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Chemical Modification of Nanosilica Toward Dispersive Solid Phase Extraction of Trace Triazine Herbicides from Environmental Water Samples

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Abstract

An easy and fast pathway in preparation of organo-functionalized silica in nanosize range with phenyl-terminated group via co-condensation method is reported. Fourier transform infrared (FTIR) spectra confirmed the grafting process and scanning electron microscopy (SEM) image corroborated formation of nanosized material. Applicability of phenyl-modified nanosilica was examined as a sorbent in dispersive solid phase extraction (DSPE) of triazine herbicides. The effect of the different parameters affecting DSPE efficiency, such as sample pH, extraction time was studied. The amount of enrichment factors for triazines using proposed method were found in the range of 31-43. Calibration curves of triazines showed linearity in the range of 0.5-200, 1.0-200, 1.5-200 and 2.0-1000 $\mu\text{g L}^{-1}$ for analytes. In addition, the detection limits for the analytes were in the range of 0.2-0.6 $\mu\text{g L}^{-1}$. The values of relative standard deviation (RSD%) for $n=3$ at the concentration level of 10 $\mu\text{g L}^{-1}$ were obtained lower than 3.5% for all analytes. The proposed method was also applied to the extraction of triazine herbicides from environmental samples and satisfactory relative recoveries were obtained.

Keywords: *Phenyl-modified nanosilica, Dispersive solid phase extraction, Triazine herbicides, High performance liquid chromatography-UV detection, Environmental water sample.*

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Introduction

Triazine herbicides have been widely utilized in agricultural field. These compounds are extensively used as pre- and post-emergent weed control agents to improve crop yields. The monitoring of these herbicides has been attracted lots of interest. This fact is due to the toxicity and persistency of triazines in ecosystem and their potential for the transformation into more polar compounds [1]. Gas chromatography (GC), high performance liquid chromatography (HPLC), and also capillary electrophoresis have been used for their analysis [2-7]. However, a pre-concentration step is usually mandatory before these analytical systems to meet the essential sensitivity. Solid phase extraction (SPE) [8], micro-SPE [9], solid phase microextraction (SPME) [10,11], solvent microextraction (SME) [5,12] have been used for isolation and enrichment of triazines prior to instrumental analysis.

Among solid-phase sorbents, nanosilica is one of the most common materials has been used in sample preparation field due to low cost, high surface area and its accessibility [13-16]. The grafting of organosilane coupling agents on nanosilica surface had been performed to prepare modified composite materials exhibit markedly improved properties as compared with the neat one [17-22]. In this way, the surface becomes more hydrophobic and exhibit augmented affinity to organic compounds, as well [23,24]. In this study phenyl group was chosen to graft on nanosilica surface due to capability to establish π - π interaction with triazine ring of selected herbicides. Applicability of phenyl-modified nanosilica was examined as a sorbent in dispersive solid phase extraction (DSPE) of triazine herbicides from environmental water samples.

Experimental

Chemicals and Reagents

Hexane, acetonitrile, acetone, methanol, and ethanol were of analytical grade and obtained from Merck (Darmstadt, Germany). HPLC grade water was purchased from Caledon (Ontario, Canada). Ammonium acetate and sodium chloride were also prepared from Merck. The SiO₂ nanoparticles with diameter of about 12 nm were obtained from Degussa Company (Darmstadt, Germany). Trimethoxyphenyl silane (97%) was obtained from Sigma-Aldrich (St. Louis, USA). A solution containing 100 mg L⁻¹ of seven triazine herbicides (simazine, prometon, atrazine, propazine, ametryne, prometryne, and terbutryne) was obtained from Supelco INC (Bellefonte, PA, USA). Standard solutions were prepared by diluting stock solution with methanol.

Moreover, working solutions were prepared daily by dilution of stock solution with double distilled water.

Apparatus

An Agilent 1200 series HPLC system including a G1311A quaternary pump and a UV detector were used for the separation and determination of the analytes. The separation was performed on Zorbax Eclipse XDB-C18 (150 mm× 4.6mm ID, 5µm) column. The solvents used as mobile phase were acetonitrile and 10 mM ammonium acetate buffer (pH=7). The chromatographic data were collected and recorded using ChemStation software. The direct sample introduction was carried out using a Rheodyne manual injector (Rohnert Park, CA, USA) with a 20 µL loop. Column temperature was kept constant at 25 °C using a thermostatted column compartment. Chromatographic separations were carried out using the isocratic elution with the mixture of acetonitrile and buffer solution (33:67). The flow rate was 2 mL/min and detection was performed at 220 nm [25]

Synthesis procedure

For the purpose of synthesis, an amount of 2.5 g trimethoxyphenyl silane was added into 2.5 g of nanosilica solution in 50ml n-hexane. The mixture was refluxed for 6 h in 60 °C and filtered. The precipitate was rinsed thoroughly with n-hexane. The product was dried at room temperature and stored in a desiccator [26, 27].

DSPE procedure

In order to perform DSPE process, a volume of 5 mL sample containing triazines at concentration level of 100 µg L⁻¹ and 20% (m v⁻¹) NaCl was transferred into a test tube to perform extraction. Following 50 mg modified nanosilica was added the extraction was performed for 15 min at 30 °C while stirring at 750 rpm with a magnetic stirrer. Then the mixture was centrifuged and after washing the sorbent, desorption process was carried out using 200 µL of methanol in 5 min. The eluent was dried using a gentle flow of N₂ gas. The residue was dissolved in 50 µL methanol and then injected into the HPLC system.

Results and discussion

Characterization of phenyl-modified silica composite

The FTIR spectra of nanosilica and phenyl-modified nanosilica are shown in Figure 1. The peaks in 1104cm^{-1} and 471cm^{-1} can be ascribed to Si-O-Si asymmetric stretching vibration and bending vibration, respectively. Moreover, nanosilica FTIR spectrum displayed clearly the characteristic peak in 951cm^{-1} and 807cm^{-1} which were assigned to Si-OH vibration and Si-O-Si symmetric vibration respectively. The synthesized composite spectrum showed peaks in 1634cm^{-1} and 3378cm^{-1} which can be ascribed to C=C and C-H stretching vibration of phenyl group [28].

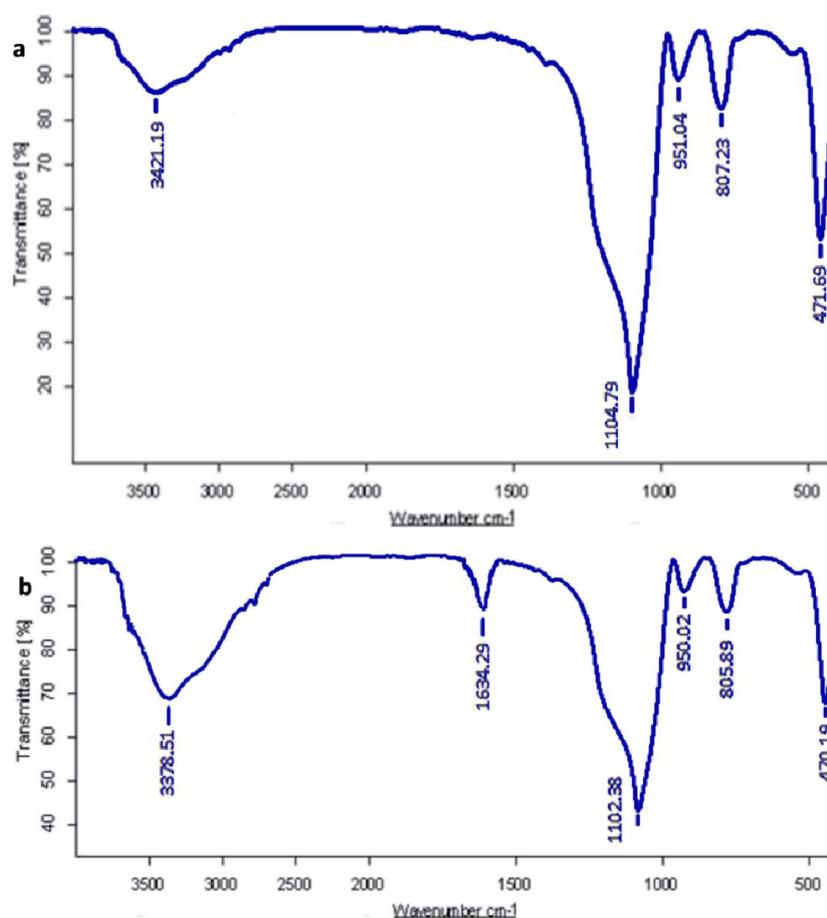


Figure 1. FT-IR spectra of a) nanosilica, and b) phenyl-modified nanosilica.

Figure 2 displays SEM image of phenyl-modified silica particles. The diameters of the diameters of the sphere-like composite were in the range of 31–74 nm. These images show a rather high surface area for the composite and obviously indicate the formation of nanoparticles.

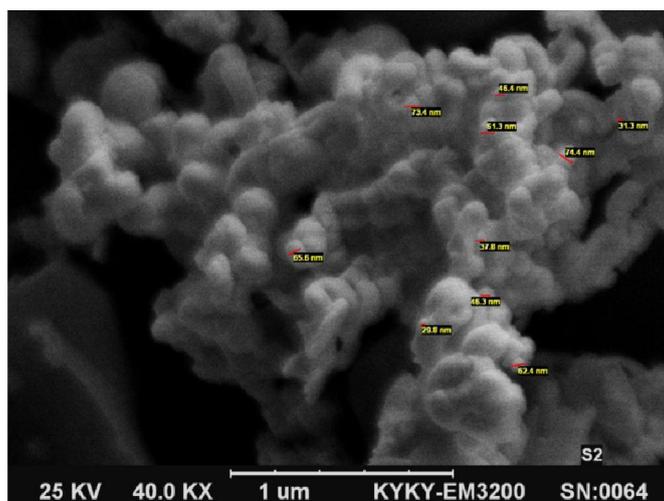


Figure 2. SEM images of phenyl-modified nanosilica.

DSPE Optimization Process

The effects of influential parameters on Triazines DSPE method including pH, extraction time, ionic strength, extraction temperature, and desorption condition were studied. A univariate approach was employed to optimize the influential factors. Moreover, the peak area was used to assess the extraction efficiency under investigated condition. Since the pKa values for triazines range from 1.6 for simazine to 4.3 for prometon [29], the pH of all aqueous samples was adjusted at 6, in order to be sure that analytes remain neutral. However, a further increase of pH to 9 by adding sodium hydroxide did not improve the extraction efficiency.

Dispersive solid phase extraction process was investigated in the range of 5 to 60 min. As demonstrated in Figure 3a, there has been a rise for all compounds up to 15 min and steady responses were observed afterwards. Hence, an extraction time of 15 min was used as optimized time. Generally, engagement of water molecules in the hydration spheres around the salt ions would decrease solubility of organic solutes in the aqueous solution. Study on salt amount was investigated in the range of 0-30% ($w v^{-1}$) of NaCl. According to the results (Figure 3b), the best DSPE recoveries were obtained at 20%.

The effect of temperature on extraction performance was studied at 30, 40, 50 and 60 °C and an adverse effect was observed. So, all further extractions were performed at 30 °C. In order to select the most suitable desorption solvent for desorption process in DSPE, acetone, acetonitrile, methanol and mobile phase mixture were utilized. The best results were obtained from methanol that could be attributed to greater solubility of the analytes in this solvent. Subsequently, the

volume of methanol as desorption solvent were studied in the range of 50 to 400 μL . According to Figure 3c, desorption process was carried out using 200 μL of methanol. Desorption time were also studied in the range of 1 to 15 min. As demonstrated in Figure 3d, desorption time of 5 min is quite suitable.

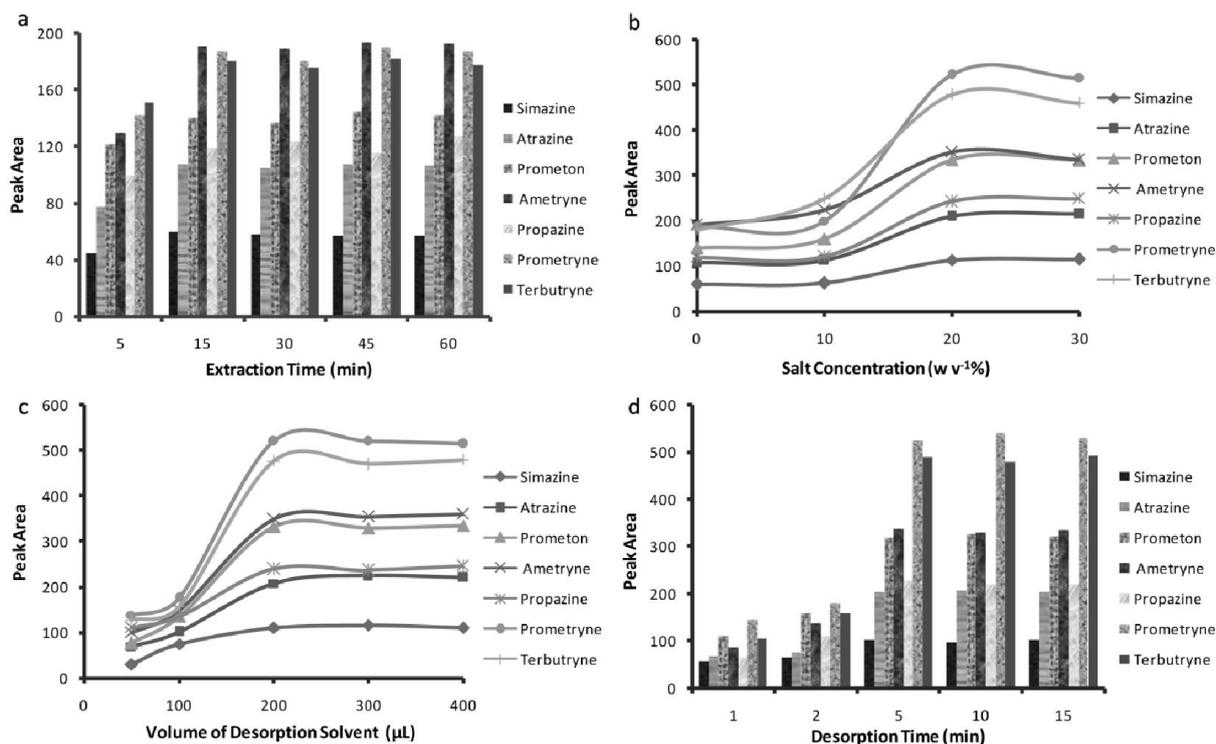


Figure 3. Effect of a) extraction time, b) ionic strength, c) desorption solvent volume, and d) desorption time on DSPE efficiency.

Method Validation

In order to evaluate proposed method using phenyl-modified nanosilica, quantitative analysis was performed under optimized conditions. As tabulated in the Table 1, the dynamic ranges of 2-200 $\mu\text{g L}^{-1}$, for simazine, 1.0-1000 $\mu\text{g L}^{-1}$, for propazine and atrazine, 1.5-200 $\mu\text{g L}^{-1}$, for ametryne, and prometon and 0.5-200 for prometryne and terbutryne, along with good R^2 values were acquired. Reproducibility of the method based on RSD% ($n=3$) values were assessed. These values were ranged between 1.4 and 3.5% at the concentration level of 10 $\mu\text{g L}^{-1}$. The amounts of limit of detection (LOD) based on the signal to noise ratio of 3 were ranged from 0.2-0.6 $\mu\text{g L}^{-1}$. The amounts of enrichment factors were from 31, for propazine, to 43 for prometryne.

To evaluate the applicability of the proposed method, experiments were performed using Caspian Sea and Zayandeh rood river water samples. The chromatograms for three samples confirmed the absence of triazines in non-spiked samples. In order to evaluate the matrix effect on extraction performance, the samples were spiked at the concentration level of $5 \mu\text{g L}^{-1}$ of triazines and they were analyzed using developed method. Figure 4a and 4b typically demonstrated the chromatograms for Caspian Seawater sample before and after spiking.

Table 1. Analytical data obtained from DSPE/HPLC-UV of triazine herbicides using phenyl-modified nanosilica sorbent.

Compound	LDR ($\mu\text{g L}^{-1}$)	R^2	LOD ($\mu\text{g L}^{-1}$)	RSD% (n=3)	EF
Simazine	2.0-200	0.997	0.6	1.4	37
Atrazine	1.5-200	0.998	0.5	1.8	36
Prometon	1.0-200	0.998	0.3	1.6	33
Ametryne	1.0-200	0.999	0.3	2.5	37
Propazine	1.5-200	0.998	0.5	3.5	31
Prometryne	0.5-200	0.993	0.2	2.8	43
Terbutryne	0.5-200	0.995	0.2	3.1	41

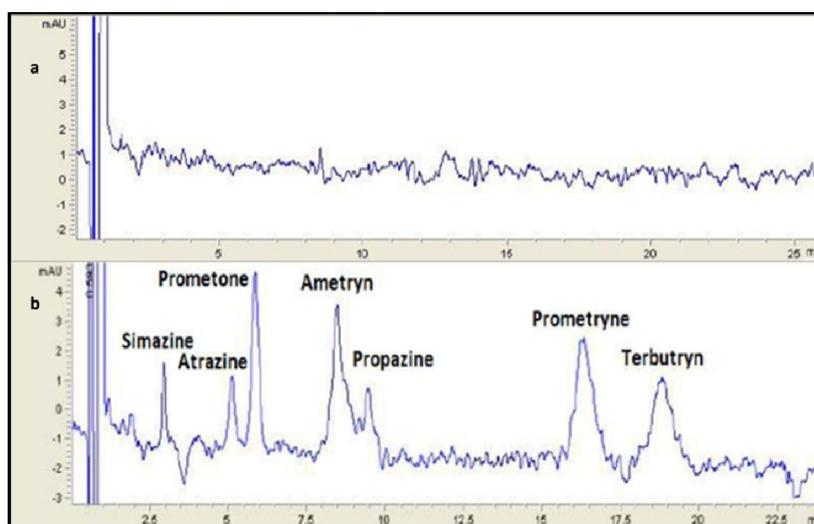


Figure 4. Chromatograms obtained from Caspian Sea water sample a) before and b) after being spiked with triazines at concentration level of $5 \mu\text{g L}^{-1}$; DSPE condition: 5 ml sample solution at pH=6 containing 20% NaCl, 50 mg sorbent, extraction in 15 min time at 30°C , desorption using $200 \mu\text{L}$ methanol in 5 min.

As tabulated in Table 2, the amounts of relative recoveries were ranged 80-96% and the RSD% values were calculated less than 4%. The results reveal water matrices had little effect on DSPE-HPLC-UV method using phenyl-modified nanosilica sorbent.

Table 2. DSPE-HPLC-UV analysis of triazines in two environmental water samples after being spiked at concentration level of 5 $\mu\text{g L}^{-1}$.

Sample		Simazine	Atrazine	Prometon	Ametryne	Propazine	Prometryne	Terbutryne
Caspian Sea water	Initial concentration*	-	-	-	-	-	-	-
	Found concentration*	4.3	4.2	4.8	4.7	4.6	4.5	4.5
	Relative recovery (%)	86	84	96	94	92	90	90
	RSD%	1.9	2.1	1.7	3.0	3.8	2.9	3.3
Zayandeh rood river water	Initial concentration	-	-	-	-	-	-	-
	Found concentration	4.1	4.0	4.1	4.5	4.3	4.0	4.3
	Relative recovery (%)	82	80	92	90	86	80	86
	RSD%	2.1	2.0	1.9	2.9	4.0	3.0	2.8

*All concentrations are in $\mu\text{g L}^{-1}$

Conclusion

Phenyl-modified nanosilica was synthesized by using a simple and efficient method via co-condensation process. The dispersive solid phase extraction, using the nanocomposite, along with HPLC-UV system proved good sensitivity, reproducibility and sufficient enrichment factor for studied triazines. Efficient π - π interaction between surface phenyl groups and aromatic moiety of analytes has provided a prospective opportunity to the efficient performance of phenyl-modified nanosilica as an adsorbent.

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