



## Sol–gel-based silver nanoparticles-doped silica – Polydiphenylamine nanocomposite for micro-solid-phase extraction



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### HIGHLIGHTS

- A sol–gel-based silver nanoparticles doped silica-polydiphenylamine nanocomposite was synthesized.
- The sorbent was applied to micro-solid-phase extraction of some selected pesticides in water samples.
- Separation and determination of the selected pesticides were performed by GC–MS.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A nanocomposite of silica-polydiphenylamine doped with silver nanoparticles (Ag–SiO<sub>2</sub>-PDPA) was successfully synthesized by the sol–gel process. For its preparation, PDPA was mixed with butanethiol capped Ag nanoparticles (NPs) and added to the silica sol solution. The Ag NPs were stabilized as a result of their adsorption on the SiO<sub>2</sub> spheres. The surface characteristic of nanocomposite was investigated using scanning electron microscopy (SEM). In this work the Ag–SiO<sub>2</sub>-PDPA nanocomposite was employed as an efficient sorbent for micro-solid-phase extraction (μ-SPE) of some selected pesticides. An amount of 15 mg of the prepared sorbent was used to extract and determine the representatives from organophosphorous, organochlorine and aryloxyphenoxy propionic acids from aqueous samples. After the implementation of extraction process, the analytes were desorbed by methanol and determined using gas chromatography–mass spectrometry (GC–MS). Important parameters influencing the extraction and desorption processes such as pH of sample solution, salting out effect, type and volume of the desorption solvent, the sample loading and eluting flow rates along with the sample volume were experimentally optimized. Limits of detection (LODs) and the limits of quantification (LOQs) were in the range of 0.02–0.05 μg L<sup>-1</sup> and 0.1–0.2 μg L<sup>-1</sup>, respectively, using time scheduled selected ion monitoring (SIM) mode. The relative standard deviation percent (RSD %) with four replicates was in the range of 6–10%. The applicability of the developed method was examined by analyzing different environmental water samples and the relative recovery (RR %) values for the spiked water samples were found to be in the range of 86–103%.

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## 1. Introduction

Sol–gel process is a well-known method for preparing organo–inorganic hybrid materials in which the desirable sorptive properties are provided while it would be quite difficult to achieve purely organic or inorganic materials. The sol–gel process has several advantages such as high purity, low temperature processing, ultra homogeneity and also the possibility to incorporate additives such as nanoparticles into the first stage of the sol preparation without inhibiting formation of the silica network. This technology has found increasing applications in many areas such as sorbents for SPE. In order to achieve an efficient sample extraction it is rather necessary to prepare novel sorbents with high extraction and anti-interference ability. Sol–gel technology provides a resourceful approach to synthesize polymer or composite under extraordinary mild conditions. It can be therefore used to obtain products of various sizes, shapes and formats [1,2]. On the other hand, NPs offer a significantly higher surface area-to-volume ratio which could be led to much greater extraction capacity and efficiency. In most of the applications, the nanoparticles should necessarily be chemically stable, uniform in size, and well dispersed in the media [3,4].

Silica has been reported to be a suitable supporting matrix to immobilize noble metal nanoparticles such as Ag NPs and avoid their aggregation [5]. Synthesis of a nanocomposite of SiO<sub>2</sub> colloidal particles containing homogeneously dispersed Ag NPs appears to be a useful approach. Also, SiO<sub>2</sub>-conductive polymer [6,7] could be used as a substrate to stabilize the Ag NPs. With addition of polymer to the nanocomposite, the advantages of conducting polymers and nanoparticles can be used simultaneously.

$\pi$ -Conjugated polymers specially polyaniline (PANI) has attracted a great deal of attention due to its ease of synthesis by chemical or electrochemical methods, well behaved electrochemistry, moderately high conductivity upon doping with simple Bronsted acid and good environmental stability [8,9]. Despite these characteristics, the major disadvantage of PANI is its insolubility in common organic solvents and its infusibility because of the stiffness of the PANI backbone and the hydrogen-bonding interactions between the amine moieties of adjacent chains. In the search for new conducting polymers of the aniline type, investigations have been directed towards anilines modified by substituents in the ring or at the nitrogen atom [10–12]. Among these PANI-like structures, poly diphenylamine (PDPA), a polymer of N-aryl substituted aniline, looks interesting. Many properties of that include electrochemistry, conductivity, luminescence and electrochromism are found to be different from PANI and also from polymers of other N-substituted aniline derivatives. The limited solubility of DPA in conventional inorganic acids justifies the selection of solvents such as H<sub>2</sub>SO<sub>4</sub>. DPA has been reported to polymerize through C–C phenyl–phenyl coupling resulting to p-diphenylene and aniline repeat units in the polymer [13,14].

Pesticides are widely applied in cropping to prevent and control pest or disease. Their bioaccumulation in animal and human body

have eventually shown their adverse effects, like: cancer, hormone disruption, birth defect and neurological effects. There is therefore a growing need to introduce and develop new, sensitive, reproducible and rapid methods for monitoring of pesticide residues in surface water samples at trace levels. Numerous methods such as dispersive micro-solid phase extraction [15], membrane-assisted solvent extraction [16], microwave-micro solid phase extraction [17], stir bar sorptive extraction [18], matrix solid phase dispersion [19], vortex-assisted -based demulsified dispersive LLME [20] and direct immersion or headspace solid phase micro extraction [21,22], have been reported for determination of trace residues and contaminants in water samples. Among these methods,  $\mu$ -SPE is a suitable technique that could be applicable to a range of different matrixes, such as wastewater, biological fluids and sewage sludge [23,24]. The use of adsorbents with different shape, size and hydrophobic and hydrophilic properties, the  $\mu$ -SPE may be used to selectively adsorb some specific compounds [25]. The recent  $\mu$ -SPE applications has shown to be an effective way to reduce solvent consumption, extraction time, sorbents amount and improve the sample handling. For the first time in this work the nanocomposite of Ag–SiO<sub>2</sub>-PDPA was synthesized and applied as sorbent in  $\mu$ -SPE for extraction and clean-up of some selected analytes from three major classes of pesticides.

## 2. Experimental

### 2.1. Reagent and standards

Certified standards of lindane, diazinon, fenthion, ethion, Piperonyl-butoxide and fenoxaprop-p-ethyl (Table 1) were supplied from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The stock solution of these compounds were prepared in methanol at concentration of 1000 mg L<sup>-1</sup> and stored at –20 °C. Tetramethoxysilane (TMOS) with purity higher than 98% and diphenylamine (DPA) were purchased from Aldrich (Darmstadt, Germany). Sodium hydroxide (NaOH), hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), Sodium chloride (NaCl), ethanol (EtOH), methanol (MeOH), chloroform, hexane, dichloromethane (DCM) and acetonitrile (ACN) (all analytical reagent grades), silver nitrate (AgNO<sub>3</sub>), butanethiol (BuSH), sodium borohydride, ammonium peroxydisulfate (APS) and cetyltrimethylammonium chloride (CTAB) were purchased from Merck (Darmstadt, Germany). Aqueous solutions of reagents were prepared using distilled water.

### 2.2. Apparatuses

A gas chromatograph model a Hewlett–Packard (HP, Palo Alto, USA) HP 6890 series GC equipped with a split/splitless injector and a HP 5973 mass-selective detector system were used. The MS was operated in the EI mode (70 eV). The separation of analytes was carried out using a capillary column TRB-5MS (Teknokroma, Barcelona, Spain) (30 m, 0.25 mm i.d.) with 0.25  $\mu$ m film thickness. The carrier gas was helium (99.999%) at a flow rate of 1 mL min<sup>-1</sup> the

**Table 1**  
Name, chemical class and some physicochemical properties of the selected pesticides.

Compounds	Chemical class	MW	log Kow	pKa
Lindane	Organochlorine	290	5.2	no sensitivity
Diazinon	Organophosphorus	304	3.3	2.6
Fenthion	Organothiophosphorus	278	4.1	7.4
Ethion	Organophosphorus	384	5.1	NA
Piperonyl-butoxide	Organochlorine	207	4.7	NA
Fenoxaprop-p-ethyl	Aryloxyphenoxy propionic acid	361	4.3	4.1

NA: not detected.

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