 10 % NaCl were passed through the cartridge at approximately 5 mL·min^{-1} using a Büchi Vac V-500 vacuum pump (Flawil, Switzerland) connected to an extraction manifold manufactured by Waters (Milford, MA, USA). Next, the sorbent was washed with 5 mL of ultrapure water to remove co-adsorbed matrix components and, finally, it was dried by passing air first and then N$_2$ for 5 min each.

Subsequently, the retained compounds were eluted from the sorbent with 2 mL of ethyl acetate and, next, the eluate was evaporated to dryness with a gentle N$_2$ flow. Finally, the extract was re-dissolved in 0.5 mL methanol:ultrapure water (20:80, v/v) and 5 µL were injected in the UPLC-QqQ-MS/MS system.

2.5 UPLC-QqQ-MS/MS procedure

The UPLC-QqQ-MS/MS instrument and the column used were described in a previous paper [40]. For the separation of the selected PCPs, the binary mobile phase was composed of 5 mM ammonium formate/0.1 % formic acid in ultrapure water:methanol (98:2, v/v) as solvent A and 5 mM ammonium formate/0.1 % formic acid in methanol as solvent B at a constant flow rate of 0.5 mL·min^{-1}. The injection volume was 5 µL. The UPLC gradient program started with 20 % B for 1 min, which was increased up to 100 % B in four steps: 50 % B in 0.5 min, 60 % B in 4.5 min, 80 % B in 0.5 min and, finally, 100 % B in 0.5 min plus 2.0 min under these last conditions. Initial mobile phase conditions (20 % B) were reached in 2.0 min and maintained during 2 additional min.

The mass spectrometer was equipped with a jet-stream electrospray ion source (ESI), operating in both positive and negative ionization (PI and NI, repectively). The conditions of the ESI source were as follows: fragmentor voltage, 380 V; capillary voltage, 3000 V; drying gas temperature, 120 °C at 13 L·min^{-1} flow rate; super-heated sheath gas temperature, 375 °C at 10 L·min^{-1} flow rate; nebulizer pressure, 45 psi. Nitrogen (high purity) was used as the nebulizer and collision gas. Multiple reaction monitoring (MRM) mode was chosen for the quantification and identification of the analytes.

For control and data analysis, the Agilent MassHunter QQQ Acquisition and Quantification Analysis B.07.00 software using Dynamic MRM software features with a retention time window of 0.8 min was used.

3. Results and discussion

3.1 Optimization of the UPLC-QqQ-MS/MS method

For the optimization of the best conditions for the analysis of the target compounds by UPLC-QqQ-MS/MS, the main variables affecting chromatographic separation (mobile phase composition and flow rate) and MS signal intensity were evaluated. According to previously published papers, methanol or acetonitrile with additives such as formic acid, acetic acid or mixtures of both with their corresponding ammonium salts were selected as mobile phases to achieve the highest sensitivity and selectivity in the determination of UVFs and/or PBs by LC-MS/MS. Thus, formic acid/acetonitrile, formic acid/ammonium formate/acetonitrile, ammonium acetate/acetic acid/methanol and formic acid/methanol mobile phases and PI mode have been used for the analysis of UVFs [42–48], whereas ammonium acetate/methanol,

ammonium fluoride/ methanol, ammonia/acetonitrile mobile phases and NI mode have been employed for the analysis of PBs [47–54].

To achieve the simultaneous determination of both UVFs and PBs, LC-MS/MS methods have been developed using acetic acid/ammonium acetate and methanol [55], ammonia and methanol [56] and ammonium acetate/acetonitrile [57] as mobile phases in both PI and NI modes.

In the present work, we have tested different mobile phases using methanol with different additives (formic acid, acetic acid and ammonium formate) as the organic solvent for the simultaneous determination of both types of PCPs by UPLC-QqQ-MS/MS.

Firstly, individual standard solutions at 100 µg·L^{-1} of each analyte in methanol:water (1:1, v/v) were injected into the UPLC-QqQ-MS system in full scan mode with a mass range of 50–800 m/z at a constant flow rate of 0.3 mL·min^{-1}. The precursor ion and the two most intense transitions were selected for each analyte. Working solutions of the analytical standards of each compound were analyzed using both PI and NI modes and the most intense signal for each UVF and PB was obtained working in NI and PI, respectively. The highest MS signals were found using the previously described mobile phase.

Next, the separation of the target compounds was optimized using different gradient programs to achieve enough resolution between chromatographic signals, especially between the two isomers iPrPB and PrPB. These co-eluting compounds showed the same two transitions, although for iPrPB the most intense transition was 178.9>137.0 and for PrPB the most intense one was 179.0>92.1. As an example, **Figure S1** (see ESM) shows the chromatograms obtained for iPrPB and PrPB with different mobile phase compositions and flow rates. It can be observed that overlapped peaks were obtained for the two isomers using the mobile phase composition showed in **Figure S1a** (0.3 mL·min^{-1} flow rate), whereas a good resolution was found for these peaks with the mobile phase composition showed in **Figure S1b** (same flow rate). However, in the last case, the retention time (R_t) was increased by approximately 2 min. In order to decrease the analysis time, the flow rate of the last mobile phase composition (**Figure S1b**) was increased up to 0.5 mL·min^{-1} (**Figure S1c**) and a good separation was found for both isomers with lower R_t.

Figure S2 (ESM) shows a full scan chromatogram of the selected analytes in the optimized UPLC-QqQ-MS/MS procedure. **Table S2** (ESM) summarizes the optimized UPLC-QqQ-MS/MS parameters for each compound as well as their retention time, the precursor ion, the two most intense transitions (SRM1 and SRM2), their corresponding collision energies (CE), their ratio SRM2/SRM1 and the ionization mode. UVFs and PBs were determined using PI and NI ionization modes, respectively.

3.2 Characterization of MCM-41-SO$_3$H

The presence of a sulfonic acid (-SO$_3$H) moiety on the functionalized mesoporous material was confirmed by elemental analysis and Raman spectroscopy, the latter being more sensitive than infrared spectroscopy (IR) towards this moiety.

The elemental analysis was carried out in triplicate and the content (%) of C, H and S was 24.85, 5.54 and 2.93, respectively.

he Raman spectrum (**Figure 1a**) shows the absence of the intense peak at 2585 cm^{-1}, which is characteristic of the –SH group vibration, and the presence of bands at around 1038 cm^{-1} and 1195 cm^{-1}, which can be attributed to the symmetric and asymmetric vibrational modes of SO$_3^-$ [58].

The XRD patterns exhibited a single intense peak at 2θ range of 2.5° (**Figure 1b**), corresponding to the d$_{100}$ reflection of a *p6mm* hexagonal symmetry, characteristic of an MCM-41 structure. This peak appears shifted towards a diffraction angle slightly higher than the one corresponding to MCM-41 (~2.2°), which can be explained by a slight decrease in the pore size as a consequence of the incorporation of sulfonic moieties into the MCM-41 pores [59]. The absence of the d$_{110}$ and d$_{200}$ reflections indicates that the material has a slightly distorted hexagonal structure, as stated elsewhere [60].

The textural parameters were obtained from N$_2$ adsorption-desorption isotherms at 77 K using the standard BET method and the BJH equation. **Figure 1c** shows the N$_2$ adsorption-desorption isotherms, which correspond to a type IV without hysteresis loop. The sharpness of the step-in nitrogen adsorption reflects a total uniformity of the pore size.

The adsorption and desorption processes are highly reversible, as can be deduced from the perfect coincidence of the two isotherm branches. The material presented a BET surface area of 515 $m^2 \cdot g^{-1}$, BJH pore volume of 0.23 $cm^3 \cdot g^{-1}$ and an average pore diameter of *ca.* 25.2 Å. These values differ from those found in a previous work by us for MCM-41, which were 1095.60 $m^2 \cdot g^{-1}$, 0.613 $cm^3 \cdot g^{-1}$ and 22.32 Å, respectively [41]. It is evident that the impregnation of the internal and external surface of the material by sulfonic groups considerably affects its surface area and pore volume. This results from the numerous -SO_3H groups trapped inside the pores, which strongly reduces the pore volume from 0.61 to 0.23 $cm^3 \cdot g^{-1}$. Therefore, the internal surface is no longer accessible to the nitrogen molecule, which drastically decreases the value of the porous surface of the material. The average pore diameter changes very little, as it is specific to the MCM-41 material.
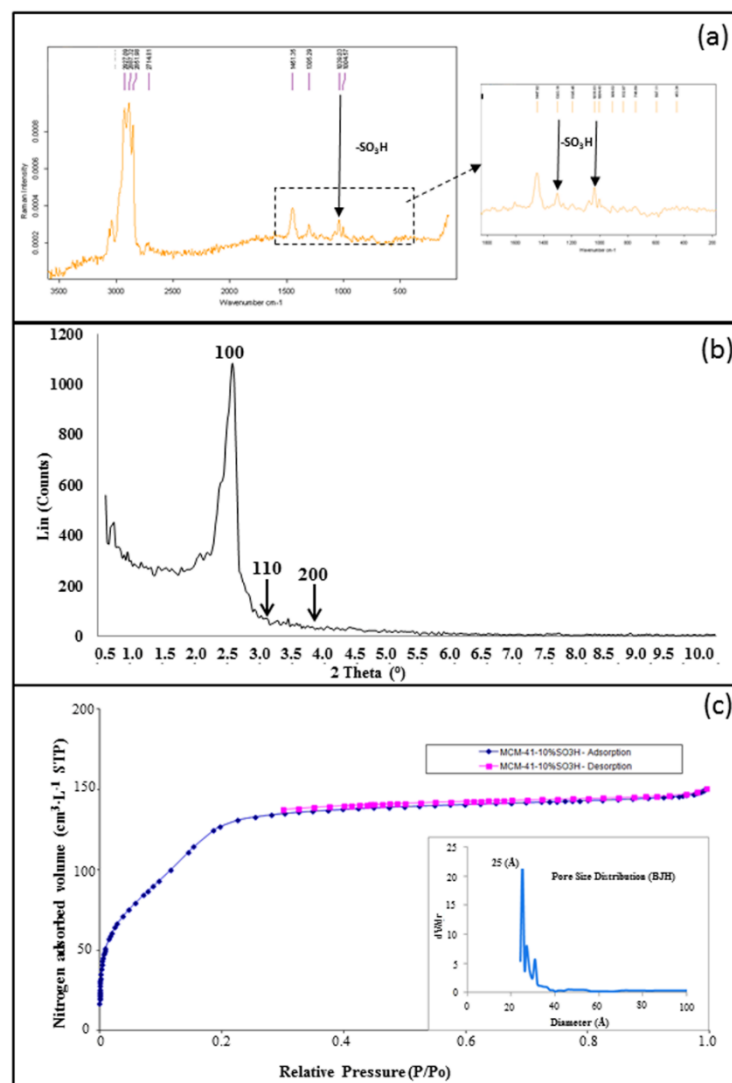

Figure 1. *(a) Raman spectrum; (b) XRD powder diffraction and (c) Nitrogen sorption isotherm at 77 K of the mesoporous MCM-41-SO₃H sample*

The particle morphology and pore arrangement are given in **Figure 2**. SEM micrographs showed that faceted particles with a wide dimension distribution, ranging from a few to ten microns, were obtained for MCM-41-SO₃H (**Figure 2a**). HRTEM micrographs confirmed that the functionalized material is characteristic of an MCM-41 type with a highly parallel channel-like porous structure packed in a hexagonal symmetry (**Figure 2b and 2c**). The functionalization did not affect the hexagonal structure of MCM-41.
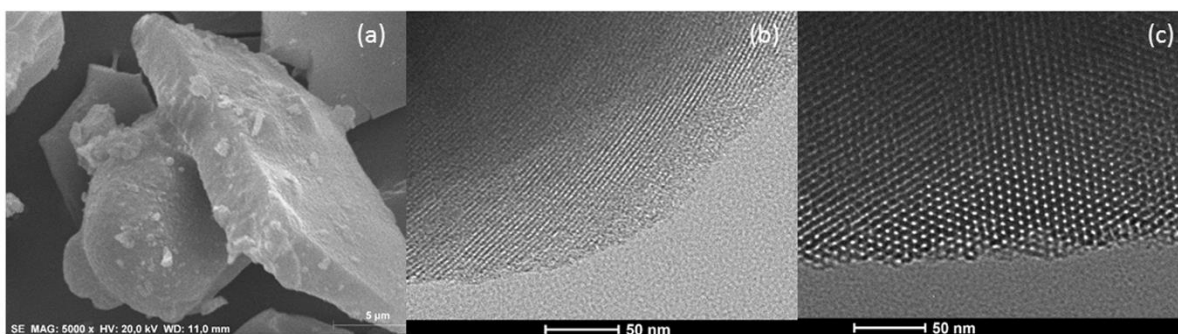
Figure 2. SEM micrograph (a) and HR-TEM (b) and (c) of a MCM-41-SO$_3$H sample

3.3 Optimization of the SPE procedure

3.3.1 Type and volume of eluent solvent

Firstly, the organic solvent for the elution of analytes from the SPE sorbent was optimized. Aliquots of 25 mL of ultrapure water spiked at a concentration level of 1 µg·L^{-1} of each PCP were passed through SPE cartridges packed with 50 mg of the MCM-41-SO$_3$H material (previously pre-conditioned with 5 mL of ultrapure water) at a flow rate of about 5 mL·min^{-1}. After drying the sorbent with air and N$_2$, the elution step was performed with 3 mL of organic solvents with different polarities (methanol, acetonitrile, ethyl acetate, dichloromethane or *n*-hexane). Then, the organic extracts were evaporated to dryness under a gentle N$_2$ current, reconstituted in 0.5 mL of methanol:ultrapure water (20:80, v/v) and, finally, 5 µL were injected in the UPLC-QqQ-MS/MS system. The best recovery values were obtained with the use of ethyl acetate as the elution solvent, whereas no analyte was eluted from the sorbent when using *n*-hexane. For the rest of the organic solvents assayed, the recoveries were in all cases lower than those obtained using ethyl acetate.

Once ethyl acetate was selected as the eluent, the optimum volume was studied. With that purpose, after the pre-concentration of spiked ultrapure water aliquots as described above, the sorbent was sequentially eluted with increasing volumes of ethyl acetate (ranging from 1 mL to 4 mL). The obtained results showed that 2 mL of ethyl acetate were enough to achieve the complete elution of all of the compounds retained in the sorbent, this volume being selected for the subsequent experiments.

3.3.2 Sample pH and ionic strength

Sample pH plays a significant role in the retention of the analytes (ionic or neutral state) onto the sorbent. As can be observed in **Table S1**, all compounds are basic with *p*K$_a$ values between 7.72 and 8.20. To assess the effect of sample pH on the retention of the selected compounds onto the MCM-41-SO$_3$H, aliquots (50 mL) of ultrapure water samples containing 1 µg·L^{-1} of each PCP were adjusted to different pH values between 2 and 9.5. The samples were pre-concentrated through SPE cartridges containing 50 mg of MCM-41-SO$_3$H according to the procedure described above and the content of PCPs in each sample extract was determined by UPLC-QqQ-MS/MS. As shown in **Figure 3a** (mean recovery versus sample pH), the retention of PBs on the sorbent surface was not affected by the sample pH, even though the recovery obtained for MePB (the most polar of them) was slightly below 70 %. However, the retention of UVFs onto the sorbent improved when the sample pH increased up to 6.5 and then it remained constant or decreased slightly. Therefore, this pH value was selected to be used in successive experiments.

Previous studies about SPE pre-concentration [61] showed that salts increase the ionic strength of water and decrease the solubility of the compounds in it (salting out effect), thus improving the extraction efficiency. As real water samples contained different salt concentrations, which can affect the retention of the target compounds onto the sorbent in different ways, the effect of the salt content on the retention of the PCPs was evaluated. With this aim, ultrapure water samples spiked with 1 µg·L^{-1} of each PCP, containing increasing amounts of sodium chloride (0.1 to 15 %, w/v) and adjusted at the optimum pH 6.5, were pre-concentrated according to the SPE procedure. The results obtained, summarized in **Figure 3b,** show that the recoveries for most PCPs were similar for samples containing between 0.1 and 12.5 % NaCl, whereas for higher salt concentrations the retention decreased for all compounds. Therefore, 10 % NaCl was added to the water samples before pre-concentration.
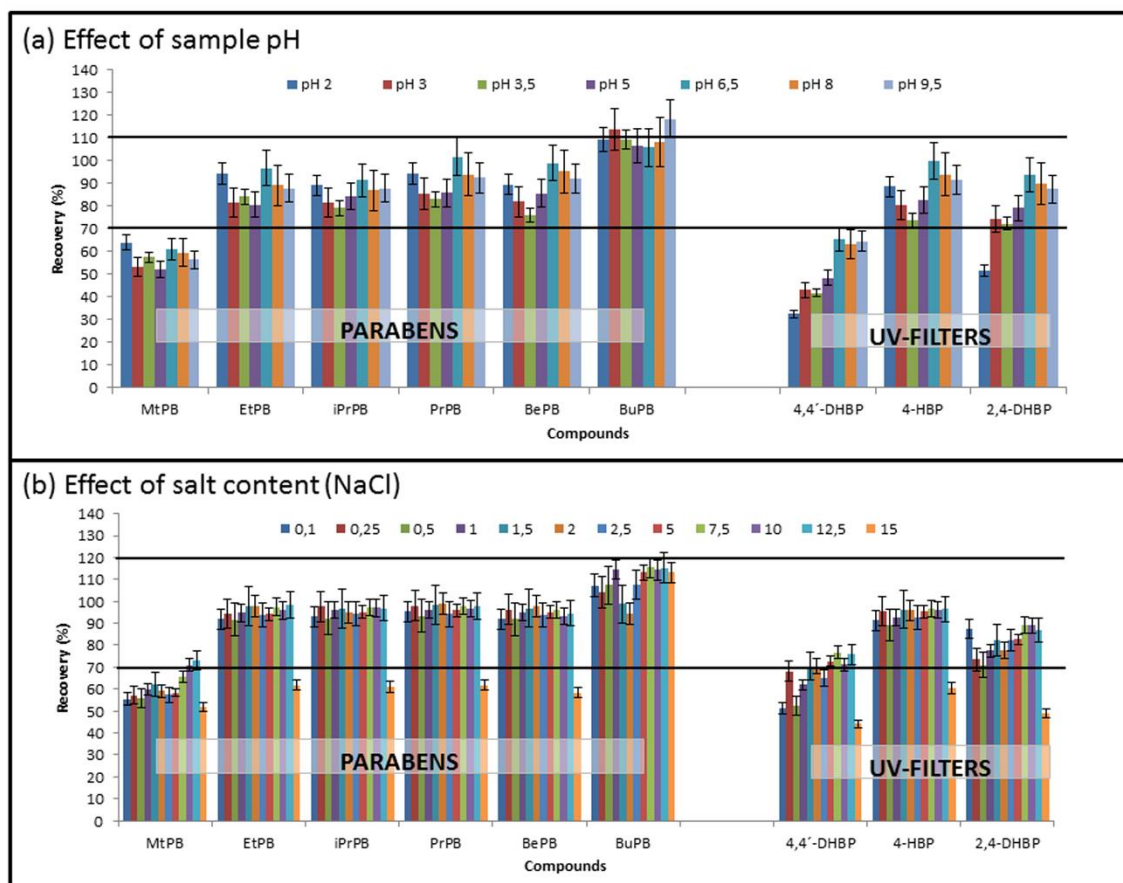
Figure 3. *Mean recovery (%) and error bar (RSD, %) obtained for three replicates in the optimization of the main parameters affecting adsorption/elution of the PCPs in the mesoporous MCM-41-SO$_3$H: (a) sample pH and (b) salt content in the sample*

3.3.3 Sorbent amount

In order to improve the retention of the most polar compounds (MePB and 4,4´-DHBP), the sorbent amount was optimized. Ultrapure water samples (50 mL adjusted at pH 6.5 and modified with 10 % NaCl) were spiked at a concentration level of 1 μg·L^{-1} of each PCP and pre-concentrated using 50, 75 and 100 mg of the MCM-41-SO$_3$H sorbent (**Table 1**).

The retention for most compounds was close to 100 % with 50 mg of sorbent and remained constant even though the sorbent amount was increased. However, for the three most polar PCPs (MePB, 4,4´-DHBP and 2,4-DHBP), the recoveries increased with the amount of sorbent. According to the results obtained, 75 mg of sorbent were enough for the full retention of 4,4´-DHBP and 2,4-DHBP but, for MePB (the most polar compound), 100 mg were necessary. Therefore, 100 mg of MCM-41-SO$_3$H were selected for the SPE pre-concentration of the target compounds.

3.3.4 Sample loading volume (breakthrough)

Another factor that affects the retention of the target analytes is the breakthrough volume (sample volume for pre-concentration). To select the maximum volume of water to be pre-concentrated, several experiments using 100 mg of sorbent and increasing volumes of ultrapure water samples (between 50 and 250 mL) spiked with the same concentration of PCPs were conducted.

In all experiments, satisfactory recoveries (between 70 % and 120 %) were obtained for all compounds except for MePB and EtPB, whose recoveries decreased when the water sample volume increased from 50 mL to 100 mL and 150 mL, respectively (**Table 1**). Therefore, 50 mL of water sample were chosen as the maximum volume, the pre-concentration factor being 100 for all compounds.

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Table 1. *Mean recovery (%) and RSD (%) obtained for the selected compounds using different MCM-41-SO$_3$H amounts (50 mL of water) and different volumes of water (100 mg of sorbent)*

Compounds	Sorbent amount (mg)*			Sample volume (mL)*				
	50	**75**	**100**	**50**	**100**	**150**	**200**	**250**
MePB	59.8 (5.7)	69.0 (6.4)	72.7 (7.3)	72.7 (7.3)	38.9 (5.4)	27.9 (4.2)	18.6 (2.1)	18.2 (3.4)
EtPB	98.8 (10.1)	101.5 (7.8)	99.5 (5.9)	99.5 (5.9)	94.9 (7.8)	77.7 (6.7)	54.1 (4.6)	54.3 (6.1)
iPrPB	102.6 (9.1)	100.8 (8.3)	101.2 (7.6)	101.2 (7.6)	103.0 (9.1)	102.5 (10.3)	100.0 (6.1)	103.5 (9.1)
PrPB	102.6 (6.1)	101.0 (7.9)	101.1 (6.0)	101.1 (6.0)	103.1 (5.3)	102.7 (9.1)	101.8 (8.3)	108.4 (6.3)
BePB	100.8 (5.7)	99.9 (8.3)	101.2 (5.6)	101.2 (5.6)	102.4 (8.4)	103.0 (5.6)	102.2 (5.2)	110.6 (7.5)
BuPB	120.3 (12.4)	119.0 (9.2)	120.7 (7.3)	120.7 (7.3)	107.1 (7.9)	109.5 (7.2)	114.3 (7.1)	109.3 (10.5)
4,4´-DHBP	76.2 (4.4)	98.9 (5.7)	98.5 (8.3)	98.5 (8.3)	93.4 (8.1)	97.7 (7.2)	97.2 (8.5)	108.1 (6.4)
4-HBP	102.5 (11.2)	101.0 (7.4)	101.8 (8.2)	101.8 (8.2)	105.8 (11.2)	103.5 (9.6)	102.8 (9.7)	111.4 (7.8)
2,4-DHBP	83.1 (7.5)	93.7 (9.4)	98.9 (7.3)	98.9 (7.3)	92.6 (6.5)	90.0 (5.2)	95.6 (5.8)	101.1 (6.1)

* RSD(%) in parentheses (n=3)

3.4 Method validation

Validation parameters [62] for the analysis of PCPs were evaluated using standards in solvent and in spiked blank extract of WWTP effluent.

Linearity was assessed by the injection of six PCP standard solutions (prepared in methanol:ultrapure water, 20:80, v/v) at concentrations ranging between 1 and 100 µg·L^{-1}. Good linearity was achieved with R^2 values higher than 0.995 and residuals lower than 20 % in the studied range (**Table S3,** ESM). Intra-day and inter-day precision were evaluated by the injection of a standard mixture of 25 µg·L^{-1} of the target analytes in solvent, the RSDs (%) being lower than 9 % in all cases (**Table S3**, ESM).

Matrix effect (ME) was evaluated by comparing the slopes of external and matrix-matched calibration graphs, the latter built by using WWTP effluent blank extracts, i.e. extracts of a WWTP which did not contain the target analytes (**Table S3**, ESM). All analytes exhibited a low or negligible matrix effect (ME ≤ |20 %|), the exception being iPrPB (ME = -27 %). Therefore, in this specific case, the quantification in real samples should be performed with matrix-matched calibration curves or with the standard addition method.

Table 2. Recovery and precision values obtained for the target PCPs in a spiked WWTP blank effluent using MCM-41-SO$_3$H as SPE sorbent

| PPCs | WWTP effluent (0.05 µg.L^{-1} PPCs)* | | WWTP effluent (0.20 µg.L^{-1} PPCs)* | | ME(%) |
	External calibration	**Standard addition calibration**	**External calibration**	**Standard addition calibration**	
MePB	73.4 (3.9)	71.1 (0.7)	66.7 (1.8)	75.0 (13.0)	-11.8
EtPB	105.0 (3.7)	93.8 (1.8)	98.0 (2.5)	82.4 (8.0)	-11.2
iPrPB	81.5 (7.9)	91.4 (9.0)	85.3 (8.8)	99.1 (4.1)	-27.1
PrPB	113.4 (6.4)	85.4 (4.3)	103.8 (4.6)	80.4 (6.5)	-15.5
BePB	115.2 (8.1)	85.7 (2.8)	95.8 (4.4)	77.9 (2.9)	-12.2
BuPB	103.8 (8.9)	92.5 (9.1)	98.7 (4.6)	80.5 (6.3)	-13.8
4,4´-DHBP	76.1 (2.8)	74.7 (2.1)	72.8 (1.8)	71.0 (1.8)	2.5
4-HBP	82.0 (4.6)	84.5 (3.2)	82.5 (1.1)	80.0 (3.0)	0.1
2,4-DHBP	95.1 (6.8)	99.6 (7.0)	82.9 (1.6)	77.3 (4.4)	4.0

**R*SD in parentheses; (n=3)

The method quantitation limit (MQL) was determined as the minimum detectable amount of analyte for which the quantifier selected reaction monitoring (SRM1 transition) provides a signal-to-noise ratio 10:1, using blank WWTP effluent extracts spiked at low concentrations of the selected PCPs (**Table S3**, ESM). MQLs were 0.5 ng·L^{-1} for PrPB and 2,4-DHBP, 1.0 ng·L^{-1} for MePB and 4,4´-DHBP, and 5.0 ng·L^{-1} for the rest of the analytes in the WWTP effluent samples (taking into account the pre-concentration factor).

The proposed method was evaluated in terms of accuracy and precision with the use of blank WWTP effluent samples spiked at two concentrations levels, 0.05 and 0.20 µg·L^{-1}. Although the ME was low for most analytes, the standard addition methodology [63] was selected for quantification and the results were compared with those obtained using external calibration curves (**Table 2**). As can be seen, the recoveries obtained by using both approaches are similar, but slightly better results were obtained for the standard addition methodology. An exception was iPrPB, with ME=-27%, whose recoveries at 0.05 and 0.20 µg·L^{-1} increased when using this last calibration method, as could be expected; the

same behavior was observed for MePB at 0.20 μg·L⁻¹. Therefore, the use of the standard addition calibration is highly advisable in the analysis of WWTP effluent samples.

Finally, blank WWTP effluent extracts were spiked in triplicate with the concentrations of the analytes corresponding to the MQLs, and their quantitation was performed with the standard addition calibration. The recoveries ranged between 68.9 % (MePB) and 93.2 % (iPrPB), and the RSDs were lower than 8.5 %.

3.5 Analysis of real samples

The proposed method was applied to the analysis of selected PCPs in WWTP effluent and swimming pool water, the quantification being performed by the standard addition approach in both cases. Trace levels of four PBs were identified in both WWTP effluent and swimming pool water at different concentration levels (**Table 3**). In WWTP effluent samples, concentrations higher than their corresponding MQLs were found for MePB, PrPB and BePB, whereas for BuPB the concentration was slightly lower than its MQL. The concentration levels found for these compounds in swimming pool water were higher than their corresponding MQLs for MePB and PrPB, and lower for BePB and BuPB.

Table 3. *Levels of PCPs (ng·L⁻¹) found in a WWTP effluent and in a swimming pool water samples*

PCPs	SRM2/SRM1 range	WWSTP effluent		Swimming pool water	
		Concentration (ng·L⁻¹)	SRM2/SRM1	Concentration (ng·L⁻¹)	SRM2/SRM1
MePB	24.7-45.9	10.0	36.4	4.0	46.6
EtPB	38.6-71.6	-	-	-	-
iPrPB	53.2-98.8	-	-	-	-
PrPB	23.9-44.5	10.0	33.8	6.0	27.5
BePB	43.1-80.1	6.0	59.9	2.0*	63.6*
BuPB	23.7-43.9	3.0*	40.9*	2.0*	35.9*
4,4´-DHBP	9.0-16.8	-	-	0.1*	13.6*
4-HBP	58.1-107.9	4.0*	84.4*	1.0*	84.7*
2,4-DHBP	15.3-28.3	-	-	-	-

*The quantification was performed using standard addition method; * The concentration level was lower than the MQLs*

As for UVFs, 4-HBP has been found in both WWTP effluent and swimming pool water at concentration levels lower than their MQL. In addition, 4,4'-DHBP was also detected in swimming pool water at the same concentration that 4-HBP. When the concentration level of a certain compound was lower than its MQL, the identification was possible because the SRM1/SRM2 ratio was within the ±30 % range of the one corresponding to its standard. Therefore, a semi-quantitative analysis was performed in these cases.

As an example, **Figure 4** shows the two transitions (SRM1 and SRM2) of PrPB in the WWTP effluent sample as well as the same information for a 1 μg·L⁻¹ standard of this, in addition to the SRM1/SRM2 ratios. These transitions and their ratios confirm the presence of PrPB in water.
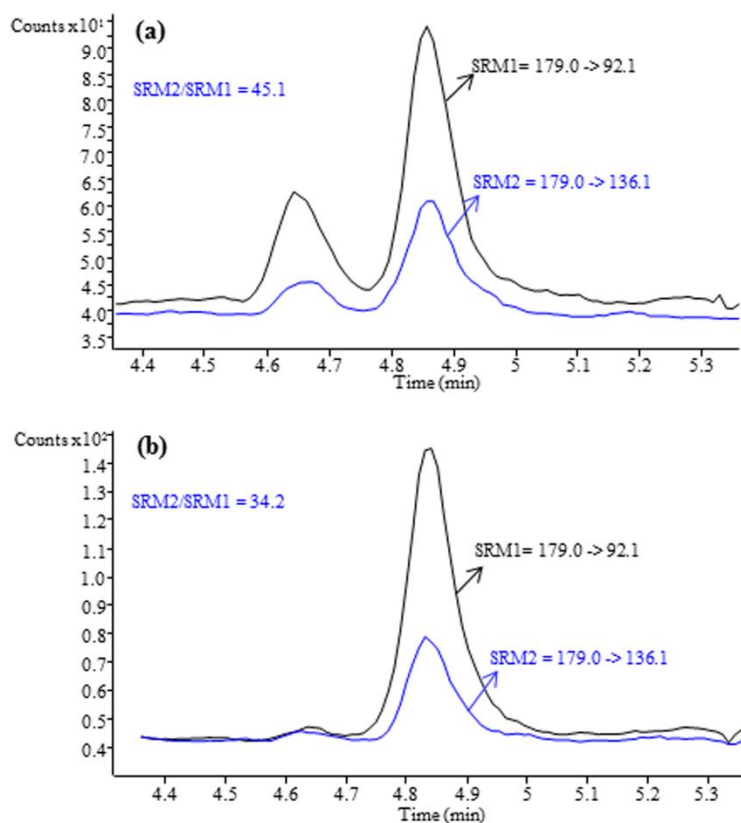
Figure 4. *Extracted ion chromatograms corresponding to the two SRM transitions of PrPB in: (a) 1 μg.L⁻¹ standard solution and (b) the WWTP effluent sample*

3.6 Interaction sorbent-analytes

With the aim of justifying the different recoveries obtained for UVFs and PBs (ketonic and ester derivatives, respectively), two main factors should be discussed. On one hand, charge delocalization, that is key in order to understand real interactions between the analytes and the adsorbent surface and, on the other, steric hindrance imposed by the nature of the alkyl groups located in the paraben esters.

When a benzene ring has two substituent groups, each exerts an influence on subsequent interactions or even reactivity. It is commonly accepted that the ring activation or deactivation can be predicted by the sum of the individual effects of these substituents. The site at which a new substituent is introduced depends on the orientation of the existing groups and their individual directing effects in terms of charge delocalization or resonance. Two general behavior categories can be identified: (1) groups oriented in such a manner that their directing influences act in concert, reinforcing the outcome and (2) groups whose influence is opposed or antagonistic to each other. The final behavior in each category changes depending on whether the groups have similar or opposite individual directing effects. In the case of 2,4-DHBP, for instance, the molecule contains two hydroxyl moieties located at relative positions 1 and 3, so the final effect is reinforced (R2 in **Scheme 1**). A similar cooperative situation occurs when one of the attached groups is electron-donating, the other one is electron-withdrawing and both moieties are placed at *para* positions (R1 in **Scheme 1**). The latter case occurs in all of the analyzed analytes, although this reinforced effect is stronger in ketones (UVFs) than in esters (PBs), since the carbon directly attached to the arene is less electropositive. Finally, a reinforcing orientational R3 type (**Scheme 1**) occurs in 2,4-DHBP, where and electron-donating and electron-withdrawing groups are located at *ortho* positions.

Interestingly, in the UVFs group of analytes, the compound with the best recovery, with a value of 99.6 % (see **Table 2**), is the one that contains the three orientational effects shown in **Scheme 1**, i.e. 2,4-DHBP. Within the ketonic compounds, the second most retained analyte is 4-HPB and then 4,4'-DHBP. **Scheme 2** shows the charge delocalization of these two compounds.

D = Electron donating group
W = Electron withdrawing group
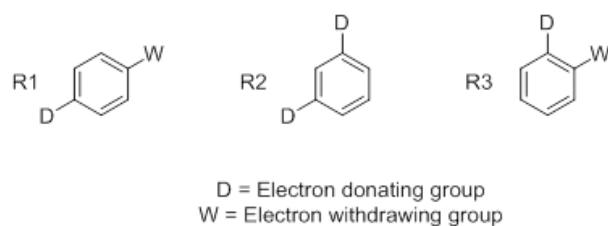
*Scheme 1. Reinforcing or cooperative interactions found in the analyzed PCPs*

In 4-HBP, both aromatic rings have opposite signs, with the phenyl group behaving as a source of electrons. In 4,4'-DHBP, the hydroxyl groups located at positions 4 and 4' are both electron-donating groups and they convert the two phenyl rings in electron-rich systems. The former effect allows a better retention onto the adsorbent, whereas the latter configuration inhibits such effect lowering the retention to 74.7 %.
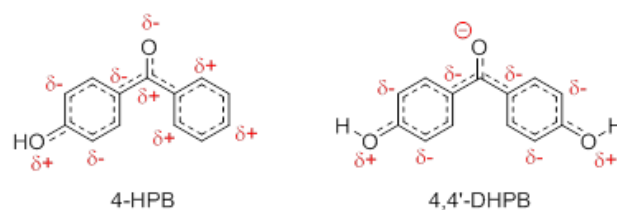
Scheme 2. Charge delocalization on 4-HPB and 4,4´-DHPB

In the analysis of PBs, the steric hindrance and conformational effects should also be considered. When the alkyl groups are sterically more demanding, i.e. Et, Pr, i-Pr, Bu and Be, the recoveries are in the range of 85.7-93.8 %. On the contrary, in the paraben MePB, the adsorption decreases to 71.1 %, probably due to the smaller size of the analyte and, consequently, a poorer retention onto the mesoporous material surface may take place.

The interaction between the MCM-41-SO$_3$H adsorbent and the analytes is, therefore, driven by hydrogen bondings and electrostatic interactions. The fact that the pK$_a$ values of all the assayed analytes are higher than the pH of the aqueous solutions makes the interactions to be established between the analytes with charge delocalization and the SO$_3^-$ groups of the adsorbent surface. **Scheme 3** illustrates some of the most plausible interaction modes that may take place in the adsorption process.
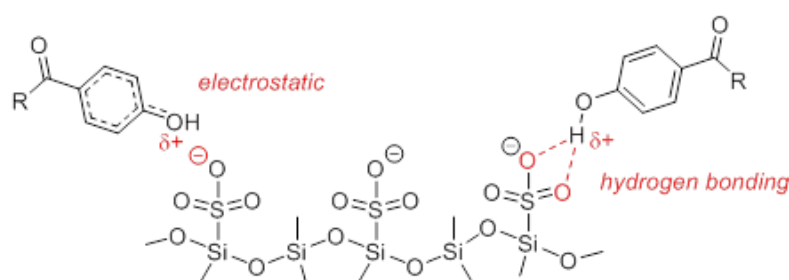
Scheme 3. Proposed interaction mechanism between MCM-41-SO$_3^-$ adsorbent and PCPs (an paraben has been selected as model)

4. Comparative study of MCM-41-SO$_3$H performance

The target PCPs have been previously extracted from aqueous samples by using conventional sorbents, the most frequent one being Oasis HLB, and they have been determined by LC-MS/MS. The performance of methods reported in the literature and our proposed method is summarized in **Table S4** (ESM).

Using 100 mg of MCM-41-SO₃H and 50 mL of water samples, the LOQs of the target PCPs were in the same order or lower than the published values, obtained using Oasis HLB and sample volumes of 100 or 250 mL. The obtained LOQs using Oasis HLB were lower only when 1000 mL of water samples were pre-concentrated.

The recoveries achieved for MePB, EtPB and PrPB with the proposed method were slightly lower than those found in the literature with two exceptions [27,28] and, for BePB and BuPB, the recoveries were higher than the previously reported ones [8,27,28].

On the other hand, iPrPB has been determined for the first time and the recoveries obtained were excellent (between 91 and 99 %). As for the UVFs, the recoveries were in the same order [29,64] or higher [27] than the ones found in the literature.

5. Conclusions

A silica-based mesoporous material functionalized with sulfonic acid groups (MCM-41-SO₃H), was synthesized and used as sorbent to pre-concentrate three UVFs and six PBs in WWTP effluent and swimming pool water at trace levels.

The presence of S was detected by elemental analysis and the –SO₃H moiety was identified by Raman sprectroscopy. The XRD patterns demonstrated the presence of a hexagonal symmetry characteristic of an MCM-41 structure, which was somewhat distorted, in addition to a slight decrease in the pore size as consequence of the incorporation of the –SO₃H groups. Moreover, the HRTEM studies confirmed the hexagonal structure of this material.

Ultrapure water was used in the preconditioning step, thus avoiding the use of organic solvents in this stage. Furthermore, a clean-up step was not necessary prior to the desorption of analytes retained on the sorbent.

The most polar compound (MePB) was retained with 100 mg of the sorbent and 50 mL was the maximum water volume that could be pre-concentrated without breakthrough for MePB and EtPB.

The only PCP showing a significant matrix effect (ME = -27 %) was iPrPB, which was corrected by the standard addition method.

The UPLC-MS/MS method was sensitive enough to allow MQLs ranging between 0.5 and 5.0 ng·L^{-1}, depending on the compound.

The results obtained (accuracy and precision) in the determination of the target PCPs demonstrate that this material is useful even when the interaction with the analytes is not the most expected (strong cation-exchange retention mechanism in this case).

Some of the target PCPs were found in WWTP effluent (MePB, PrPB, BePB, BuPB and 4-HBP) and in swimming pool water (MePB, PrPB, BePB, BuPB, 4-HBP and 4,4'-DHBP).

The possibility of synthesize functionalized mesoporous materials in the laboratory offers the possibility of addressing specific problems, thus improving the sample treatment step.

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CRediT authorship contribution statement

M. Mokhtari: Validation, Writing - original draft. **H. Hamaizi:** Investigation, Visualization. **M.D. Gil García:** Conceptualization, Methodology, Project administration. **M. Martínez Galera:** Resources, Writing - original draft, Supervision.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.microc.2019.104515.

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Graphical abstract
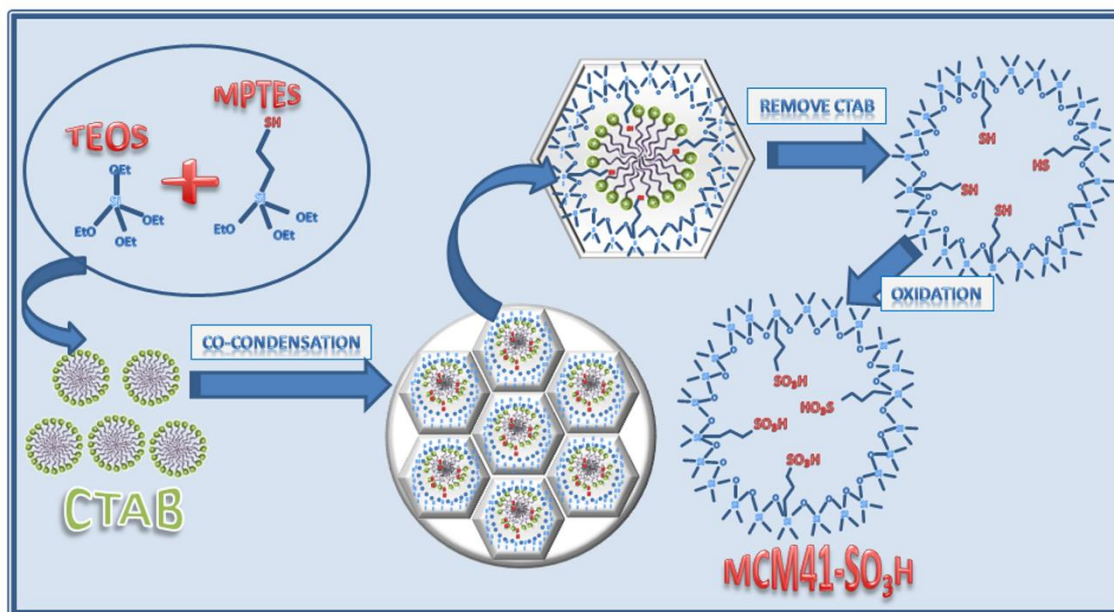
Highlights

- Nine personal care products were determined in wastewater and swimming pool water
- The MCM-41-SO$_3$H sorbent was efficiently used for enrichment and clean-up
- The personal care products were determined by UPLC with MS/MS detection
- Recoveries were excellent, except for the most polar MePB