



Study of silica-structured materials as sorbents for organophosphorus pesticides determination in environmental water samples



Enric Pellicer-Castell^a, Carolina Belenguer-Sapiña^a, Pedro Amorós^b, Jamal El Haskouri^b, José Manuel Herrero-Martínez^a, Adela Mauri-Aucejo^{a,*}

^a Department of Analytical Chemistry, Faculty of Chemistry, University of Valencia, Dr Moliner 50, 46100 Burjassot, Valencia, Spain

^b Institut of Material Science (ICMUV), University of Valencia, Catedrático José Beltrán 2, 46980 Paterna, Valencia, Spain

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ABSTRACT

A novel sorbent based on a UVM-7 mesoporous silica doped with Ti has been synthesized and used for solid-phase extraction of several organophosphorus pesticides in environmental water samples followed by gas chromatography coupled to a nitrogen-phosphorus selective detector. Thus, mesoporous silica materials doped with Ti and Fe as well as immobilized cyclodextrin silica-based supports were prepared and morphologically characterized by several techniques such as transmission electronic microscopy, nitrogen adsorption-desorption and X-ray diffraction. These sorbents were comparatively evaluated, and Ti25-UVM-7 material was selected as the best solid phase. After optimization of extraction parameters such as amount of solid-phase, type and volume of eluent, pH and ionic strength and breakthrough volume, recoveries between 81% and 104.5% were achieved, with RSD values below 7.8% and 12% for intra-day and inter-day repeatability respectively. Moreover, limits of quantification in the range 0.5–4.4 $\mu\text{g L}^{-1}$ were achieved for all target compounds using mass spectrometry detector. In addition, the developed method was applied for analysis of real water samples and it was validated with commercial C18 cartridges. Matrix effect was demonstrated in complex environmental matrices and the good reusability of synthesized material was also proved.

1. Introduction

Organophosphorus pesticides have been widely used in agriculture to protect crops and plantations due to their insecticidal properties. However, after their use the remains of these pesticides can reach drinking or superficial waters affecting the human health as they show carcinogenic and mutagenic effects. Thus, the presence of residues of these compounds in waters must be controlled and monitored. According to drinking water guidelines, the maximum acceptable concentrations established by the European Union (98/83/EC) [1] are 0.1 and 0.5 $\mu\text{g L}^{-1}$ for individual or total pesticides respectively. In this sense, the determination of pesticides at these low concentration values requires the development of sensitive and selective techniques, mainly based on GC or LC combined with selective detectors such as NPD [2] or sophisticated detection techniques such as mass spectrometry [3].

In any case, the monitoring and detection of OPP residues in water sources with complex matrices requires the development of pre-treatment and sampling steps in order to enhance sensitivity. In this sense, different sample preparation techniques such as the classical LLE [4] and DLLME [5], as well as other novel techniques such as SBSE [6] have been used for the extraction of OPPs from water samples, whereas SPE with C18-based material [7,8] and SPME [9] are the most common techniques used for enrichment of these analytes. However, these SPE methods have some disadvantages, such as limited selectivity and poor reusability, whereas for SPME the fibers are fragile and relatively expensive [3,10]. In this sense, there is a considerable interest in developing new selective and efficient materials for extracting and isolating components from complex environmental matrices [11].

Mesoporous silica materials have received a lot of attention due to their favorable properties (e.g. mechanical, thermal and chemical

Abbreviations: OPP, Organophosphorus pesticides; GC, Gas chromatography; LC, Liquid chromatography; NPD, Nitrogen-phosphorus detector; MS, Mass spectrometry; LLE, Liquid-liquid extraction; DLLME, Dispersive liquid-liquid extraction; SBSE, Stir bar sorptive extraction; SPE, Solid phase extraction; SPME, Solid phase microextraction; TEOS, Tetraethyl orthosilicate; CTAB, Cetyl trimethylammonium; CD, Cyclodextrin; MeOH, Methanol; ACN, Acetonitrile; TEA, Triethanolamine; TBOT, Tetrabutyl orthotitanate; HRTEM, High-resolution transmission electron microscopy; EDX, Energy-dispersive X-ray; WWTP, Wastewater treatment plant; LOD, Limit of detection; LOQ, Limit of quantification; EF, Enrichment Factor

* Corresponding autor.

E-mail address: adela.mauri@uv.es (A. Mauri-Aucejo).

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stability), low density, good biocompatibility, easy and diverse controlling of particle size and morphologies [12]. Due to these unique features, they can be used as size-selective scaffolds to allow the adsorption of small molecules as well as large molecules by size-exclusion mechanism. In addition, they show high surface areas (up to 1000 m² g⁻¹) and pore volumes, jointly with a wide range of post-modification functionalities, which makes these materials attractive SPE sorbents [13].

The preparation of mesoporous silica materials can be achieved through the atrane route, where the introduction of surfactants as “templates” permits a fine control of the mesopore range compared to the classical sol-gel process thus expanding the range of applications of silica-based materials [14]. In this route, TEOS is commonly used as a silicon source, whereas the usually used surfactant is the CTAB. Within mesoporous silicas, MCM-41 is the most studied and applied material; however, other silicas such as UVM-7, which can be considered as a nanometric version of MCM-41, have been described. The most outstanding feature concerning of these materials is their peculiar architecture: a continuous network constructed from aggregated small mesoporous nanoparticles that generate a non-ordered system of large pores (between large-meso and macro). It results in a material with high surface area and a highly accessible pore system [15]. In addition, these mesoporous materials can be easily modified by incorporation of different elements to these silica structures, in order to improve their selective properties. In fact, several materials with M-UVM-7 structure containing a diversity of dopant agents have been prepared [16,17]. In this sense, the addition of titanium and iron to the silica network could be addressed in order to enhance the adsorption properties of these materials towards for P-containing compounds, such as OPPs [18,19]. In this sense, amino-modified UVM-7 materials have been only used as sorbents in few studies, focused on environmental analysis, for the determination of metallic ions [20].

On the other hand, sorbents based on conventional sol-gel process have been used in the extraction of wide range of analytes by SPME [21,22]. However, a few studies focused on applications of hybrid sol-gel materials as SPE sorbents have been reported [10,23]. In this sense, we have recently developed cyclodextrin-silica microporous composites (as host-guest complexes) as sorbent phases applied either in air samplers [24] or SPE cartridges [25] to the effective retention of several pollutants from environmental samples.

The aim of this work is to study the potential use of mesoporous silica materials based on UVM-7 structure doped with Ti and Fe as SPE sorbents for extraction of OPPs in water samples followed their analysis by GC-NPD. In addition, a comparison with silica materials modified with immobilized CDs was initially done. The material that provided the best extraction performance was selected and its relevant features (such as breakthrough volume, reusability, etc.) were established. The optimal SPE procedure was then applied to the preconcentration of OPPs in environmental water samples. Additionally, these results were compared with those obtained with a commercial C18 SPE sorbent.

2. Experimental

2.1. Chemicals and reagents

OPP standards such as ethoprophos, diazinon, methyl chlorpyrifos (chlorpyrifos-m), methyl tolclofos (tolclofos-m), fenitrothion, malathion, chlorpyrifos and parathion were from Sigma-Aldrich (St. Louis, MO, USA). Ultrapure water from an Adrona (Riga, Latvia) purification system was employed. All solvents used in extraction and analysis procedures were from HPLC grade quality: ethanol, n-hexane, dichloromethane, ethyl acetate from Scharlau (Barcelona, Spain) and MeOH, ACN, tetrahydrofuran and acetone from VWR Chemicals (Radnor, PA, USA).

For synthesis of silica-based materials, the following reagents were used: TEOS, triethanolamine, CTAB, tetrabutyl orthotitanate, iron

chloride (II) tetra hydrate and ethanol were used from Fluka (Buchs, Switzerland), 3-isocyanatepropyltriethoxysilane from Sigma-Aldrich, β - and γ -CD from CycloLab (Budapest, Hungary).

A standard stock multicomponent solution of OPPs was prepared. Working standard solutions were prepared by dilution of this stock mixture with ultrapure water. All pesticide solutions were stored in darkness at 4 °C.

Additionally, for sample analysis commercial C18 cartridges (Varian Bond Elut, 200 mg) were used as reference sorbents for sample enrichment of OPPs.

2.2. Instrumentation

HRTEM images of silica-based materials were obtained using Jeol (Tokyo, Japan) model JEM-2100F microscope operated at 200 kV. Images were obtained using a MegaView III camera provided with the Analysis image data acquisition system. Moreover, EDX data was collected by using an XL30 ESEM scanning electron microscope.

Surface area, pore size and volume were measured by porosimetry using nitrogen adsorption-desorption isotherms. The isotherms were recorded at 77 K with a Micrometrics ASAP2010 automated sorption analyzer. The specific surface areas were calculated from the adsorption data in low-pressure range using BET model. Likewise, X-ray diffractograms were obtained using Cu K α radiation (Seifert 3000TT θ - θ).

A Vac Elut 20 connected to a vacuum pump system (CKNF model N 0.26.3 AN 18) was employed to treat the samples through SPE. Samples were previously filtered with nylon 0.45 μ m Sartorius Stedim Biotech filters.

OPP were determined using an Agilent 7890 A GC system from Agilent Technologies Inc. (Waldbronn, Germany) equipped with an ALS-7693A autosampler with a NPD system. The analytical column was an Agilent HP-5 (30 m x 0.32 mm x 0.25 μ m film thickness). Separation was carried out using nitrogen as carrier gas at 1 mL min⁻¹ flow rate, sample injection (0.5 μ L) was done in splitless mode using the following temperature gradient: 60 °C for 1 min, followed by a ramp at 5 °C min⁻¹ up to 170 °C (hold 3 min), and ramp at 2 °C min⁻¹ to 195 °C (hold 1.5 min). Under these conditions, a good resolution was achieved for all pesticides with the exception of chlorpyrifos and parathion pair. Also, some analytical figures of merit were evaluated using an Agilent 5977 A GC chromatogram coupled to a single quadrupole MS detector. For this purpose, the same separation conditions indicated above were used and selective on monitoring mode was used for pesticide analysis. The specific ions monitored for each pesticide are given in Table S1.

On the other hand, to evaluate the non-retained OPPs in the sorbents, a LaChrom chromatograph was used, which was equipped with a LaChrom L-7100 pump, a Hitachi oven, a VWR L-7614 degasser, an Agilent Interface 35900E processor and a LaChrom L-7614 UV-Vis detector at 225 nm. The separation was carried out using a C18 ZORBAX Eclipse Plus column (4.6 \times 100 mm, 3.5 μ m particle size) at 30 °C and at a constant flow of 1 mL min⁻¹, with MeOH:water as mobile phase under elution gradient conditions as follows: from 0 to 7 min from 50:50 (v/v) MeOH-H₂O increasing progressively up pure MeOH (to 60:40 (v/v) for 7–12 min; 80:20 (v/v) for 12–15 min, and 100% MeOH for 2 more min). The injection volume was 20 μ L. In this case, all analytes were separated properly under described conditions.

2.3. Preparation of mesoporous silica materials

The synthesis of UVM-7 materials was based in a previous work [14] and they were prepared by a one-pot surfactant-assisted procedure, which is a modification of the so-called atrane route [17,26]. All of them were prepared by the same general method, and using the following molar ratios of reagents: 2-x Si: x M:7 TEA:0.5 CTAB:180H₂O. In a typical synthesis of UVM-7 pure silica, 11.2 mL of TEOS and 25 mL of TEAH were mixed at 140 °C, and then 4.56 g of CTAB were added to the mixture at 120 °C. Afterwards, 180 mL of water were slowly added with

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