

## **Solid phase extraction of pesticides from environmental waters using an MSU-1 mesoporous material and determination by UPLC-MS/MS**

L. Kharbouche<sup>c</sup>, M.D. Gil García<sup>a,b</sup>, A. Lozano<sup>a,b</sup>, H. Hamaizi<sup>c</sup>, M. Martínez Galera<sup>a,b\*</sup>

<sup>a</sup>*Department of Chemistry and Physics, Area of Analytical Chemistry, University of Almería, 04120 La Cañada de San Urbano, Almería, Spain*

<sup>b</sup>*Campus de Excelencia Internacional Agroalimentario CeiA3, La Cañada de San Urbano, 04120 Almería, Spain*

<sup>c</sup>*Department of Chemistry, University Ahmed Ben Bella 1, Oran, Algeria*

### **ABSTRACT**

This paper describes the synthesis of a silica based MSU-1 mesoporous solid and its application as sorbent in solid-phase extraction to pre-concentrate thirteen pesticides of low-high polarity (methomyl, cymoxanil, carbofuran, monolinuron, isoproturon, methidathion, methiocarb, malathion, phosalone, diazinon, penconazole, neburon and chlorotoluron) in ground and river water. The synthesis was based in an H-bonding interaction assembling ( $I^0N^0$ ) between two non-ionic components (the inorganic silica surface,  $I^0$  and the polyethylene oxide template,  $N^0$ ) by adding tetraethoxysilane to the non-ionic surfactant Brij@100, the latter previously dissolved in HCl 1M. 50 mL water samples adjusted at pH=3.5 were passed, at a flow rate of 5 mL/min, through a home-made cartridge containing 50 mg of MSU-1 sorbent, pre-conditioned with 5 mL of ultrapure water; then, the cartridge was washed with 5 mL of ultrapure water. Following elution with 5 mL of acetonitrile, the pesticides were determined by ultra performance liquid chromatography coupled to triple quadrupole-mass spectrometry. Two selected reaction monitoring transitions were monitored per compound, the most intense one being used for quantification and the second one for confirmation. Three points were used for identification, as established in the Directive 96/23/EC for LC-MS/MS analysis, which deals with confirmatory methods for organic residues and contaminants listed in the Group B (veterinary drugs and contaminants). Medium matrix effect ( $|20\%| > ME < |50\%|$ ) was found for methiocarb and malathion, whereas diazinon and phosalone showed strong matrix effect ( $ME \geq |50\%|$ ). Therefore, the standard addition methodology was applied by adding an adequate amount of the pesticide standard mixture to the final sample extract. All pesticides were quantified using this approach for practical reasons, thus avoiding two different calibrations. The method quantification limit (MQL) of pesticides was 0.01 µg/L for all of them, except for diazinon (0.1 µg/L). Recoveries of the target pesticides at MQL and 0.25 µg/L concentration levels in blank river water were in the range 70.1-113.5% and 86.7-107.3%, respectively, with RSDs lower than 16.3% and 15.7%, respectively. Four ground water samples and three river water samples, taken from Almería (Spain), were analyzed by the proposed method and only phosalone at a concentration level of 0.05 µg/L was found in one river water sample.

**Keywords:** Mesoporous silica material (MSU-1); Pesticides; Solid phase extraction (SPE); UPLC-QqQ-MS/MS; Environmental water

---

\*Corresponding author: M. Martínez Galera. E-mail address: [mmartine@ual.es](mailto:mmartine@ual.es)

## 1. Introduction

Pesticides are being used in agriculture to control pests for better yield and production. Today, the prevailing trend is to use pesticides that act only in accordance with their intended action and do not harm humans or other flora and fauna. However, unfortunately, the absolute selectivity is impossible to achieve in practice [1], in such a way that the application of these compounds has become a problem due to the possibility of contamination of ground and surface waters and its consequent impact on the environment and public health [2]. Thus, some reviews have been published in the literature dealing with the risk posed by these contaminants to human health [3-5] and aquatic ecosystems [6-10].

Pesticides reach water bodies by different routes including run-offs or spray drifting from agricultural fields and gardens, thus deteriorating their quality and affecting the living organisms [11] as they adversely affect the biodiversity, alter the functions of the ecosystem and impact the interspecies communication [12]. Numerous compounds have been detected in surface water, groundwater, and water supplies related to agricultural activities and human cases of environmental contamination [13,14]. Therefore, it is necessary to monitor residue pesticide levels in the environmental water for its quality assurance.

To determine pesticides in complex matrices, such as ground and surface waters, sample treatment for pre-concentration and clean up is a crucial step, which has been defined as a bottleneck in the whole analytical process [15]. In the last decades, solid phase extraction (SPE) has been the most popular sample treatment technique and significant efforts have been carried out to develop new formats and advanced sorbent materials improving selectivity or specificity towards target analytes, sorptive capacity and physicochemical or mechanical stability [16]. Thus, research in new advanced materials has involved different disciplines such as materials science, nanotechnology, polymer synthesis and analytical chemistry [15].

Silica based mesoporous materials (SMMs) are being increasingly used in sample preparation because of their advantageous characteristics, which have been described elsewhere [17]. The most commonly used SMMs are the small pore hexagonal MCM-41 and cubic MCM-48, the large pore hexagonal SBA-15 and cubic SBA-16 [18], which have been applied in sample preparation with and without functionalization [17,19].

MCM-41, the firstly synthesized and most studied member of the M41S family, is distinguished by its long range (hexagonal) pore order, but its low wall thickness (1-1.5 nm) leads to low chemical and hydrothermal stabilities, which could be crucial properties for certain adsorption and catalysis applications [20]. MCM-41 and its derivatives were synthesized in ethanol-water basic medium.

Later, mesoporous silica materials belonging to the MSU-X family were prepared by hydrolysis-condensation at acidic medium for charge neutrality of silica surfaces ( $I^0$ ) in presence of non-ionic polyethylene oxide (PEO) templates ( $N^0$ ). These mesostructures are assembled through H-bonding interactions between the electrically neutral surfactants and inorganic precursors [21] and the materials are characterized by their thicker walls (hence improved hydrothermal stability) and short range mesopore order (so-called 3D worm-hole structure) [22]. In MSU-X ( $X=1-4$ ) materials, X refers to the surfactant molecules, which can be either alkyl-PEO, alkyl-aryl PEO, polypropylene oxide PEO block-copolymers or ethoxylated derivatives of the fatty esters of sorbitan (Tween) [23]. B. Fotoohi et al. [24] provided a classification of the different members of this group of materials, including their inherent features. Thus, Brij surfactants form MSU-1 structures because their hydrophobic hydrocarbon tails are aliphatic, whereas the mesostructures obtained using Triton are named MSU-2 because of the presence of phenyl rings in their hydrophobic tails.

Previously, we have used MCM-41 as an SPE sorbent to pre-concentrate organic contaminants with very different polarity, including fourteen pharmaceuticals ( $\beta$ -blockers, NSAIDs and paracetamol) [25] and eight pesticides (organophosphates, carbamates and triazoles) [26] in environmental waters. These works describe two simple and inexpensive SPE procedures that provided right recoveries, avoiding derivatization processes of the material, except for the very polar analytes atenolol, methomyl and cymoxanil, which showed recoveries around 70, 20 and 70%, respectively.

In the present work, an MSU-1 mesoporous silica material was synthesized using Brij® S100 as template directing agent and used as sorbent to pre-concentrate thirteen pesticides of different polarity (methomyl, cymoxanil, carbofuran, monolinuron, isoproturon, methidathion, methiocarb, malathion, phosalone, diazinon, penconazole, neburon and chlorotoluron) present in surface waters. The quantification was carried out using UPLC-MS/MS and the results improved those obtained using other sorbents, especially for polar analytes.

## 2. Experimental

### 2.1. Chemicals and reagents

Pesticide analytical standards (>98%) of methomyl, cymoxanil, carbofuran, monolinuron, isoproturon, methidathion, methiocarb, malathion, phosalone, diazinon and penconazole were purchased from Sigma-Aldrich (Germany) and other pesticides such as neburon and chlorotoluron were purchased from Riedel de-Haën (Germany). Organic solvents of pesticide residue analysis grade (acetone, methanol, acetonitrile, dichloromethane and n-hexane) were purchased from Sigma-Aldrich. Individual pesticide stock solutions were prepared in acetonitrile for all compounds and stored at -20 °C with concentrations ranging from 990 to 1500 mg/L, being stable for at least three months. Working standard solution mixtures of all pesticides were prepared daily by appropriate dilution of individual stock standard solutions in acetonitrile-ultrapure water (20:80, v/v).

Polyoxyethylene (100) stearyl ether (Brij® S100) non-ionic surfactant and tetraethyl orthosilicate (TEOS) were both purchased from Sigma-Aldrich. A 3 mL polypropylene body syringe and two polyethylene frits were used to prepare the SPE cartridges, both supplied by Supelco (Spain).

### 2.2. Instruments and software

An UPLC-MS/MS method was developed for the determination of thirteen pesticides in environmental water. It consisted of an Agilent UHPLC 1290 series coupled to an Agilent 6490 Triple Quadruple-UPLC/MS. Chromatographic separation was performed with a Zorbax Eclipse Plus C8 column (1.8µm×2.1mm×100mm) from Agilent, maintaining the temperature at 35°C. The UPLC mobile phase consisted of a mixture of 0.1% formic acid in ultrapure water (mobile phase A) and 0.1% formic acid and 5% ultrapure water in acetonitrile (mobile phase B) at a constant flow rate of 0.3 mL/min, and the injection volume was 5 µL. The elution gradient program was as follows: 20% of B (initial conditions) for 2 min, a linear gradient up to 100% of B in 13 min plus 2 min more under isocratic mode (100% B). Subsequently, initial mobile phase conditions (20% B) were reached in 2.5 min and were maintained during 2 additional min before the next injection.

The UPLC system was coupled to the Triple quadrupole (QQQ) with a jet-stream electrospray ion source (ESI) operating in positive ionization mode (PI), with 380 V as the fragmentor voltage and 3000 V for the capillary voltage. The configuration of ESI source was as follows: 120 °C for the drying gas temperature at a flow rate of 13 L/min, 375 °C for the sheath gas temperature at a flow rate of 10 L/min and 45 psi for the nebulizer pressure. Nitrogen (high purity) was used as the nebulizer gas and collision gas.

To optimize the MS parameters, individual pesticide standard solutions of 100 µg/L in acetonitrile:water (1:1, v/v) were infused directly into the MS system in full-scan mode with a mass range of 50–800 m/z. The most intense ion was selected as the precursor ion for each analyte. Next, optimal collision energy (CE) were selected for the two most intense transitions of each analyte in product ion mode, the most intense of them being the quantifier ion (SRM1) and the second one, the qualifier ion (SRM2).

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

### 2.3. Synthesis and characterization of the MSU-1 sorbent

The protocol for the preparation of MSU-1 sorbent with Brij® S100 non-ionic surfactant and TEOS as silica precursor was based on a previous work developed by us [27], but with some modifications.

Brij® S100 (2 g) was dissolved in distilled water (30 g) with vigorous stirring (~1100 rpm) for 10 min at 40°C before adding HCl 1 mol/L (120 mL). The mixture was maintained under vigorous stirring for 1 h. Then, TEOS (9 g) was added to this homogeneous mixture and kept under vigorous stirring for 1 h more. Afterwards, it was introduced into a sealed polyethylene tube and it was maintained overnight in refrigerator (6°C). Next, it was placed in the oven at 120 °C for 24 h and the resulting white solid was recovered by filtration, washed several times with water, dried at 60 °C and, finally, calcined at 550 °C for 6 h under air. In these conditions, approximately 2 g of MSU-1 sorbent (a white fine powder) were obtained.

The characterization of the synthesized MSU-1 was performed by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption-desorption isotherms.

The powder XRD patterns were obtained on an EMPYREAN PAN analytical spectrometer using the Cu K $\alpha$  radiation and operating at 45 kV and 40 mA within the 2 $\theta$  range of 0.7 and 10° and with 0.01 2 $\theta$  steps. The sample was placed between two films of kapton.

The SEM micrographs were obtained on a HITACHI S-3500N Scanning Electron Microscope after coating the sample with a 14.4 nm thickness gold film, using a voltage of 10 kV and a working distance of 14.4 mm. The TEM images were obtained on a FEI Talos F200X TEM electron microscope, operating at 200 kV. The sample was crushed in an agate mortar, dispersed in ethanol and a single drop was poured onto a formvar-carbon film covered copper grid.

The nitrogen adsorption-desorption isotherms were measured at 77 K using an ASAP 2420 volumetric adsorption analyzer (Micromeritics). Prior to adsorption measurements, the samples were outgassed at 400 °C in a nitrogen flow for 6 h. The surface area was obtained by the Brunauer–Emmett–Teller (BET) method using adsorption data in the relative pressure range from 0.05 to 0.2. The pore size distribution was calculated from the adsorption.

## 2.4. Water samples

Two types of environmental waters were analyzed, including four groundwater (GW) samples and three river water (RW) samples, taken from Almeria (Spain). All of them were collected in plastic bottles, filtered through 20-25  $\mu$ m cellulose membranes and stored at 4 °C before analysis.

A river water (BRW) sample was collected in a scarcely populated area, analyzed to confirm the absence of pesticide residues and used as the blank for optimization and validation studies according to the EURACHEM Guide [28].

## 2.5. SPE procedure

The SPE cartridges were home made by packing 50 mg of the MSU-1 sorbent in 3 mL body syringes. Before pre-concentration, the SPE cartridges were pre-conditioned with 5 mL of ultrapure water (pH=3.5  $\pm$  0.1) and then, 50 mL of water samples adjusted at pH=3.5  $\pm$  0.1 were passed through the cartridges at an appropriate flow rate (approximately 5 mL/min) using a Büchi Vac V-500 vacuum pump (Flawil, Switzerland), connected to an extraction manifold of Waters (Milford, MA, USA). Next, the MSU-1 sorbent was washed with 5 mL of ultrapure water to remove co-adsorbed matrix substances and it was dried by passing air for 5 min plus N<sub>2</sub> for 5 min.

Subsequently, the pesticides, retained on the MSU-1 sorbent, were eluted with 5 mL of dichloromethane and the eluate was evaporated to dryness with a gentle N<sub>2</sub> flow. Finally, the extract was redissolved in 0.5 mL acetonitrile:ultrapure water (20:80,v/v) and then injected in the UPLC-MS/MS system.

# 3. Results and discussion

## 3.1. Synthesis and characterization of MSU-1

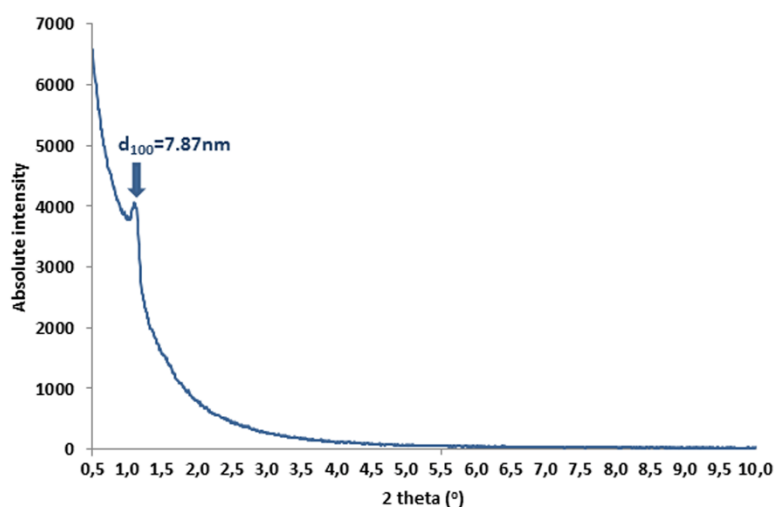
The MSU-1 material was synthesized using TEOS as silica precursor and the non-ionic surfactant Brij® S100 (C<sub>18</sub>H<sub>37</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH, n~100) in which the hydrophobic alkyl group consists of 18 carbon units and the hydrophilic head group contains 100 ethylene oxide (EO) units. Working in acidic medium (HCl 1 M), the N<sup>0</sup>I<sup>0</sup> templating strategy was followed with H-bonding interactions [21] between the neutral silica (I<sup>0</sup>) and the PEO (polyethylene oxide) template (N<sup>0</sup>).

The XRD patterns recorded on the calcined samples exhibited a single peak in the 2 $\theta$  range of 0.5-2° (**Figure 1**), indicating a poorly ordered mesostructure lacking long-rang structural order, such as the one observed for mesostructured solids with worm-like pores [23], which means that pores are regular in terms of size but not spatially ordered. On the other hand, the correlation distance deduced from the main XRD peak (d<sub>100</sub>) can be attributed to the pore-pore distance, giving a value of 7.87 nm, in agreement with the one found by S.A. Bagshaw et al. [29] when they obtained an MSU-1 silica material by using TEOS and the PEO surfactant Tergitol 15-S-n (C<sub>11-15</sub>H<sub>23-31</sub>O(CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>20</sub>).

SEM micrographs (**Figure 2a**) showed well defined spherical particles (A) with sizes ranging between 5 and 12  $\mu$ m, in addition to a small number of particles with hexagonal shape (B), which is in agreement with the results obtained by TEM (**Figure 2b**).

Nitrogen adsorption/desorption isotherm is type IV, according to the characteristics of mesoporous solids, with a hysteresis of type H2, suggesting narrow diameters at the end of the pores (**Figure S1a** in Electronic Supplementary Material, ESM). Textural parameters indicate a narrow BJH desorption average pore diameter distribution centered at

4.24 nm (**Figure S1b** in ESM); presumably, the surfactant molecule, which has a hydrophilic chain constituted of 100 ethylene oxide segments, is subject of torsions resulting in size reduction before forming micelles. Furthermore, the BET surface area is 813.88 m<sup>2</sup>/g, and the BJH adsorption cumulative volume of pores is 0.597 cm<sup>3</sup>/g.



**Figure 1.** X-ray diffraction pattern of MSU-1

The meso- and micropores are interconnected at the silica wall, which shows a very large value of its thickness (~3 nm), obtained by calculating the difference between the pore-pore distance and the mean pore diameter. This means that the hydrothermal stability is high for this mesoporous material.

### 3.2. UPLC-QqQ-MS/MS analysis

UPLC is based on the use of normal-sized columns packed with particles with a diameter lower than 2 μm in such a way that the column efficiency increases significantly and becomes nearly independent of the mobile phase flow rate. [30].

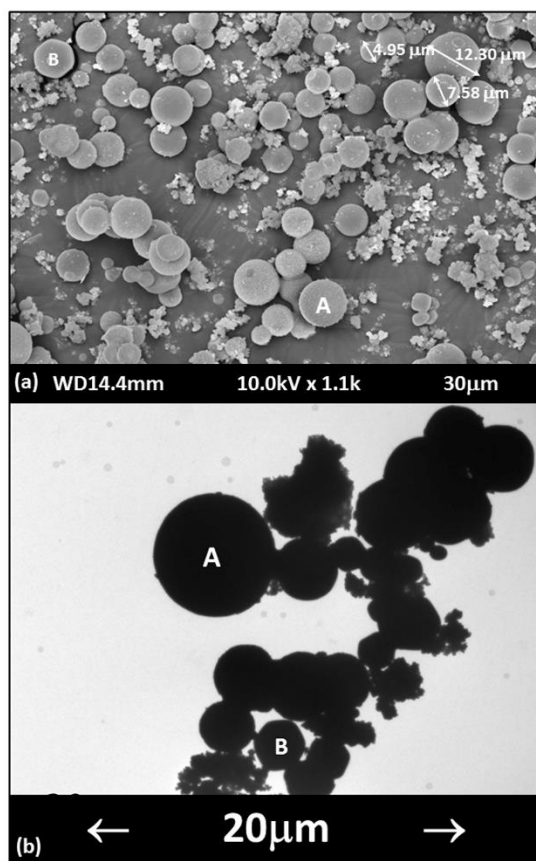
In this work an UPLC-QqQ-MS/MS method has been developed for quantification and identification of a group of pesticides in environmental waters, according to the EU guidelines [31]. **Table 1** shows the operational parameters for identification and quantitation of target pesticides by the UPLC-MS/MS method. It includes the retention time (Rt) and two SRM transitions for each pesticide (SRM1 and SRM2) with their corresponding collision energies for MS/MS operation mode and the SRM ratio (the relationship between the abundance of two selected transitions, SRM2/SRM1), obtained by injection of a pesticide standard solution of 100 μg/L in acetonitrile:water (1:1, v/v).

The most intense transition (SRM1) was used for quantification and three points were used for identification, as established in the Directive 96/23/EC [32] which deals with confirmatory methods for organic residues and contaminants listed in the Group B (veterinary drugs and contaminants), analyzed by LC-MS/MS, in real samples [31]:

(1) The Rt of the analyte in the test sample shall correspond to that of the calibration standard with a tolerance of ± 2,5 %

(2) One precursor ion and two product ions should be selected for each analyte

(3) The relative intensities of the two detected ions (SRM2 and SRM1), expressed as a percentage of the intensity of the most intense ion or transition, shall correspond to those of the calibration standard, either from calibration standard solutions or from spiked samples, at comparable concentrations, measured under the same conditions, within tolerances between ± 20% and ± 50%) depending on the relative intensity among SRM2 and SRM1.



**Figure 2.** (a) SEM and (b) TEM images of MSU-1

### 3.3. Optimization of the enrichment procedure

#### 3.3.1. Selection of type and volume of eluent

25 mL of ultrapure water samples, spiked at a concentration level of 1 μg/L, were passed through cartridges packed with 50 mg of MSU-1 material at a flow rate of about 5 mL/min. The elution step was performed with 5 mL of different solvents (methanol, acetonitrile, acetone, dichloromethane and n-hexane). The organic extracts were evaporated to dryness under a N<sub>2</sub> stream, were reconstituted in 0.5 mL of acetonitrile:ultrapure water (20:80,v/v) and then, 5 μL of each extract was injected in the UPLC-QqQ-MS/MS system.

It was found (**Table S1**, included in ESM) that acetonitrile and dichloromethane led to good recoveries for all pesticides, but acetonitrile was selected rather than dichloromethane due to its lower toxicity, as well as the slightly better recoveries for methomyl and cymoxanil.

In addition, the recoveries for the less polar pesticides increased with the volume of acetonitrile, being satisfactory (between 87 and 107%) when using 5 mL, whereas 7 mL of acetonitrile did not improve these values. For that reason, 5 mL of acetonitrile were utilized in the following experiments to reach a complete elution and save time and reagents.

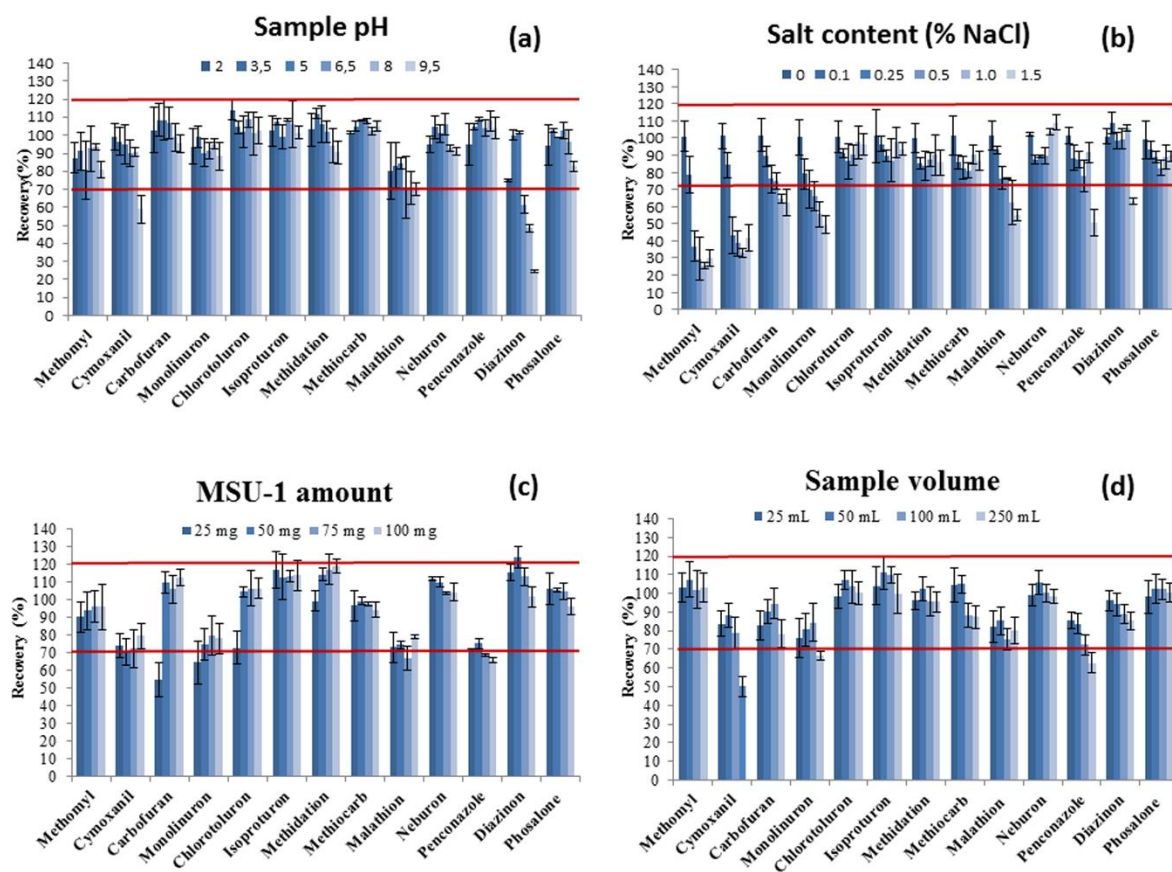
#### 3.3.2. Optimization of sample pH and ionic strength

Sample pH could be an important factor that affects the retention of pesticides onto the SPE sorbent because it can affect the existing forms of the pesticides with acidic or basic properties, as well as the surface charge of the silica sorbent.

The pH effect in the retention of the pesticides onto the MSU-1 sorbent was evaluated at a pH range between 2.0 and 9.5. With this aim, 25 mL aliquots of ultrapure water, spiked at a concentration level of 1 μg/L of each pesticide, were adjusted a different pH values with HCl 0.1 mol/L or NaOH 0.1 mol/L and they were passed through the SPE cartridges packed with 50 mg of MSU-1 at a flow rate of 5 mL/min. Similar recoveries were obtained over the studied pH range for most pesticides (**Figure 3a**). The exception was for pesticides with acidic and basic properties (cymoxanil

and diazinon, respectively), whose recoveries remained constant between pH 2 and 5 for diazinon ( $pK_a=2.6$ ) and between pH 2 and 8 for cymoxanil ( $pK_a=9.3$ ). At pH values higher than 8 the recoveries decreased significantly. This behavior can be explained because at  $pH > pK_a + 2$ , the pesticides are fully in their basic forms and are strongly retained by the sorbent through anionic exchange and hydrophobic interactions. Thus,  $pH=3.5$  was selected as the optimum sample pH to achieve the highest recoveries for all pesticides.

The study of salt content effect (**Figure 3b**) was carried out by adding amounts of NaCl, ranging from 0 to 2%, to water samples (adjusted at pH 3.5 and spiked at 1  $\mu\text{g/L}$  of each pesticide).



**Figure 3.** Mean recovery (%) and error bar (RSD, %) obtained in the optimization of the main parameters affecting adsorption/elution of the pesticides in the MSU-1 sorbent: (a) sample pH, (b) salt content in the sample, (c) sorbent amount and (d) breakthrough volume

The addition of salts (commonly sodium chloride) increases the ionic strength and decreases the solubility of target analytes (salting out effect), thus increasing the partition of the analytes onto the sorbent phase and, therefore, their extraction efficiency.

The explanation of the salting-out phenomenon is that water molecules form hydration spheres around the ionic salt molecules, thus reducing the amount of water available to dissolve the analyte [33].

However, the addition of salts can also lead to a decrease of the extraction efficiency, which can be due to two phenomena: (i) polar molecules may participate in electrostatic interactions with the salt ions in solution, thereby reducing the rate of mass transfer [33], and (ii) the addition of salt may increase the viscosity of the sample matrix, which would hamper the transfer of the analytes to the sorbent [34].

**Table 1.** Operational parameters of the LC-QqQ-MS/MS method for pesticide residues analysis in environmental water

<b>Pesticide</b>	<b>Rt (min)</b>	<b>DP (V)</b>	<b>SRM<sub>1</sub></b>	<b>CE<sub>1</sub> (eV)</b>	<b>SRM<sub>2</sub></b>	<b>CE<sub>2</sub> (eV)</b>	<b>SRM<sub>2</sub>/SRM<sub>1</sub>*</b>
Methomyl	3.03	380	163.1>106.0	4	163.1>84.0	2	56
Cymoxanil	6.15	380	199.1>128.0	4	199.1>110.9	12	27
Carbofuran	8.58	380	222.0>165.0	10	222.0>123.0	15	89
Monolinuron	9.02	380	215.1>126	16	215.1>148.1	8	67
Chlorotoluron	9.38	380	213.1>72.0	20	213.1>140.0	20	5
Isoproturon	9.86	380	207.2>72.1	10	207.2>165.1	20	5
Methidathion	10.19	380	302.9>145.0	2	302.9>85.1	15	53
Methiocarb	10.87	380	226.1>169	5	226.1>121.1	12	79
Malathion	11.27	380	331.0>127.1	15	331.0>285.0	5	92
Neburon	12.18	380	275.1>57.1	20	275.1>88.1	12	29
Penconazole	12.30	380	284.0>70.0	42	284.0>159.0	45	33
Diazinon	12.51	380	305.0>169.2	15	305.0>153.0	20	16
Phosalone	12.60	380	368.0>182.0	8	368.0>111.0	44	17

\* Expressed as a percentage



For those pesticides with very low logKow (methomyl and cymoxanil, with values of 0.09 and 0.67, respectively), slight increases in the NaCl concentration lead to significant negative effects (**Figure 3b**), whereas for the rest of pesticides, slight (carbofuran, monolinuron and malathion, with logkow in the range 1.8-2.75) or negligible (the rest of pesticides, with logKow in the range 2.50-4.01) effects were observed.

Taking into account the above considerations, it can be concluded that the mechanism involved in the low recoveries for the very polar methomyl and cymoxanil and the less polar carbofuran, monolinuron and malathion is the interaction of these molecules through electrostatic interactions with the salt ions, thus reducing the rate of mass transfer. Subsequent experiments were carried out without salt addition to the water samples.

### 3.3.3. Sorbent effect

25 mL of ultrapure water samples (adjusted at pH 3.5 and spiked at a concentration level of 1 µg/L) were passed through cartridges packed with MSU-1 at increasing amounts in the range 25-100 mg, at a flow rate of 5 mL/min. As it is shown in **Figure 3c**, the recoveries of all pesticides were between 70 and 120% with 50 mg of MSU-1 sorbent, whereas when the sorbent amount was 25 mg, the recoveries of carbofuran and monolinuron were lower, indicating that this amount was not enough to retain these two pesticides. In contrast, when the sorbent amount was increased (75 mg or 100 mg) the recovery for penconalozole was lower than 70% because it was incompletely eluted and more volume of acetonitrile should be added for elution. Therefore, 50 mg of MSU-1 were used in the subsequent experiments.

### 3.3.4. Sample breakthrough

Sample breakthrough depends on the strength of the interaction between analytes and sorbent, on the sample volume and on the amount of sorbent [35]. The sample breakthrough volume was evaluated by applying the optimized procedure to sample volumes from 25 to 250 mL, spiked with the same amounts of pesticides. **Figure 3d** shows that the recoveries for all pesticides were satisfactory (between 70% and 120%) with sample volumes up to 100 mL and they decreased below 70% with volumes of 250 mL for cymoxanil, monolinuron and penconazole. Therefore, a 100 mL volume of water sample was selected as the maximum sample volume, being the pre-concentration factor 100 for all pesticides.

## 3.4. Method validation

The applicability of the proposed SPE method for the target pesticides in real water samples was validated, according to the EURACHEM Guide [28].

Linearity was evaluated by injecting (in triplicate) pesticide standard solutions prepared in solvent and in blank river water extract, at five concentration levels (between 1.0 µg/L and 100.0 µg/L). Acceptable linearity (with  $R^2$  higher than 0.99) was found for all the pesticides in solvent and in matrix matched solutions and different linear ranges were obtained (**Table 2**), according to the pesticide.

The effect of the matrix compounds on the pesticide signals was evaluated by comparing the slopes of solvent-based and matrix-matched calibration graphs. According to the results summarized in **Table 2**, most pesticides showed low or negligible matrix effects ( $ME < |20\%|$ ). Methiocarb and malathion showed medium matrix effect ( $|20\%| > ME < |50\%|$ ) and diazinon and phosalone showed strong matrix effects ( $ME > |50\%|$ ). Therefore, quantification of the mentioned pesticides in real samples should be performed with matrix-matched calibration curves or with the standard addition method. In this case, the standard addition methodology was applied, by adding increasing amounts of the pesticide standard mixture to the final sample extract.

Method quantification limits (MQLs) of the pesticides were determined from standards of the pesticides prepared in blank river water extract at low concentrations and they were based on the  $S/N=10$  criterion. According to their sensibilities, MQLs were 0.01 µg/L for methomyl, cymoxanil, chlorotoluron, isoproturon and neburon, 0.05 µg/L for carbofuran, monolinuron, methidathion, methiocarb, malathion, penconazole and phosalone, and the highest one, 0.1 µg/L, for diazinon.

Recovery and precision studies were carried out in river water blank samples ( $n=5$ ) spiked at two concentration levels. The lowest one was the MQL for each pesticide and the highest was 0.25 µg/L, all of them expressed as pesticide concentrations in river water samples.

Recoveries between 70.1% and 113.5% and precision values lower than 16.3% (**Table 3**) proved the suitability of MSU-1 as sorbent to pre-concentrate pesticides of different polarity in environmental surface waters.

### 3.5. Comparative study of MSU-1 sorbent recoveries

The studied pesticides have been pre-concentrated in aqueous samples by using conventional SPE sorbents, the most frequent being OASIS HLB. The chromatographic methods, sorbents, recoveries sample volumes and variables involved in the pre-concentration step are included in **Table S2** [26,36-49].

In a recent work, 100 mg of MCM-41 [26] and 30 mg of MWCNTs (multiwalled carbon nanotubes) [36] were used by us to pre-concentrate some of the pesticides of this study (methomyl, cymoxanil, methidathion, malathion, penconazole, diazinon, parathion-methyl and phosalone) in surface water, and they were then determined by LC-QqLIT.

The recoveries obtained for the very polar methomyl and cymoxanil with the MSU-1 sorbent (82-75% and 91-95%) were higher than the ones obtained using MCM-41 (16-29% and 67-78%) [26] and MWCNTs (43%-60% and 57%-86%) [36], and they were comparable to the ones obtained using Oasis HLB, being 96-105% for methomyl [37] and 83-102% for cymoxanil [39]. In addition, when using the MSU-1 sorbent, the recoveries obtained with Oasis HLB [39,42,44,49] were also improved for carbofuran (92%-110% vs 70%-120%), monolinuron (107-113% vs 56-57%), chlorotoluron (80-101% vs 75-85%), methidathion (86-108% vs 78-84%), penconazole (102%-108% vs 76%-89%), methiocarb (99%-111% vs 25%) and neburon (70-87% vs 67-77%) and were in the same order for diazinon (87%-106% vs 81%-113%) and isoproturon (82-97% vs 86-89 %).

In addition, 50 mg of MSU-1 sorbent were enough to pre-concentrate 50 mL of water samples, whereas 200 mg of Oasis HLB were used to preconcentrate 100-500 mL of water, according to the results found in the literature [37,39,40,42-44,49].

Regarding the cost of the compared sorbents, the price of one Oasis HLB cartridge was 7.5 euros, whereas the MSU-1 cartridge used in this work cost 1.5 euros, including the polypropylene syringe and frits. That difference involved a cost reduction of 80%.

### 3.6. Real samples

The proposed SPE-UPLC-QqQ-MS/MS method was applied to the determination of the target pesticides in four ground water samples and three river water samples, all of them from Almería (Spain).

Only phosalone was found in one river water sample at a concentration of 0.05 µg/L, which was below the threshold level established by the EU Commission in drinking water [50]. **Figure S2** shows two extracted ion chromatograms (EIC) corresponding to a standard of phosalone at 50 µg/L prepared in river water blank extract (corresponding to 0.05 µg/L in the water sample) and the pesticide present in the real river water sample. According to the identification criteria established by the EU guidelines [31], phosalone has been unequivocally identified in the river water.

## 4. Conclusions

A silica based mesoporous material MSU-1 was synthesized, using TEOS and the nonionic surfactant Brij@100 in strong acidic medium. The mesoporous material showed a poorly ordered mesostructure, similar to that of mesostructured solids with worm-like pores.

Pesticide residues in environmental waters were determined by UPLC-QqQ-MS/MS. Strong matrix effect (ME > 50%) was found only for diazinon, which was overcome by the standard addition approach.

The MSU-1 material was used for the first time to pre-concentrate thirteen pesticides of different polarity (logKow= 1.8-4.01) with satisfactory results, which improved the ones obtained previously by us using MCM-41 and MWCNTs for the very polar methomyl and cymoxanil. In other cases, the results were better than those published in the literature using Oasis HLB.

The flexibility linked to the synthesis of mesoporous materials at the laboratory allows their tailored design to resolve specific problems in sample treatment, such as the pre-concentration of polar pesticides.

The sensitivity provided by the use of UPLC-MS/MS allowed MQLs as low as 0.01 µg/L for all pesticides except diazinon, using only 50 mL of water samples in the pre-concentration step.

Despite the extensive use of pesticides, mainly insecticides, in the agricultural areas of Almería (Spain), phosalone was the only one detected, as an isolated case in a river water sample.

**Table 2.** Linear range and matrix effect (ME) values obtained for the target PCPs by UPLC-QqQ-MS/MS

Pesticides	Solvent		River water SPE extract		ME(%)*
	Linear range (µg/L)	R <sup>2</sup>	Linear range (µg/L)	R <sup>2</sup>	
Methomyl	1.0-100.0	0.9998	1.0-100.0	0.9989	-18
Cymoxanil	1.0-100.0	0.9977	1.0-100.0	0.9993	4
Carbofuran	1.0-100.0	0.9996	5.0-100.0	0.9948	-3
Monolinuron	1.0-100.0	0.9996	5.0-100.0	0.9901	-7
Chlorotoluron	1.0-100.0	0.9994	1.0-100.0	0.9987	-8
Isoproturon	1.0-100.0	0.9993	1.0-100.0	0.9995	-2
Methidathion	1.0-100.0	0.9998	5.0-100.0	0.9994	-7
Methiocarb	5.0-100.0	0.9992	10.0-100.0	0.9995	43
Malathion	1.0-100.0	0.9999	5.0-100.0	0.9978	-23
Neburon	1.0-100.0	0.9988	1.0-100.0	0.9962	-10
Penconazole	1.0-100.0	0.9966	5.0-100.0	0.9996	-12
Diazinon	5.0-50.0	0.9928	5.0-50.0	0.9964	-84
Phosalone	1.0-100.0	0.9996	5.0-100.0	0.9908	-50

\* ME(%) = ((slope matrix/slope solvent)-1) × 10

**Table 3.** Recovery and precision values obtained for the target pesticides using MSU-1 as SPE sorbent in river water samples

Pesticides	MQL ( $\mu\text{g/L}$ )*		0.25 $\mu\text{g/L}$ *	
	Mean recovery (%)	RSD (%)	Mean recovery (%)	RSD (%)
Methomyl <sup>(a)</sup>	82.1	13.3	75.4	14.0
Cymoxanil <sup>(a)</sup>	90.8	5.3	94.7	14.6
Carbofuran <sup>(b)</sup>	110.1	12.4	91.9	12.7
Monolinuron <sup>(b)</sup>	113.5	16.3	107.3	10.3
Chlorotoluron <sup>(a)</sup>	80.3	12.1	101.5	14.1
Isoproturon <sup>(a)</sup>	82.2	12.2	97.5	15.7
Methidathion <sup>(b)</sup>	86.4	10.1	108.1	13.2
Methiocarb <sup>(b)</sup>	111.1	10.5	98.7	12.5
Malathion <sup>(b)</sup>	110.6	6.5	94.2	11.3
Neburon <sup>(a)</sup>	70.1	6.8	87.4	9.1
Penconazole <sup>(b)</sup>	108.4	12.7	102.2	8.3
Diazinon <sup>(c)</sup>	106.3	7.1	86.7	10.3
Phosalone <sup>(b)</sup>	91.7	13.5	104.9	11.5

<sup>(a)</sup> 0.01  $\mu\text{g/L}$ ; <sup>(b)</sup> 0.05  $\mu\text{g/L}$  and <sup>(c)</sup> 10  $\mu\text{g/L}$ ; \*n=5

## **Acknowledgements**

The authors are grateful to “Campus de Excelencia Internacional Agroalimentario” (CeIA3) and to “Central Research Services of the University of Almería”.

## **CRedit authorship contribution statement**

**L. Kharbouche:** Literature research, Laboratory work Validation. **M.D. Gil García:** Conceptualization, Methodology, Supervision, Writing - original draft. **A. Lozano:** Laboratory work, Supervision, **H. Hamaizi:** Investigation, Visualization. **M. Martínez Galera:** Resources, Supervision, Writing - original draft.

## **Appendix A. Supporting information**

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.talanta.2019.02.092](https://doi.org/10.1016/j.talanta.2019.02.092).

## References

- [1] M. Tankiewicz, J. Fenik, M. Biziuk, Solventless and solvent-minimized sample preparation techniques for determining currently used pesticides in water samples: A review, *Talanta* 86 (2011) 8– 22. DOI:10.1016/j.talanta.2011.08.056
- [2] A.M. Rodrigues, V. Ferreira, V.V. Cardoso, E. Ferreira, M.J. Benoliel, Determination of several pesticides in water by solid-phase extraction, liquid chromatography and electrospray tandem mass spectrometry, *J. Chromatogr. A*, 1150 (2007) 267–278. DOI:10.1016/j.chroma.2006.09.083
- [3] M. Giulivo, M. López de Alda, E. Capri, D. Barceló, Human exposure to endocrine disrupting compounds: Their role in reproductive systems, metabolic syndrome and breast cancer. A review, *Environ. Res.* 151 (2016) 251–264. <http://dx.doi.org/10.1016/j.envres.2016.07.011>
- [4] J.P. Myers, M.N. Antoniou, Blumberg, L. Carroll, T. Colborn, L.G. Everett, M. Hansen, P.J. Landrigan, B.P. Lanphear, R. Mesnage, L.N. Vandenberg, F.S. vomSaal, W.V. Welshons, C.M. Benbrook, Concerns over use of glyphosate-based herbicides and risks associated with exposures: a consensus statement, *Environ. Health* 15 (2016) 1-13. DOI: 10.1186/s12940-016-0117-0
- [5] K.-H. Kima, E. Kabir, S.A. Jahan, Exposure to pesticides and the associated human health effects, *Sci. Total Environ.* 575 (2017) 525–535. <http://dx.doi.org/10.1016/j.scitotenv.2016.09.009>
- [6] T. Katagi, H. Tanaka, Metabolism, bioaccumulation, and toxicity of pesticides in aquatic insect larvae, *J. Pestic. Sci.* 41 (2016) 25–37. DOI: 10.1584/jpestics.D15-064
- [7] M. Iqbal, *Vicia faba* bioassay for environmental toxicity monitoring: A review, *Chemosphere* 144 (2016) 785–802. <http://dx.doi.org/10.1016/j.chemosphere.2015.09.048>
- [8] Z.R. Staley, V.J. Harwood, J.R. Rohr, A synthesis of the effects of pesticides on microbial persistence in aquatic ecosystems, *Crit. Rev. Toxicol.* 45 (2015) 813-836. <https://doi.org/10.3109/10408444.2015.1065471>
- [9] A.K. Prusty, D.K. Meena, S. Mohapatra, P. Panikkar, P. Das, S.K. Gupta, B.K. Behera, Synthetic pyrethroids (Type II) and freshwater fish culture: Perils and mitigations, *Int. Aquat. Res.* 7 (2015) 163–191. DOI: 10.1007/s40071-015-0106-x
- [10] C.A. Morrissey, P. Mineau, J.H. Devries, F. Sanchez-Bayo, M. Liess, M.C. Cavallaro, K. Liber, Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: A review, *Environ. Int.* 74 (2015) 291–303. <http://dx.doi.org/10.1016/j.envint.2014.10.024>
- [11] S. Ullah, A. Zuberi, M. Alagawany, M.R. Farag, M. Dadar, K. Karthik, R. Tiwari, K. Dhama, H.M.N. Iqbal, Cypermethrin induced toxicities in fish and adverse health outcomes: Its prevention and control measure adaptation, *J. Environ. Manage.* 206 (2018) 863-871. <https://doi.org/10.1016/j.jenvman.2017.11.076>
- [12] M.E. Shuman-Goodier, C.R. Propper, A meta-analysis synthesizing the effects of pesticides on swim speed and activity of aquatic vertebrates. *Sci. Total Environ.* 565 (2016) 758-766. <http://dx.doi.org/10.1016/j.scitotenv.2016.04.205>
- [13] A. Masiá, J. Campo, A. Navarro-Ortega, D. Barceló, Y. Picó, Pesticide monitoring in the basin of Llobregat River (Catalonia, Spain) and comparison with historical data. *Sci. Total Environ.* 503–504 (2015) 58–68. <http://dx.doi.org/10.1016/j.scitotenv.2014.06.095>
- [14] A. Masiá, M. Ibáñez, C. Blasco, J.V. Sancho, Y. Picó, F. Hernández, Combined use of liquid chromatography triple quadrupole mass spectrometry and liquid chromatography quadrupole time-of-flight mass spectrometry in systematic screening of pesticides and other contaminants in water samples. *Anal. Chim. Acta* 761 (2013) 117– 127. <http://dx.doi.org/10.1016/j.aca.2012.11.032>
- [15] Y. Wen, L. Chen, J. Li, D. Li, L. Chen, Recent advances in solid-phase sorbents for sample preparation prior to chromatographic analysis, *Trends Anal. Chem.* 59 (2014) 26–41. <http://dx.doi.org/10.1016/j.trac.2014.03.011>
- [16] J. Płotka-Wasyłka, N. Szczepańska, M. de la Guardia, J. Namieśnik, Modern trends in solid phase extraction: New sorbent media, *Trends in Analytical Chemistry* 77 (2016) 23–43. <http://dx.doi.org/10.1016/j.trac.2015.10.010>

- [17] L. Zhao, H. Qin, R. Wu, H. Zou, Recent advances of mesoporous materials in sample preparation, *J. Chromatogr. A* 1228 (2012)193–204. DOI: 10.1016/j.chroma.2011.09.051
- [18] A. Walcarius, L. Mercier, Mesoporous organosilica adsorbents: nanoengineered materials for removal of organic and inorganic pollutants, *J. Mater. Chem.* 20 (2010) 4487–4511. DOI: 10.1039/b924316j
- [19] N. Casado, D. Pérez-Quintanilla, S. Morante-Zarcero, I. Sierra, Current development and applications of ordered mesoporous silicas and other solegel silica-based materials in food sample preparation for xenobiotics analysis, *Trends Anal. Chem.* 88 (2017) 167-184. <http://dx.doi.org/10.1016/j.trac.2017.01.001>
- [20] B. Fotoohi, L. Mercier, Some considerations regarding the mesopore structure and order in MSU-3 and MSU-F (organo)silicas, *Micropor. Mesopor. Mat.* 211 (2015) 38-48. <http://dx.doi.org/10.1016/j.micromeso.2015.02.045>
- [21] T.R. Pauly, T.J. Pinnavaia, Pore size modification of mesoporous HMS molecular sieve silicas with wormhole framework structures, *Chem. Mater.* 13 (2001) 987-993. DOI: 10.1021/cm000762t
- [22] G.J. Soler-Illia, C. Sanchez, B. Lebeau, J. Patarin, Chemical strategies to design textured materials: from microporous and mesoporous oxides to nanonetworks and hierarchical structures, *Chem. Rev.* 102 (2002) 4093-4138. DOI: 10.1021/cr0200062
- [23] C. Boissière, A. Larbot, A. van der Lee, P.J. Kooyman, E. Prouzet, A new synthesis of mesoporous MSU-X silica controlled by a two-step pathway, *Chem. Mater.* 12 (2000) 2902-2913. DOI: 10.1021/cm991188s
- [24] B. Fotoohi, L. Mercier, Modification of pore structure and functionalization in MSU-X silica and application in adsorption of gold thiosulfate, *Microporous Mesoporous Mater.* 190 (2014) 255-266. DOI: 10.1016/j.micromeso.2014.02.020
- [25] S. Dahane, M. Martínez Galera, M.E. Marchionni, M.M. Socías Viciano, A. Derdour, M.D. Gil García, Mesoporous silica based MCM-41 as solid-phase extraction sorbent combined with micro-liquid chromatography–quadrupole-mass spectrometry for the analysis of pharmaceuticals in waters, *Talanta* 152 (2016) 378-391. <http://dx.doi.org/10.1016/j.talanta.2016.02.013>
- [26] M.D. Gil García, S. Dahane, F.M. Arrabal-Campos, M.M. Socías Viciano, M.A. García, I. Fernández, M. Martínez Galera, MCM-41 as novel solid phase sorbent for the pre-concentration of pesticides in environmental waters and determination by microflow liquid chromatography-quadrupole linear ion trap mass spectrometry, *Microchem. J.* 134 (2017) 181–190. <http://dx.doi.org/10.1016/j.microc.2017.06.008>
- [27] G. Benbakhta, M. Mokhtari, H. Hamaizi, M. Martínez Galera, M.D. Gil García, Extraction of creatinine by adsorption onto pure micro- and mesoporous silica materials, *J. Biotech Research* 8 (2017) 113-122. ISSN: 1944-3285
- [28] B. Magnusson, U. Örnemark (eds.) *Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics*, 2nd ed. (2014). ISBN 978-91-87461-59-0. Available from <http://www.eurachem.org>
- [29] S.A. Bagshaw, E. Prouzet, T.J. Pinnavaia, Templating of Mesoporous Molecular Sieves by Nonionic Polyethylene Oxide Surfactants, *Science, New Series* 269 (1995) 1242-1244. <https://www.jstor.org/stable/2888004>
- [30] H.V. Botitsi, S.D. Garbis, A. Economou, D.F. Tsipi, Current mass spectrometry strategies for the analysis of pesticides and their metabolites in food and water matrices, *Mass Spectrometry Reviews* 30 (2011) 907– 939, DOI: 10.1002/mas.20307
- [31] Commission Decision 2002/657/EC of 12<sup>th</sup> August 2002, Implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results, *Off. J. Eur. Commun.* L221, Brussels, Belgium, (2002) 8–36
- [32] Council Directive 96/23/EC of 29 April 1996 on measures to monitor certain substances and residues thereof in live animals and animal products and repealing Directives 85/358/EEC and 86/49/EEC and Decisions 89/187/EEC and 91/664/EEC, *Off. J. Eur. Commun.* L125/10, Brussels, Belgium, (1996) 10-32
- [33] S.P. Huang, S.D. Huang, Determination of organochlorine pesticides in water using solvent cooling assisted dynamic hollow-fiber-supported headspace liquid-phase microextraction, *J. Chromatogr. A* 1176 (2007) 19–25. DOI: 10.1016/j.chroma.2007.10.073

- [34] Z. Huang, H.K. Lee, Micro-solid-phase extraction of organochlorine pesticides using porous metal-organic framework MIL-101 as sorbent, *J. Chromatogr. A* 1401 (2015) 9–16. <http://dx.doi.org/10.1016/j.chroma.2015.04.052>
- [35] M.J.M. Wells, *Handling large volume samples: applications of SPE to environmental matrices*, Taylor & Francis Group, Cookeville, Tennessee (2000).
- [36] S. Dahane, M.D. Gil García, A. Uclés Moreno, M. Martínez Galera, M.M. Socías Viciano, A. Derdour, Determination of eight pesticides of varying polarity in surface waters using solid phase extraction with multiwalled carbon nanotubes and liquid chromatography-linear ion trap mass spectrometry, *Microchim. Acta* 182 (2015) 95–103. DOI: 10.1007/s00604-014-1290-x
- [37] A. Belmonte Vega, A. Garrido Frenich, J.L. Martínez Vidal, Monitoring of pesticides in agricultural water and soil samples from Andalusia by liquid chromatography coupled to mass spectrometry. *Anal Chim Acta* 538 (2005) 117–127. DOI:10.1016/j.aca.2005.02.003
- [38] S. Lissalde, N. Mazzella, V. Fauvelle, F. Delmas, P. Mazellier, B. Legube, Liquid chromatography coupled with tandem mass spectrometry method for thirty-three pesticides in natural water and comparison of performance between classical solid phase extraction and passive sampling approaches, *J. Chromatogr. A* 1218 (2011)1492-1502. DOI:10.1016/j.chroma.2011.01.040
- [39] A. Mourão Rodrigues, V. Ferreira, V. Vale Cardoso, E. Ferreira, M.J. Benoliel, Determination of several pesticides in water by solid-phase extraction, liquid chromatography and electrospray tandem mass spectrometry, *J Chromatogr A*. 1150 (2007) 267-278. DOI: 10.1016/j.chroma.2006.09.083
- [40] E. Herrero-Hernández, M.S. Andrades, A. Alvarez-Martín, E. Pose-Juan, M.S. Rodríguez-Cruz, M.J. Sánchez-Martín, Occurrence of pesticides and some of their degradation products in waters in a Spanish wine region, *J Hydrol* 486 (2013) 234–245. <http://dx.doi.org/10.1016/j.jhydrol.2013.01.025>
- [41] M.S. Talebianpoor, S. Khodadoust, A. Mousavi, R. Mahmoudi, J. Nikbakht, J. Mohammadi, Preconcentration of carbamate insecticides in water samples by using modified stir bar with ZnS nanoparticles loaded on activated carbon and their HPLC determination: Response surface methodology, *Microchem. J.* 130 (2017) 64–70. <http://dx.doi.org/10.1016/j.microc.2016.08.002>
- [42] F.F. Donato, N.M.G. Bandeira, G.C. dos Santos, O.D. Prestes, M.B. Adaime, R. Zanella, Evaluation of the rotating disk sorptive extraction technique with polymeric sorbent for multiresidue determination of pesticides in water by ultra-high-performance liquid chromatography–tandem mass spectrometry, *J. Chromatogr. A* 1516 (2017) 54–63. <http://dx.doi.org/10.1016/j.chroma.2017.08.025>
- [43] E. De Gerónimo, Virginia C. Aparicio, S. Bárbaro, Portocarrero, S. Jaime, J.L. Costa, Presence of pesticides in surface water from four sub-basins in Argentina, *Chemosphere* 107 (2014) 423–431. <http://dx.doi.org/10.1016/j.chemosphere.2014.01.039>
- [44] J. Robles-Molina, F. J. Lara-Ortega, B. Gilbert-López, J.F. García-Reyes, A. Molina-Díaz, Multi-residue method for the determination of over 400 priority and emerging pollutants in water and wastewater by solid-phase extraction and liquid chromatography-time-of-flight mass spectrometry, *J. Chromatogr. A* 1350 (2014) 30–43. <http://dx.doi.org/10.1016/j.chroma.2014.05.003>
- [45] S. Wang, P. Zhao, G. Min, G. Fang, Multi-residue determination of pesticides in water using multi-walled carbon nanotubes solid-phase extraction and gas chromatography-mass spectrometry, *J. Chromatogr. A* 1165 (2007) 166–171. DOI: 10.1016/j.chroma.2007.07.061
- [46] J. Patsias, E. Papadopoulou-Mourkido, Rapid method for the analysis of a variety of chemical classes of pesticides in surface and ground waters by off-line solid-phase extraction and gas chromatography-ion trap mass spectrometry, *J. Chromatogr. A* 740 (1996) 83-98. DOI: 10.1016/0021-9673(96)00099-4
- [47] Y.S. Al-Degs, M.A. Al-Ghouti, A.H. El-Sheikh, Simultaneous determination of pesticides at trace levels in water using multiwalled carbon nanotubes as solid-phase extractant and multivariate calibration, *J. Hazar. Mater.* 169 (2009) 128–135. DOI: 10.1016/j.jhazmat.2009.03.065
- [48] M. Guardia Rubio, A. Ruiz Medina, M.I. Pascual Reguera, M.L. Fernández de Córdoba (2007) Multiresidue analysis of three groups of pesticides in washing waters from olive processing by solid-phase extraction-gas chromatography



with electron capture and thermionic specific detection, *Microchem. J.* 85 (2007) 257-264. DOI: 10.1016/j.microc.2006.06.005

[49] N. Stamatis, D. Hela, I. Konstantinou, Occurrence and removal of fungicides in municipal sewage treatment plant, *J. Hazard. Mater.* 175 (2010) 829–835. DOI:10.1016/j.jhazmat.2009.10.084

[50] Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy, *Off. J. Eur. Commun.* L226, Brussels, Belgium, (2013) 1-18

## Highlights

- Thirteen pesticides were determined in surface waters at trace levels
- The packed MSU-1 silica based sorbent was efficiently used for enrichment and cleanup
- The pesticides were determined by UPLC with MS/MS detection
- The recoveries of some pesticides were better than those obtained using Oasis HLB