

SYNTHESIS AND APPLICATIONS OF NEW CYANOPROPYLTRIETHOXY-  
SILANE AND CYANOPROPYLTRIETHOXYSILANE NANOMATERIALS  
AS SORBENTS OF SELECTED ORGANOPHOSPHORUS  
PESTICIDES ANALYSIS

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*To my beloved Family*

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## ABSTRACT

Conventional extraction methods such as liquid-liquid extraction for organophosphorus pesticides (OPPs) are tedious, time consuming, environmental unfriendly, hazardous to the operator, and use large volumes of organic solvents. These problems are addressed by the synthesis and development of two extraction methods based on two new in-house sol-gel nanosorbents for use in solid phase-based extraction. The two new nanomaterials, namely cyanopropyltriethoxysilane (CNPrTEOS) and silica nanoparticles functionalized with CNPrTEOS (SiO<sub>2</sub>-NPs-CNPrTEOS) were prepared via a sol-gel process. Synthesized sorbents were characterized by using Fourier transform infrared spectroscopy, field emission scanning electron microscopy, thermogravimetric and nitrogen adsorption analysis. The particle sizes of both nanomaterials were between 20 to 500 nm with high surface areas of 379 m<sup>2</sup> g<sup>-1</sup> and 570 m<sup>2</sup> g<sup>-1</sup> for CNPrTEOS and SiO<sub>2</sub>-NPs-CNPrTEOS, respectively. The effects of several sol-gel synthesis parameters were evaluated to optimize sorbent extraction efficiency and increase the extraction of polar and non-polar OPPs simultaneously. The selected OPPs were analysed using high performance liquid chromatography with ultraviolet detector. The synthesized CNPrTEOS was successfully applied as a solid phase extraction (SPE) sorbent to extract three selected OPPs, namely dicotophos, diazinon and chlorpyrifos. The synthesised SiO<sub>2</sub>-NPs-CNPrTEOS material was used as new sorbent in SPE and dispersive micro solid phase extraction (D- $\mu$ -SPE). Several effective extraction parameters in SPE and D- $\mu$ -SPE were optimized. The proposed SPE method based on CNPrTEOS and SiO<sub>2</sub>-NPs-CNPrTEOS exhibited good linearity between 0.3-100  $\mu\text{g L}^{-1}$ , high enrichment factor (833-1666) and low (0.088-0.214  $\mu\text{g L}^{-1}$ ) limits of detection (LODs =  $3 \times SD/m$ ). Finally, the proposed D- $\mu$ -SPE method based on the SiO<sub>2</sub>-NPs-CNPrTEOS successfully determined the selected polar and non polar OPPs in water samples with excellent recoveries (101.21-109.12%). LODs at ultra-trace level (0.047-0.059  $\mu\text{g L}^{-1}$ ) were obtained with 10 min of extraction time, small amount of sorbent (50 mg) and low organic solvent volume (150  $\mu\text{L}$ ). The LODs obtained using the proposed SPE and D- $\mu$ -SPE methods were well below the maximum residue limit (MRL) set by the European Union and LODs of commercial CN-SPE cartridges. The developed environmentally friendly methods using SPE-CNPrTEOS, SPE-SiO<sub>2</sub>-NPs-CNPrTEOS and D- $\mu$ -SPE-SiO<sub>2</sub>-NPs-CNPrTEOS provided precise, accurate and excellent recoveries of OPPs from water samples. These new sol-gel materials showed high potential for use as sorbent in solid phase-based extraction of pesticides of variety polarity.

## ABSTRAK

Kaedah pengekstrakan konvensional seperti pengekstrakan cecair-cecair untuk pestisid organofosforus (OPPs) adalah membosankan, memakan masa, tidak mesra alam, berbahaya kepada pengguna, dan menggunakan pelarut organik yang banyak. Masalah ini boleh ditangani dengan mensintesis dan membangunkan dua kaedah pengekstrakan berasaskan dua pengerap sol-gel baharu dalaman untuk digunakan dalam pengekstrakan berasaskan fasa pepejal. Kedua-dua bahan nano ini iaitu sianopropiltrietoksisilana (CNPrTEOS) dan nanozarah silika berfungsi CNPrTEOS (SiO<sub>2</sub>-NPs-CNPrTEOS) telah disediakan melalui proses sol-gel. Pengerap yang disintesis telah dicirikan menggunakan analisis spektroskopi infra-merah transformasi Fourier, mikroskopi imbasan elektron pancaran medan, termogravimetri dan analisis penjerapan nitrogen. Saiz zarah kedua-dua bahan nano adalah antara 20 hingga 500 nm dengan luas permukaan yang tinggi, iaitu 379 m<sup>2</sup> g<sup>-1</sup> dan 570 m<sup>2</sup> g<sup>-1</sup> masing-masing untuk CNPrTEOS dan SiO<sub>2</sub>-NPs-CNPrTEOS. Kesan beberapa parameter sintesis sol-gel telah dinilai untuk mengoptimumkan kecekapan pengekstrakan optimum pengerap dan meningkatkan pengekstrakan OPPs berkutub dan tak berkutub secara serentak. Analit OPPs terpilih ini telah dianalisis menggunakan kromatografi cecair berprestasi tinggi dengan pengesan ultralembayung. CNPrTEOS yang disintesis telah digunakan dengan jayanya sebagai pengerap pengekstrakan fasa pepejal (SPE) untuk mengekstrak tiga OPPs terpilih, iaitu dikrotofos, diazinon dan klorpirifos. Bahan SiO<sub>2</sub>-NPs-CNPrTEOS yang disintesis telah digunakan sebagai pengerap baharu dalam SPE dan pengekstrakan serakan mikro fasa pepejal (D- $\mu$ -SPE). Beberapa parameter pengekstrakan yang berkesan dalam SPE dan D- $\mu$ -SPE telah dioptimumkan. Kaedah SPE yang dicadangkan berasaskan CNPrTEOS dan SiO<sub>2</sub>-NPs-CNPrTEOS menunjukkan kelinearan yang baik antara 0.3-100  $\mu\text{g L}^{-1}$ , faktor pengayaan yang tinggi (833-1666) dan had pengesanan (LODs =  $3 \times SD/m$ ) yang rendah (0.088-0.214  $\mu\text{g L}^{-1}$ ). Akhir sekali, kaedah D- $\mu$ -SPE yang dicadangkan berasaskan SiO<sub>2</sub>-NPs-CNPrTEOS telah berjaya menentukan OPPs berkutub dan tak berkutub dalam sampel air dengan pengembalian semula yang cemerlang (101.21-109.12%). LODs pada tahap ultra surihan (0.047-0.059  $\mu\text{g L}^{-1}$ ) telah diperolehi dengan masa pengekstrakan 10 min, jumlah pengerap yang kecil (50 mg) dan isipadu pelarut organik yang rendah (150  $\mu\text{L}$ ). LODs yang diperolehi menggunakan kaedah SPE dan D- $\mu$ -SPE yang dicadangkan adalah di bawah had residu maksimum (MRL) yang ditetapkan oleh Kesatuan Eropah dan LODs bagi kartrij komersial CN-SPE. Kaedah mesra alam yang dibangunkan ini menggunakan SPE-CNPrTEOS, SPE-SiO<sub>2</sub>-NPs-CNPrTEOS dan D- $\mu$ -SPE-SiO<sub>2</sub>-NPs-CNPrTEOS memberikan pengembalian semula OPPs yang tepat, tepat dan cemerlang daripada sampel air. Bahan sol-gel baharu ini menunjukkan potensi tinggi untuk kegunaan sebagai bahan pengerap dalam pengekstrakan berasaskan fasa pepejal bagi pestisid pelbagai kekutuban.

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150 mL sample volume, 150  $\mu$ L DCM as desorption  
solvent, 10 min extraction time, 3 min desorption time

**LIST OF ABBREVIATION**

CNPr	-	Cyanopropyl
CNPrTEOS	-	Cyanopropyltriethoxysilane
D- $\mu$ -SPE	-	Dispersive micro solid phase extraction
DCM	-	Dichloromethane
DOA	-	Department of Agriculture
DW	-	Deionized water
EtOH	-	Ethanol
EPA	-	Environmental Protection Energy
EU	-	European Union
EII	-	Electron Impact Ionization
FAAS	-	Flame Atomic Absorption Spectrometry
FE-SEM	-	Field Emission-Scanning Electron Microscopy
FT-IR	-	Fourier Transform-Infrared Spectroscopy
GC	-	Gas Chromatography
GC-ECD	-	Gas Chromatography Electron Capture Detector
GC-FPD	-	Gas Chromatography Flame Photometric Detector
GC-MS	-	Gas Chromatography Mass Spectrometry
GC-NPD	-	Gas Chromatography Nitrogen Phosphorus Detector
h	-	Hour
HPLC	-	High Performance Liquid Chromatography
LC	-	Liquid Chromatography
LLE	-	Liquid-Liquid Extraction
LOD	-	Limit of Quantification
LOQ	-	Limit of Qualification
LPME	-	Liquid-Phase Microextraction
MeOH	-	Methanol
min	-	Minutes

MISPE	-	Molecularly Imprinted Solid Phase Extraction
MOA	-	Ministry of Agriculture and Agro-Based Industry
MRL	-	Maximum Residue Limits
MTMOS	-	Methyltrimethoxysilane
NaCl	-	Sodium chloride
NaOH	-	Sodium hydroxide
<i>n</i> -BOH	-	<i>n</i> -Butanol
NH <sub>4</sub> OH	-	Ammonium solution
NPs	-	Nanoparticles
OCPs	-	Organochlorinated Pesticides
OH-TPDMS	-	Hydroxy-terminated Polydimethylsiloxane
OPPs	-	Organophosphorus Pesticides
PAHs	-	Polycyclic Aromatic Hydrocarbons
PCBs	-	Polychlorobiphenyl
PDMS	-	Polydimethylsiloxane
PMHS	-	Poly(methylhydroxysiloxane)
PDMS-20HMe18C	-	Polydimethylsiloxane-2-hydroxymethyl-18-crown-6
<i>n</i> -PrOH	-	<i>n</i> -Propanol
PVA	-	Poly(vinyl) alcohol
RSD	-	Relative Standard Deviation
RM	-	Ringgit
SBSE	-	Stir Bar Sorptive Extraction
SFE	-	Supercritical Fluid Etraction
SPE	-	Solid Phase Extraction
SPME	-	Solid Phase Microextraction
TFA	-	Trifluoroacetic acid
TEOS	-	Tetraethoxysilane
TMOS	-	Tetramethoxysilane
UV	-	Ultra-violet

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background Information

Pesticides are large group of toxic synthesis organic compounds used in agriculture. Pesticides are used on farms as herbicides, fungicides and insecticides (Gou *et al.* 2000). Insecticides known as organophosphorus pesticides (OPPs) and organochlorine pesticides (OCPs) are commonly used against insects. OCPs (e.g., DDT) have been banned since 1972 in the US and 1983 in China (Qiu *et al.* 2004), but they are still used for crop protection.

OPPs are one of the most common highly toxic classes because of their inhibition of acetyl-cholinesterase. Due to the widespread use of OPPs in agriculture to protect product quality, they are commonly found in surface waters, foods and even honey (Amendola *et al.* 2011). Food produced for humans can contain pesticides, either from direct application to the food or bio-magnification up the food chain.

The presence of OPPs contamination in food commodities has become a growing source of concern for mammals (Shimelis *et al.* 2007). OPPs toxicity is harmful to human health. According to drinking water guidelines, the maximum acceptable concentrations established by the European Union (EU) are  $0.1 \mu\text{g L}^{-1}$  and  $0.5 \mu\text{g L}^{-1}$  for single and total OPPs, respectively (Community 1998). Due to the high toxicity of OPPs at trace levels, monitoring and detection of residues in water sources is essential for human protection. Pre-treatment and sampling are most important in analytical work because these steps typically account for over 60% of

the total analysis time and their quality largely determines the success of analysis in complex matrices (Chen and Wu 2005). Different types of techniques have been successfully developed for sample preparation and extraction of OPPs from various media: liquid-liquid extraction (LLE) (Barcelo 1993), supercritical fluid extraction (SFE) (Rissato *et al.* 2005) and stir-bar sorptive extraction (SBSE) (Baltussen *et al.* 1999, Bicchi *et al.* 2002). However, LLE is time consuming and labor-intensive, and choosing an appropriate solvent can be complicated. Moreover, it is difficult to polar and ionic compounds from water, and these methods require relatively large volumes of organic solvents and harmful chemicals that are costly to dispose of.

Method simplification and miniaturization are modern trends in analytical chemistry (Blasco 2004). Solid-phase extraction (SPE) is a convenient sampling method compared to LLE because of its simplicity and economic benefits in terms of time and solvent needs (Cacho *et al.* 2003, Lal *et al.* 2008). SPE has been successfully used to preconcentrate and clean up pesticides from different samples (Sabik *et al.* 2000, Wells and Yu 2000) and has many advantages, such as wide availability of selective sorbents, less consumption of organic solvent, low cost, short analysis time, simple equipment, simple operation, rapid sample loading and high breakthrough volume (Sabik *et al.* 2000).

SPE based on commercial sorbents, such as C<sub>18</sub> and CN, provides higher affinity for nonpolar and polar pesticides, respectively. In recent years, SPE has been developed with novel in-house sorbents with promising analytical performances: cross-linked copolymers suitable for nonpolar pesticides and reversed-phase mechanisms and interactions (Masque *et al.* 2001, Bielicka Daszkiewicz *et al.* 2006) and molecular imprinted polymers (MIPs) (Berton *et al.* 2006). Commercial sorbents and reported in-house adsorbents provide potential benefits, but they also have several drawbacks, such as low recovery, less precision, low enrichment factor, less sensitivity and low reusability.

Recently, to overcome the aforementioned limitations with polar and nonpolar OPPs, environmental friendly hybrid sol-gel based sorbents with many advantages were developed as SPE sorbents: polydimethylsiloxane-2-

hydroxymethyl-18-crown-6-coated (PDMS-20HMe18C) (Wan Ibrahim *et al.* 2010), methyltrimethoxysilane–tetraethoxysilane (MTMOS-TEOS) (Wan Ibrahim *et al.* 2012), methyltrimethoxysilane–cyanopropyltriethoxysilane MTMOS-CNPrTEOS , (Wan Ibrahim *et al.* 2013).

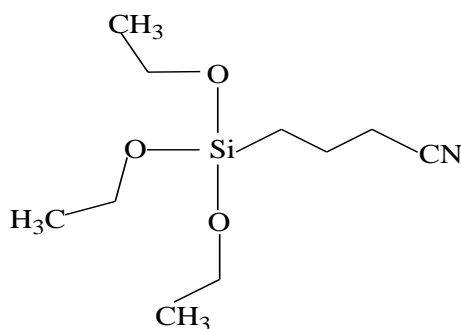
Dispersive micro solid phase extraction (D- $\mu$ -SPE) has been widely used to isolate pesticides (Jiménez-Soto *et al.* 2012). Dispersive micro-solid phase extraction is a quick, easy, cheap, effective, rugged and safe (QuEChERS) method for sample preparation, isolation and preconcentration for a wide range of samples (Han *et al.* 2014). D- $\mu$ -SPE is another mode of d-SPE that consumes small amounts of adsorbent and elution solvent, provides higher adsorption capacity, avoids channeling or blocking and is simple and less time consuming than conventional SPE (Fu *et al.* 2012, Chung *et al.* 2013, Yahaya *et al.* 2014). D- $\mu$ -SPE traps analytes on the sorbent from liquid samples followed by desorption or elution by organic solvents. D- $\mu$ -SPE exhibits high breakthrough volumes because a large volume of sample can be processed with small amounts of sorbent and solvent.

In the present study, sol-gel technology was used to prepare sorbents for SPE and D- $\mu$ -SPE because new sorbents with different properties and conditions can be developed. First, novel nanosized sorbents based on cyanopropyltriethoxysilane (CNPrTEOS) with high surface areas were synthesized using the sol-gel method and applied as SPE sorbents to preconcentrate polar and nonpolar OPPs. Second, silica nanoparticles were synthesized and functionalized with CNPrTEOS (SiO<sub>2</sub>-NPs-CNPrTEOS) followed by application as SPE and D- $\mu$ -SPE sorbents for OPP preconcentration. These proposed methods exhibited low limit of detections (LODs) with excellent enrichment factors for OPPs extraction from water samples. Polar (dicotophos) and nonpolar (diazinon and chlorpyrifos) OPPs were successfully recovered from environmental water samples (tap, river, mineral and drinking water) with high extraction recoveries and little matrix effects observed.

The proposed SPE and D- $\mu$ -SPE methods based on different types of in-house and commercial sorbents co-extracted many matrix species, resulting in a dirty extraction. As a result, selective chelating sorbent has become an active area of

research. SPE and D- $\mu$ -SPE methods can overcome these limitations by using new sol-gel materials that can extract polar and non-polar compounds via the sol-gel process. Because of its potential benefits, CNPrTEOS was used as the new material to extract polar and non-polar OPPs from environmental water samples. The cyano functional group in CNPrTEOS is very polar and impacts the extraction of polar analytes from aqueous matrices. CNPrTEOS exhibits both polar and polarizable characteristics and is among the most useful stationary phases with respect to polarity at both low and high temperatures. The cyano group attached to the siloxane backbone via a three-methylene ( $\text{CH}_2$ ) spacer is polar and strongly electron attracting, displaying dipole-dipole, dipole-induced dipole and charge-transfer interactions. The unshared electron pair in the nitrile nitrogen may form intermolecular hydrogen-bonds with suitable hydrogen donor sample molecules like phenols. These characteristics of cyano stationary phases are responsible for their increased affinity for ketones, esters and analytes bearing electrons (Kulkarni *et al.* 2006).

Methods based on CNPrTEOS have been used as sol components to synthesize inorganic-organic hybrid polydimethylsiloxane-cyanopropyltriethoxysilane (PDMS-CNPrTEOS) as extraction sorbents to analyze non-steroidal anti-inflammatory drugs (NSAIDs) by SBSE (Wan Ibrahim *et al.* 2011a). The cyano moiety in the PDMS-CNPrTEOS hybrid may improve the extraction of more polar NSAIDs through hydrogen bonding, electrostatic and  $\pi$ - $\pi$  interactions with analytes. The structure of CNPrTEOS is shown in Figure 1.1.



**Figure 1.1** The chemical structure of CNPrTEOS



## 1.2 Problem Statement

In recent years, the development of fast, accurate, sensitive, simple and inexpensive methodologies has become an important research focus. Sample preparation is generally required to determine trace levels of organic compounds in sample matrices. Liquid-liquid extraction is a versatile and multipurpose sample-preparation technique and recommended in many standard analytical methods (Tahboub *et al.* 2005). However, it is tedious, expensive, laborious, time consuming, and unable to extract polar compounds, requires multistage operation, is likely to form emulsions, uses large volumes of organic solvents and requires disposal of toxic or flammable chemicals (Pico *et al.* 2007). Solid phase extraction and solid micro phase extraction can overcome these drawbacks because they can reduce the use of organic solvents, the mass of sorbent needed and the extraction time, as well as increase the sample capacity.

Commercial SPE and D- $\mu$ -SPE sorbents are typically suitable for non-polar or polar compounds, but not for both. Non-polar sorbents show low retention of polar compounds, and the reverse is true for polar sorbents (Chan and Tsang 2007). Therefore, to overcome these limitations, new nanomaterials were synthesized using a sol-gel method that can extract polar and nonpolar compound simultaneously. These new nanosorbents have higher capacity in comparison with commercial and previous sorbents for extraction and concentration of polar and nonpolar OPPs. These new nanosorbents were sol-gel nanomaterials based on CNPrTEOS and silica nanoparticles functionalized with CNPrTEOS (SiO<sub>2</sub>-NPs-CNPrTEOS), which were used in SPE and D- $\mu$ -SPE to extract three selected OPPs with different polarities.

## 1.3 Aims and Objectives of Study

The aim of this study is to synthesize new sol-gel sorbents for SPE and D- $\mu$ -SPE to extract polar and non-polar OPPs simultaneously. The objectives are to

1. Synthesize new nanosorbents based on CNPrTEOS and SiO<sub>2</sub>-NPs-CNPrTEOS as extraction sorbents, and optimization of effective sol-gel synthesis parameters, namely water volume, solvent type, base catalyst pH value and precursor content.
2. Characterize the synthesized nanosorbents using Fourier transform infrared spectroscopy (FTIR), field scanning electron microscopy (FESEM), nitrogen adsorption, elemental analysis (EDX) and thermogravimetric analysis (TGA).
3. Evaluate the synthesized CNPrTEOS as SPE sorbent and SiO<sub>2</sub>-NPs-CNPrTEOS as D- $\mu$ -SPE and SPE sorbents for OPPs preconcentration, and optimization and validation of effective SPE and D- $\mu$ -SPE parameters.
4. Evaluate the optimum SPE and D- $\mu$ -SPE conditions for method validation to determine the linearity range, LOD, LOQ and precision of SPE and D- $\mu$ -SPE method followed by analysis of environmental samples (Tap, bottled mineral, bottled drinking and river water).

#### 1.4 Scope of Study

This study focused on the preparation of sol-gel CNPrTEOS and SiO<sub>2</sub>-NPs-CNPrTEOS as sorbents for the simultaneous extraction and preconcentration of three selected OPPs dicotophos, diazinon and chlorpyrifos, via SPE and D- $\mu$ -SPE. The functional groups, surface morphologies and thermal stabilities of the prepared sol-gel sorbents were characterized using FTIR, FESEM and TGA. Physical characteristics such as pore size, surface area, pore volume and pore size distribution were measured using N<sub>2</sub> adsorption (BET). To obtain appropriate sorbents for OPPs preconcentration, the CNPrTEOS content, pH of the base catalyst, water volume and solvent type during sol preparation were evaluated. The extraction efficiencies of the SPE and D- $\mu$ -SPE methods were successfully applied to OPPs preconcentration prior to high performance liquid chromatography equipped with UV analysis. Optimization of the proposed methods (SPE and D- $\mu$ -SPE) was carried out for sample volumes, desorption or elution solvent types, desorption or elution solvent

volumes, extraction time, desorption time and adsorbent mass. The SPE and D- $\mu$ -SPE methods were validated in terms of linearity, limit of detection and limit of quantification. The extraction recoveries of the SPE and D- $\mu$ -SPE methods based on the new nanosorbents were examined in the extraction of OPPs from environmental samples. Finally, extraction efficiencies of the newly synthesized sol-gel sorbents were compared with commercial cyanopropyl (CNPr) for polar and nonpolar OPPs that had been isolated under the optimized extraction conditions.

### **1.5 Significance of Study**

Commercial SPE sorbents (non-polar C<sub>18</sub> and polar CNPr) have limitations in the extraction of polar and nonpolar analytes from different types of samples. The newly developed sol-gel sorbents based on CNPrTEOS and SiO<sub>2</sub>-NPs-CNPrTEOS with different polarities improved the extraction performance of polar dicotophos, and nonpolar chlorpyrifos and diazinon. As extraction sorbents, the new in-house sol-gel CNPrTEOS and SiO<sub>2</sub>-NPs-CNPrTEOS materials enhanced the extraction capability of polar and nonpolar OPPs simultaneously, thereby reducing extraction time. The D- $\mu$ -SPE method using the new sol-gel sorbent is also simple, inexpensive and environmental friendly.

### **1.6 Summary**

Chapter 1 explains the background of the study concerning toxic pesticides, sampling methods, sorbent variety and sol-gel materials. The statement of problem, objectives, scopes and significance of this study are also covered.

Chapter 2 focuses on the published literature concerning pesticides, sol-gel technology, solid-phase extraction, dispersive micro solid-phase extraction and commercial and in-house sorbent materials.

Chapter 3 focuses on the methodology, followed by a description of materials, instruments, synthesis procedures for sol-gels based on CNPrTEOS and silica nanoparticles functionalized with CNPrTEOS precursors, chromatography peak identification and SPE and D- $\mu$ -SPE methods.

Chapter 4 focuses on the preparation of the new nanosized sol-gel sorbents based on CNPrTEOS as an SPE adsorbent, characterized using FTIR, BET, FESEM, and EDX. The sorbent synthesized in-house was successfully applied to the simultaneous extraction of polar (dicrotophos) and non-polar (diazinon and chlorpyrifos) OPPs from various water samples (tap, river, mineral and drinking water). The CNPrTEOS-based sorbent was sensitive to polar and nonpolar OPPs through electrostatic interactions, H-bonding and porosity. SPE based on CNPrTEOS showed good affinity for the isolation of polar and non-polar OPPs simultaneously. The preconcentrated OPPs were determined by HPLC-UV.

In chapter 5, the SiO<sub>2</sub>-NPs-CNPrTEOS nanoparticles were synthesized using sol-gel technology. Briefly, SiO<sub>2</sub> nanoparticles were prepared and functionalized using the CNPrTEOS precursor. The combined sol-gel sorbent was characterized by FTIR, BET, FESEM, EDX and TGA. The synthesized nanomaterial was used as an SPE and D- $\mu$ -SPE sorbent to extract three polar and nonpolar OPPs from environmental water samples (tap, river, mineral and drinking water). A high enrichment factor and lower LOD are the some benefits of D- $\mu$ -SPE compared with conventional SPE. The isolated OPPs were determined by HPLC-UV.

Chapter 6 is the final chapter and focuses on the conclusion and future works of the current study. This chapter summarizes the obtained analytical results, such as the optimization parameters and validation of the SPE and D- $\mu$ -SPE methods based on the novel sol-gel sorbents (CNPrTEOS and SiO<sub>2</sub>-NPs-CNPrTEOS).

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