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SOLID-PHASE EXTRACTION OF *S*-TRIAZINE HERBICIDES BASED ON NEW ORGANIC-INORGANIC HYBRID COPOLYMER

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ABSTRACT

In this study, a new organic-inorganic hybrid copolymer (P(MAA-MPTS)/Sil) was synthesized, characterized, and applied as a sorbent for s-triazines. The P(MAA-MPTS)/Sil was prepared by coupling free radical copolymerization of methacrylic acid and methacryloxypropyltrimethoxysilane and sol-gel processing, using tetramethoxysilane as a cross-linker. Scanning electron microscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis, and nitrogen adsorption-desorption measurements were used for the characterization of the copolymer particles. The extraction efficiency of hybrid copolymer toward s-triazines was studied by batch procedure. High recoveries for all studied compounds (ametryne, atrazine, propazine, simazine, simetryn, and terbuthylazine) were achieved in the pH range 7 - 8 within 30 min. Quick quantitative desorption was achieved using a mixture of methanol and acetic acid. An analytical procedure based on solid-phase extraction of s-triazines on newly synthesized hybrid copolymer and HPLC measurements was developed for their quantification in surface waters. Experiments performed with different types of waters (tap, lake, river) and determination limits achieved demonstrated the successful applicability of P(MAA-MPTS)/Sil in monitoring programs for quality control of tap and surface waters.

Keywords: organic-inorganic hybrid copolymer, solid-phase extraction, s-triazines, HPLC.

INTRODUCTION

Triazines are selective herbicides used to control a wide spectrum of grass and broadleaf weeds in cereal, oilseed, and horticultural crops [1]. Among them, the s-triazine derivatives, (especially atrazine) are the most commonly used worldwide, and are often detected in rivers, lakes and groundwaters [2]. Triazines are characterized by a low octanol-water partition coefficient (K_{ow} values between 2 and 3), which means low absorption on soil particles and easy migration into the surface and ground waters so they can be found in aquatic systems at various concentration levels. Due to their extremely high toxicity, persistence, and accumulation in the aquatic environment, they are included in European legislation as a priority pollutant for surface and ground waters, with a maximum level for each of individual herbicide at 0.1 $\mu g\ L^{-1}$ and 0.5 $\mu g\ L^{-1}$ for mixtures of triazines [3, 4]. The highly sensitive determination of s-triazines in different types of waters often requires the use of an additional preconcentration step in the developed analytical procedure [5 - 7]. A variety of preconcentration methods, such as dispersive liquid-liquid microextraction [8, 9], cloud point extraction [10, 11], deep eutectic solvent-base extraction [12, 13] and stir bar sorptive extraction [14] have been developed and used for s-triazines enrichment. Solid-phase extraction and microextraction (SPE, SPME) is the most widely used enrichment approach in water analysis [6]. Various sorbents obtained by targeted synthesis capable of efficient and selective simultaneous separation and preconcentration of s-triazines have been proposed [15 - 17]. Examples of new trends in recently used sorbents for s-triazines are: multi-walled carbon nanotubes [18], magnetic particles [19, 20], and TiO_2 nanotubes [21]. As a new alternative, hybrid organic-inorganic materials have been found to have significant advantages, such as high mechanical and thermal stability, biocompatibility and flexibility [22]. These materials have been characterized by a homogeneous distribution of organic fragments and silica moieties within the three-dimensional polymer network [23]. Recently, hybrid organic-inorganic sorbents have been used for SPE of metal ions [24], cationic dye [25], lincomycin [26], veterinary drugs [27], estrogenic hormones [28], etc. According to authors' knowledge, the hybrid organic-inorganic materials have not been used for SPE of triazine herbicides.

In this study we present the synthesis and characterization of a new organic-inorganic hybrid copolymer prepared by coupling free radical copolymerization of methacrylic acid (MAA) and methacryloxypropyltrimethoxysilane (MPTS) and a sol-gel process between the resulting copolymer and the tetramethoxysilane (TMOS) as a cross-linking agent. The characterization studies showed that the new hybrid material possessed high specific surface area, thermal stability, and high selectivity toward the target analyte. Sorption properties and extraction parameters were studied and optimized in batch mode. Under optimal conditions, the newly synthesized organic-inorganic hybrid copolymer shows high sorption selectivity and capacity toward s-triazines. An efficient SPE preconcentration procedure combined with high-performance liquid chromatography (HPLC) measurement was developed and applied successfully for the determination of triazine herbicides in various types of water samples.

EXPERIMENTAL

Materials and reagents

All reagents were of analytical reagent grade, and all aqueous solutions were prepared in deionized water (Millipore Corp., USA). A stock standard solution of a mixure of 100 mg L^{-1} for each s-triazine herbicides (ametryne, atrazine, propazine, simazine, simetryn and terbuthylazine) was purchased from Dr. Ehrenstorfer GmbH (Germany) and stored in a refrigerator. Working standard solutions were prepared daily via dilution of stock solution using pH adjusted deionized water.

Methacrylic acid (MAA), 3-(trimethoxysilyl) propyl methacrylate (MPTS), tetramethyl orthosilicate (TMOS) (Aldrich, USA) and 2,2'-azobisisobutyronitrile (AIBN) (Merck, Germany), were used without further purification to prepare the organic-inorganic hybrid copolymers. HPLC-grade methanol (MeOH), acetonitrile (ACN) and acetic acid were obtained from Labscan (Ireland).

Apparatus

HPLC analyses were carried out on an Agilent 1200 Series LC chromatographic system (Agilent Technologies, Germany) equipped with the following devices: vacuum degasser, binary pump, autosampler, thermostated column compartment, and a diode array detector (DAD). Data acquisition was performed with the software LC3D ChemStation (version Rev.B.01.03-SR2 (204); Agilent Technologies 2001-2005). An Eclipse XDB-C18 column (150 mm x 4.6 mm, 5 μm particle size from Agilent Technologies) was used. A scanning electron microscope (SEM, JEOL JSM-5500, Tokyo, Japan) was used for the surface morphology studies. The specific surface area, pore size distribution and average pore diameter of particles obtained were determined by nitrogen adsorption-desorption isotherms at 77 K using the Quantachrome NOVA 1200 apparatus (Quantachrome UK Ltd., England). FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer, Thermo Scientific (Madison, WI, USA). The samples were analyzed as KBr pellets. Thermogravimetric analysis (TGA) of organic-inorganic hybrid copolymer prepared was performed on a LABSYS EVO (Setaram, Caluire, France) apparatus with a Pt/Pt-Rh thermocouple in a corundum crucible at a heating rate of 20°C min^{-1} in a temperature range of 20 - 850°C and an atmosphere of argon. A pH meter (Mettler Toledo; Seven Compact S220-K, Switzerland) was used for pH measurements. An centrifuge EBA 20 (DJB Labcare Ltd., England) was used to separate the sorbent particles and the solutions containing the extracted *s*-triazines in the batch experiments.

Synthesis of the organic-inorganic hybrid copolymer

The organic-inorganic hybrid copolymer was prepared by using coupling free radical copolymerization and sol-gel processing as described earlier with some modifications [26]. In the first step, MAA (2.32 mmol), MPTS (2.52 mmol), and AIBN (10 mg) were dissolved in 20 mL of MeOH and sonicated for 5 min. The solution was saturated with dry nitrogen for 15 min and copolymerization was carried out at temperature 55°C for 3 h. In the second step, a TMOS solution (7.5 mmol of TMOS were dissolved in 15 mL of MeOH, acidified with 0.5 mL of 3 % HCl and stirred for condensation at room temperature for 30 min) was added to the prepolymer solution. The reaction was allowed to proceed under magnetic stirring at 55°C for 6 h. The resultant suspension was adjusted to pH 7 with sodium hydroxide solution. Finally, the gel particles obtained were recovered by centrifugation and washed several times with MeOH to remove unreacted monomers and other ingredients. The prepared organic-inorganic hybrid copolymer, named P(MAA-MPTS)/Sil, was dried in a vacuum oven at 60ºC for 24 h. Reaction scheme for P(MAA-MPTS)/Sil copolymer preparation is shown in Fig. 1.

Adsorption and desorption experiments

The extraction efficiency of organic-inorganic hybrid copolymer P(MAA-MPTS)/Sil toward s-triazine herbicides (ametryne, atrazine, propazine, simazine, simetryn, and terbuthylazine) was studied by batch experiments as follows: An aliquot of the standard solution containing 0.2 µg of a mixture of s-triazines was added to 10 mL of the test solution and adjusted to a desired pH value. Sorbent particles of ca. 50 mg were added to this solution and stirred with an electric shaker for 30 min at a temperature of 25°C. After sorption, the suspension was centrifuged at 5000 rpm, the supernatant was removed, and the sorbent particles were washed twice with water. The s-triazines were desorbed from the P(MAA-MPTS)/Sil with 2 mL MeOH - acetic acid (9:1, v/v). The eluted fraction was evaporated to near dryness under nitrogen at 25°C, and the residues were redissolved in 0.5 mL ACN for HPLC analysis. The recovery (R, %) of s-triazines was calculated by comparing the amount of s-triazines in solution after elution process (A_{el}, µg) and the initial s-triazines amount before sorption on the P(MAA-MPTS)/Sil particles (A_i, µg), using equation:

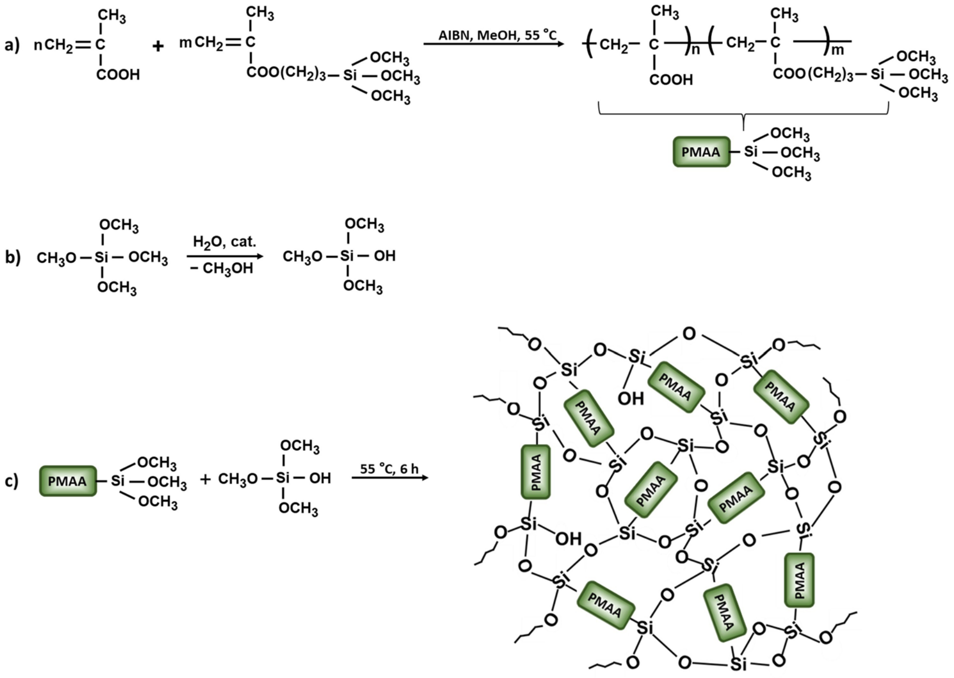


Fig. 1. Schematic representation of the organic-inorganic hybrid copolymer synthesis: (a) free radical copolymerization of MAA and MPTS, (b) hydrolysis and co-condensation of TMOS and (c) cross-linking with TMOS.

$$R = \frac{A_{el}}{A_i} \times 100 \qquad (1)$$

HPLC determination

HPLC analyses were carried out using the following gradient elution: acetonitrile initial percentage of 20 % increased linearly to 60 % in 15 min and further linearly increased to 100 % in 25 min, after which the percentage was returned to the initial conditions in 30 min. The flow rate was 1 mL min^{-1}. A thermostated column at 30°C and 20 µL of sample volume were used. The absorbance was measured continuously in the 200 - 400 nm range, and the quantification of peaks areas was carried out at 240 nm to achieve maximum sensitivity.

For identification purposes, the samples were spiked with pure standards (Dr. Ehrenstorfer, Germany). The identification was based on the retention time and UV-VIS spectra information of pure standards, while for quantification purposes calibration plots using the external standard methodology were performed. For recovery calculations, peak areas obtained for each chromatogram were compared with those obtained from the standard controls used to spike the samples.

Analytical procedure

The pH of water sample (50 mL) was adjusted in the range 7 - 8 and 50 mg P(MAA-MPTS)/Sil particles were added. The suspension was stirred for 30 min and centrifuged at 5000 rpm. The supernatant was removed, the sorbent particles were washed twice with 10 mL water, and the retained s-triazines were eluted with 2 mL MeOH - acetic acid (9:1, v/v). The eluted fraction was evaporated to near dryness under nitrogen at 25°C, and the residue was redissolved in 0.5 mL ACN for HPLC analysis.

RESULTS AND DISCUSSION

Synthesis and characterization of P(MAA-MPTS)/Sil

The principal scheme for the synthesis of organic-inorganic hybrid copolymer P(MAA-MPTS)/Sil is illustrated in Fig. 1. First, copolymer containing -COOH and $-Si(OCH_3)_3$ functional groups was prepared by solution copolymerization of MAA and MPTS via a free radical mechanism (Fig. 1a). The obtained linear pre-polymer contains the desired functional groups, which can undergo hydrolysis and condensation with TMOS under suitable conditions. Second, the TMOS hydrolysis was catalysed by HCl to produce silanol groups (Fig. 1b). Finally, the resulting homogeneous solution was mixed with the prepolymer solution to form covalent bonds between the $-OCH_3$ groups of the prepolymer and the -OH of TMOS. During the sol-gel process, which involves a series of hydrolysis and polycondensation steps, a three-dimensional network structure is obtained (Fig. 1c).

Fig. 2a shows the SEM images of the obtained organic-inorganic hybrid sorbent. Highly agglomerated and irregularly shaped copolymer particles can be seen. The surface of the particles exhibits a porous structure (Fig. 2b). The results of the BET analysis show that the newly synthesized hybrid material is characterized by a high specific surface area (321 m^2 g^{-1}), and the pore volume is 0.68 cm^3 g^{-1}. Pore size analysis shows an

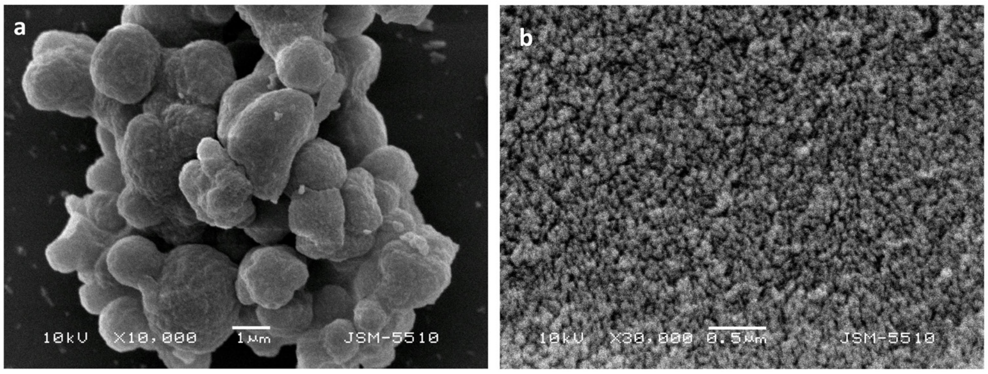


Fig. 2. Scanning electron micrographs of P(MAA-MPTS)/Sil at a ×10000 (a) and ×30000 (b) magnification.

average pore diameter of 8.4 nm. These data confirmed the formation of material with a mesoporous structure.

IR spectroscopy was used to study the chemical structure of the P(MAA-MPTS)/Sil. The characteristic C=O stretching bond, which belongs to the ester functional group in the structure of MPTS and MAA, was observed at 1725 cm^{-1} in the FT-IR spectra of the synthesized copolymer (Fig. 3a). In 1640 cm^{-1}, the residual C=C stretch of MAA and MPTS is observed. The bands at 790 and 460 cm^{-1} are due to Si−O vibrations. The observed bands at 1078 cm^{-1} and 1185 cm^{-1} are explained by Si−O−Si and Si−O−C stretching vibrations [29]. The peak at 2950 cm^{-1} is assigned to the asymmetric stretching of CH$_2$ groups present in the MPTS structure. The wide and intense band at 3446 cm^{-1} is ascribed to -OH stretching of -COOH groups in MAA and of silanol -OH groups in P(MAA-MPTS)/Sil. These results indicated that the organic and inorganic phases were covalently bonded in the polymer matrix [30].

Thermogravimetric analysis is useful for obtaining information on the thermal stability of newly synthesized materials. Samples of organic-inorganic hybrid copolymer prepared were heated in the range 20 - 850°C and the weight changes were measured. The thermogram of P(MAA-MPTS)/Sil shows a weight loss of 7.88 % over the range 100 - 250°C due to the removal of the adsorbed water and solvent (Fig. 3b) [26]. During the next stage of heating (250 - 420°C), the weight loss is probably due to the decomposition of the ester bond and the degradation of the 3-(trimethoxysilyl)propyl methacrylate) segment in MPTS, while in the temperature range 420 - 800°C, poly(methacrylic acid) segmental cleavage takes place [31]. The residue weight at 800°C is probably due to the inorganic silica content of P(MAA-MPTS)/Sil, and the weight retention is about 64 %, indicating good heat resistance [29].

Optimization of the SPE conditions for s-triazine herbicides with P(MAA-MPTS)/Sil

The parameters affecting the extraction efficiency, such as pH of the sample solution, type of the desorbing agent, sample volume, and time of sorption/desorption, were investigated.

The pH of the sample solution is an important parameter directly related to the degree of sorption because the interactions between analytes and the sorbent material are pH dependent. The pH value influences both the chemical form of the analytes (molecule or ion) and the degree of protonation/deprotonation of the functional groups in the sorbent. The binding of s-triazine molecules to P(MAA-MPTS)/Sil is mainly based on hydrogen bonds, which are expected to be formed with (1) -COOH groups of MAA, (2) C=O groups of MAA and MPTS, and (3) silanol -OH groups (Fig. 4). To evaluate these interactions, the pH of the standard solution was adjusted to values ranging from pH 3 to pH 8. According to the results presented in Fig. 5, the highest recoveries of ametryne, atrazine, propazine, simazine, simetryn, and terbuthylazine were reached at pH 7 - 8. In this pH range, the fraction of protonated carboxylic and silanol groups in the P(MAA-MPTS)/Sil is optimal and ensures the formation of hydrogen bonds with the deprotonated nitrogen atoms in s-triazine molecules. Most probably the decrease of the degree of

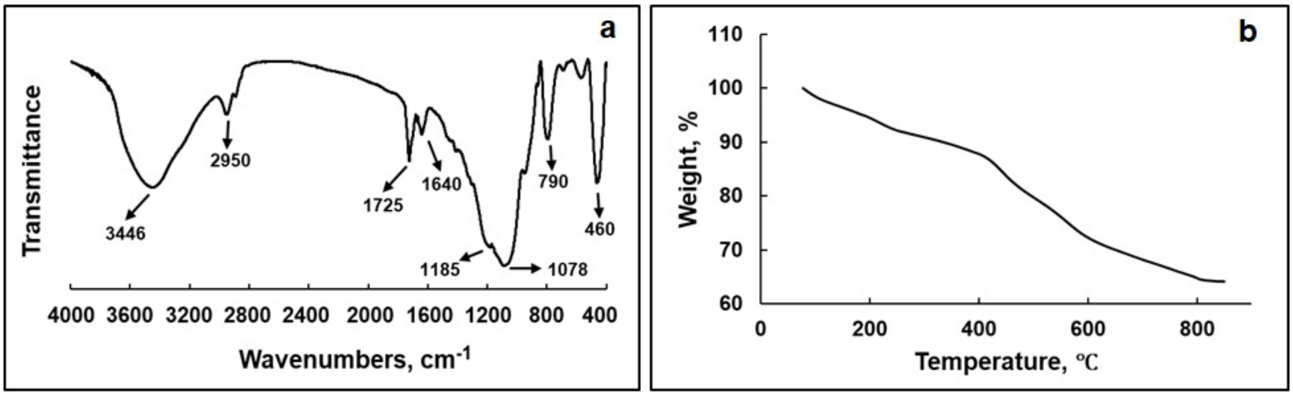
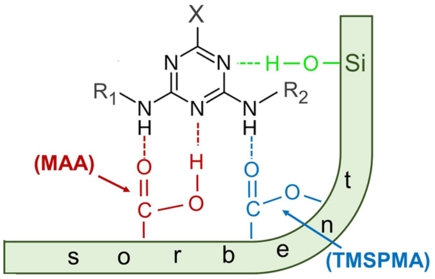


Fig. 3. FT-IR spectra (a) and thermogravimetric curve (b) of P(MAA-MPTS)/Sil.

sorption at higher acidic or basic medium resulted from the increased ionic fraction of s-triazines at pH < 5 or increased ionization of functional groups in P(MAA-MPTS)/Sil at pH > 8, which was not advantageous for hydrogen bonds formation between triazine molecules and the sorbent. These results were in good agreement with those already reported in the previous work [32]. Therefore, a pH range of 7 - 8 was selected as optimal for further experiments.

The appropriate choice of desorbing agent is an important factor determining the extraction efficiency of the sorbent. The eluent should ensure quantitative desorption of retained analytes and thus guarantee the best recoveries. Various polar solvents (acetone, ACN, and MeOH) and a mixture of MeOH - acetic acid (9:1, v/v) were studied for the optimization of the elution step, considering that polar solvents would disturb the hydrogen bonding between the s-triazine molecules and the binding sites of P(MAA-MPTS)/Sil. As seen in Fig. 6, complete desorption of s-triazines was not achieved with methanol, acetone, and ACN. Due to the strong interactions between the sorbent and s-triazines, a small amount (10 %) of acetic acid was added to MeOH to reach complete desorption. The results obtained (Fig. 6) indicated that this mixture provides the highest recovery (> 95 %) of all studied s-triazines. Subsequently, various volumes (1.0, 2.0, and 5.0 mL) of MeOH - acetic acid were investigated, and the quantitative recoveries were reached with 2.0 mL of the desorbing agent.

The kinetics of sorption/desorption processes of the s-triazines were investigated by batch procedure with P(MAA-MPTS)/Sil particles for 5 - 60 min. Quantitative recoveries (> 95 %) of all studied s-triazines were reached



herbicides	**X**	**R_1**	**R_2**
Ametryne	SCH_3	$-CH_2CH_3$	$-CH(CH_3)_2$
Atrazine	Cl	$-CH_2CH_3$	$-CH(CH_3)_2$
Propazine	Cl	$-CH(CH_3)_2$	$-CH(CH_3)_2$
Simazine	Cl	$-CH_2CH_3$	$-CH_2CH_3$
Simetryn	SCH_3	$-CH_2CH_3$	$-CH_2CH_3$
Terbuthylazine	Cl	$-CH_2CH_3$	$-C(CH_3)_3$

Fig. 4. Schematic presentation of the probable interaction of s-triazines with the functional groups in P(MAA-MPTS)/Sil.

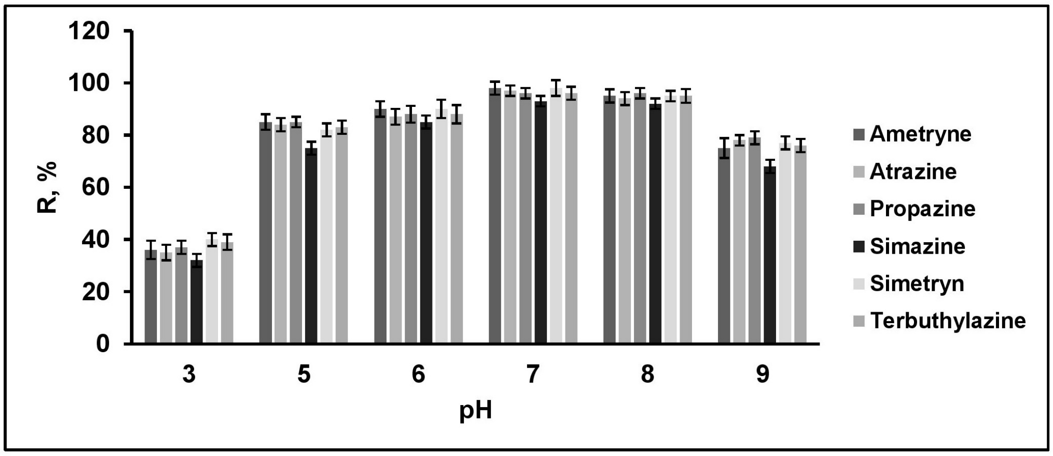


Fig. 5. Effect of pH on the recovery of *s*-triazine herbicides (0.02 µg mL^{-1}, 25°C, three parallel experiments).

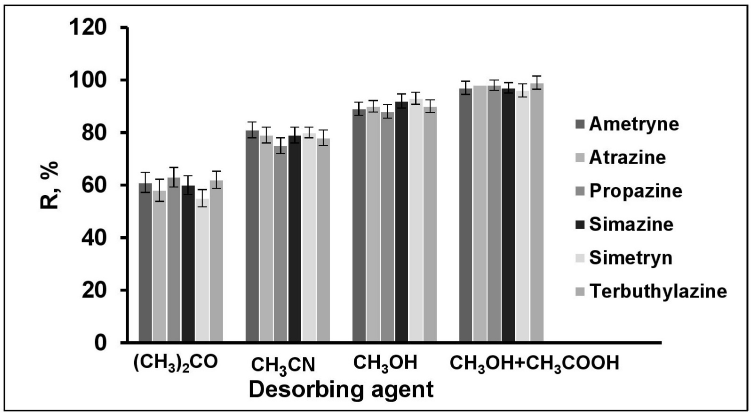


Fig.6. Effect of the type of desorbing agent on the recovery of *s*-triazine herbicides (2 mL desorbing agent, 25°C, three parallel experiments).

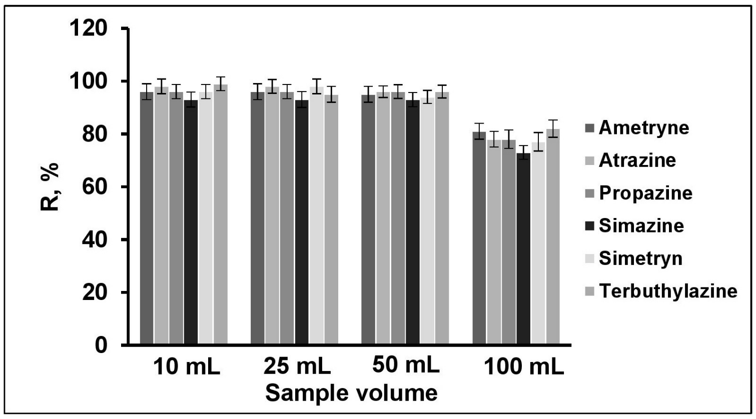


Fig. 7. Effect of the sample volume on the recovery of *s*-triazine herbicides (0.02 µg mL^{-1}, 25°C, three parallel experiments).

for 30 min for both processes of sorption and desorption.

To determine the enrichment factor, the effect of the sample volume on the recovery of *s*-triazine herbicides was studied. For this purpose, different volumes of model solutions (10 - 100 mL) were spiked with 2 µg of each of the investigated *s*-triazines (procedure described in Section Adsorption and desorption experiments). The results obtained show that 50 mL is the maximum sample volume at which quantitative recovery may be accomplished (Fig. 7). The value of the enrichment factor is 100.

To establish the minimum amount of adsorbent providing quantitative sorption of s-triazines at ecologically relevant concentrations in water systems, the capacity of the P(MAA-MPTS)/Sil was determined. The adsorption capacity (Q) is defined as the amount of each s-triazine herbicide adsorbed by 1 g of sorbent at equilibrium. To determine the adsorption capacity of P(MAA-MPTS)/Sil the following procedure was used: 50 mg of sorbent particles were equilibrated with 10 mL solution containing 0.02 - 0.10 µg mL^{-1} for each triazine herbicide under optimum conditions. The amounts of each triazine after their elution were measured by HPLC. The average adsorption capacity of P(MAA-MPTS)/Sil was found to be 7.9, 8.2, 8.4, 7.8, 7.5 and 8.5 µg g^{-1} for ametryne, atrazine, propazine, simazine, simetryn, and terbuthylazine, respectively.

Analytical application

In order to confirm the applicability of proposed sorbent P(MAA-MPTS)/Sil for the determination of s-triazines, 50 mL of uncontaminated, different types of water samples (tap, sea, river) were spiked with a standard mixture of known amounts of studied analytes at concentration levels close to those required by Directive 2013/39/EC. Experiments with spiked samples were conducted to evaluate the impact of the real sample matrix on the recovery. The results are presented in Table 1. The recovery values obtained, independently of the type of waters, are in the range 91 - 95 % with relative standard deviations (RSD) of 5 - 11 %. The exception is simazine, for which the recovery is about 83 % and the RSD is 5 - 12 %. It is worth mentioning that although the recovery of simazine is below 90 %, its values are quite reproducible. Therefore, the SPE procedure can be used to quantify simazine with proper an appropriate correction coefficient. Moreover, the results demonstrated that the matrices of the real samples, even sea water, have no considerable effect on the degree of sorption of triazines on P(MAA-MPTS)/Sil. The experiments performed with sorbent from different batches showed very good repeatability of recoveries achieved for all studied analytes, confirming the ruggedness of the synthetic procedure. To evaluate the sorbent's reusability, many adsorption/desorption cycles were carried out. The results lead to the conclusion that P(MAA-MPTS)/Sil enables at least 25 adsorption/desorption cycles without significant (less than 10 %) change of adsorption capacity and extraction efficiency. This indicates good stability and reusability of the sorbent.

Analytical figures of merit and method validation

The analytical characteristics related to the performance of the developed SPE procedure for determination of s-triazines were defined by 5 parallel analyses of model solutions containing 0.1 μg L^{-1} of each of them (Table 2). The limit of detection (LOD) and limit of quantification (LOQ), which depend mainly on the sensitivity of HPLC measurements of s-triazines under the optimized instrumental parameters, were calculated as 3 and 10 times the standard deviation of measured model solutions. The results obtained for LOD and LOQ were summarized in Table 2. The calculated RSD values varied in the range of 7 - 12 % for the studied concentration range of 0.05 - 5 μg L^{-1}, demonstrating the good precision of the developed analytical procedure. The accuracy of determining the content of s-triazines by proposed SPE-HPLC method was confirmed by analysing tap and river water using a high-sensitivity method such as LC-MS/MS. Very good agreement was observed between the results of a parallel analysis.

Table 1. Recoveries achieved for *s*-triazines studied in the presence of different types of waters.

s-Triazines	Recoveries, %		
	Tap water	Sea water	River Iskar
Ametryne	94 ± 4	91 ± 4	93 ± 3
Atrazine	95 ± 4	94 ± 4	94 ± 3
Propazine	94 ± 4	91 ± 4	92 ± 4
Simazine	83 ± 3	82 ± 3	82 ± 3
Simetryn	91 ± 4	88 ± 4	92 ± 4
Terbuthylazine	95 ± 3	96 ± 3	93 ± 3

Table 2. Figures of merit for SPE HPLC method by using P(MAA-MPTS)/Sil as a sorbent.

s-Triazines	LOD, μg L^{-1}	LOQ, μg L^{-1}	RSD, %
Ametryne	0.03	0.09	3 - 9
Atrazine	0.04	0.12	4 - 10
Propazine	0.04	0.11	4 - 9
Simazine	0.03	0.09	5 - 12
Simetryn	0.03	0.1	4 - 10
Terbuthylazine	0.03	0.08	4 - 11

CONCLUSIONS

In the present paper, a new organic-inorganic hybrid copolymer P(MAA-MPTS)/Sil was successfully prepared by a free radical polymerization followed by a sol-gel process. The synthesis procedure has very good repeatability, and the sorbent is characterized by a high specific surface area and thermal stability. A SPE procedure was developed for selective determination of s-triazines based on their preliminary quantitative retention on P(MAA-MPTS)/Sil. The whole analytical procedure is very simple, fast, reproducible, and easy to perform. The method could be applied to the determination of *s*-triazines in various types of surface waters. The method repeatability, LOD, and LOQ achieved fulfilled the technical requirements of analytical procedures used in the monitoring programs for the quality control of surface waters. The method could be introduced into routine analytical practice.

Authors' contributions: M.M.: Investigation, Writing - Original Draft, Review, Editing, Data curation; I.D.: Conceptualization, Methodology, Investigation, Writing - Original Draft, Review, Editing, Data curation.

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