NEW SOL-GEL SILICA NANOPARTICLES COATED CYANOPROPYLTRIETHOXYSILANEAS ALTERNATIVE SOLID PHASE EXTRACTION SORBENT FOR ORGANOPHOSPHORUS PESTICIDES

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Abstract. Sorbents based on silica are widely used in solid phase extraction (SPE). The most common SPE material is C18.Recently nanoparticleshave gained interest as sorbent materials for analytical purpose. In this study silica-based nanoparticles with polar and non-polar groups were synthesized using cyanopropyltriethoxysilane (CNPrTEOS) and tetraethoxysilane (TEOS) as precursor in the presence of ammonia solution as catalyst and ethanol as solvent via sol-gel technology. The sol-gel SiO_2-NPs-CNPrTEOS was used for the simultaneous extraction of three organophosphorus pesticides (OPPs) of different polarity namely dicrotophos, diazinon and chlorpyrifos prior to LC-UV detection at 270 nm. The sorbent produced was characterized using FTIR, FESEM, nitrogen gas adsorption and TGA. The surface area and average pore diameter of the sorbent are 570 $m^2 g^{-1}$ and 31Å (mesoporous), respectively. The average particle size of SiO_2-NPs-CNPrTEOS is 54 nm. The mesoporous SiO_2-NPs-CNPrTEOS showed superior extraction capability for the polar dicrotophos and also for the non-polar diazinon and chlorpyrifos compared to commercial cyano SPE. The new

SiO$_2$-NPs-CNPrTEOS exhibits high potential as a bipolar sorbent for the simultaneous extraction of polar and non-polar OPPs.

Keywords Sol-gel, Solid phase extraction, Nanoparticles sorbent, Cyanopropyltriethoxysilane, Tetraethoxysilane, Organophosphorus pesticides, Liquid chromatography-UV detection

1.0 INTRODUCTION

Sol–gel procedure include hydrolysis and condensation of inorganic salts such as sodium silicate (Na$_2$SiO$_3$) or metal alkoxides (Si(OR)$_4$) for instance tetraethylorthosilicate (Si(OC$_2$H$_5$)$_4$) in the presence of base (e.g., NH$_3$) or mineral acid (e.g., HCl) as catalyst [1, 2, 3]**.** The new sol gel method is extremely sensitive towards experimental conditions that influence the rate of hydrolysis and condensation reactions, e.g., the kind and concentration of precursor (alkoxides), H$_2$O/precursor ratio, reaction time, nature and concentration of catalyst, type of solvent, aging, drying technique and reaction temperature. Bogush and Zukoski[4] synthesized monodispersed silica with particles size in the range of 40 nm to few micrometers via modified Stober method. They believed that TEOS concentration, types of solvent, concentration of water and ammonia, and reaction temperature were the basic parameters, which controlled the particle size and particle size distribution.

Sol-gel process has been used in the production of solid phase microextraction (SPME) coating materials [5], solid phase extraction (SPE) phases and also stir bar sorptive extraction (SBSE) sorbents. Kulkarni et al. [6] developed sol-gel CN-PDMS for capillary microextraction (CME) for the extraction of polar (Alcohols) and non-polar (PAHs) analytes simultaneously from aqueous sample. The used sol-gel precursor cyanopropyltriethoxysilane (CNPrTEOS) and the prepared sol-gel CN-PDMS coating provided effective extraction of highly polar analytes by the cyanopropyl moieties. Wan Ibrahim et al. [7] used cyanopropyltriethoxysilane (CNPrTEOS) as sol component for synthesis of inorganic-organic hybrid PDMS-CNPrTEOS as extraction sorbent for analysis of non-steroidal anti-inflammatory drugs (NSAIDs) forSBSE method. The more

cyano functional group in PDMS-CNPrTEOS-derived hybrid improved the extraction of more polar NSAIDs through hydrogen bonding and π-π interaction with the selected analytes.

This study focused on the production and characterization of silica nanoparticles with cyanopropyltriethoxysilane (SiO$_2$-NPs-CNPrTEOS) coating for use as solid phase extraction sorbent. The SiO$_2$-NPs-CNPrTEOS sol–gel material was characterized using Fourier transform infrared spectroscopy (FTIR), Nitrogen gas adsorption (BET), Field emission scanning electron microscopy (FESEM) and thermogravimetric analysis (TGA). The synthesized nanocomposite was applied to the determination of three selected OPPs as test analytes namely chlorpyrifos, diazinon and dicrotophos. This is the first work to report on the development of new sol-gel SiO$_2$-NPs-CNPrTEOS as sorbent for SPE for the determination of OPPs. This new sorbent material showed superior extraction performance for the selected OPPs compared to commercial cyano sorbent.

2.0   EXPERIMENTAL

2.1   Standards and Materials

Three OPPs used as test analytes namely dicrotophos (polar), diazinon (mid-polar) and chlorpyrifos (non-polar) were purchased from Fluka Sigma-Aldrich (MO, USA). Pesticides stock solutions (1000 ppm) were prepared by using HPLC grade methanol and diluted as needed. The solutions were then stored in the refrigerator when not in use. Chemicals used were cyanopropyltriethoxysilane (CNPrTEOS), tetraethoxysilane (TEOS) and ammonium solution (NH$_4$OH) were obtained from Sigma Aldrich (MO, USA). HPLC grade toluene, methanol and ethanol were purchased from Merck (Darmstadt, Germany). Hydrochloric acids (HCl) and dichloromethane (DCM) were from Fluka (Buchs, Switzerland). Deionized water (DW) was purified by a Milipore Simplicity185 (UV) water system from Thermo Scientific (MA, USA). Commercial cyano SPE cartridge (1 mL) was purchased from Supelco (PA, USA).

2.2 Preparation of Silica Nanoparticles Coating with Cyanopropyltriethoxysilane

The starting silica nanoparticles were synthesized using sol-gel method [2].The silica nanoparticles (SiO_2-NPs) were prepared by mixing 8mLof TEOS, 25 mL of water, 1 mL of NH_4OH at pH 12 and 15 mL of ethanol as solvent into a 500 mL beaker. The mixture was stirred by using a magnetic stirrer for four hours at room temperature, left at room temperature (25ºC) for one day until gel was formed. The formed gel was washed with 3×20 mL of deionized water (DW).The washed powder was dried at 70ºC for one day till completely dried. The silica nanoparticles (SiO_2-NPs) were activated by refluxing in concentrated HCl (6 M) for 6 h. A 100 mL of round-bottom flask were introduced successively with 30 mL of anhydrous toluene, 1.0 g of activated silica and 2.5 mL of 3-cyanopropyltriethoxysilane. The solution was refluxed for 24 h under nitrogen gas, filtered and washed subsequently with toluene, dichloromethane and methanol and dried under reduced pressure at 80°C for 24 h. Through this simple procedure, the cyanopropyl-functionalized silica (SiO_2-NPs-CNPrTEOS) was obtained. The product was weighed and placed in a bottle sample.

2.3 Solid Phase Extraction Procedures

The prepared SiO_2-NPs-CNPrTEOS (100 mg) was ground using a pestle and mortar and manually packed into an empty 3 mL SPE polypropylene tube fitted with frits (top and bottom). Empty SPE tubes were purchased from Supelco (Bellefonte, PA, USA). The filled SPE cartridge was then placed in a 12-port SPE vacuum manifold from Supelco (Bellefonte, PA, USA) and conditioned by passing 5 mL methanol, followed by 10 mL of deionized water. Then 1 mL of spiked deionized water sample (1 µg mL^{-1} of each OPPs as mixture) was slowly passed through the cartridge at a flow rate of 0.5 mL min^{-1}. The sorbent was not allowed to become dry at any moment. After loading the sample into the SPE cartridge, it was dried by passing air for 30 min. The trapped pesticides were eluted from the sorbent with 2 mL dichloromethane and eluate was dried under a stream of gentle nitrogen gas. Finally, the residue obtained was reconstituted with 80 µL methanol prior to LC-UV analysis. For commercial cyano SPE sorbent from Supelco (PA, USA), a 1 mL cartridge was used for extraction and a similar procedure as the SiO_2-NPs-CNPrTEOS SPE was followed.

2.4 Liquid Chromatography Conditions

The analysis of dicrotophos, diazinon and chlorpyrifos were performed using an Agilent 1100 series high performance liquid chromatography (Agilent Technologies, USA). The HPLC system consists of a vacuum degasser, aquaternary pump, manual injector with a 20 µL Rheodyneloop and aultraviolet detector. The separation was performedon a reverse phase C18 HPLC Eclipse XDB-C18column (5 µm, 150 mm × 4.6 mm I.D.), from Agilent Technologies (Santa Clara, CA, USA). The mobile phase used was methanol and water(70:30, v/v) at a flow rate of 1.0 mL min^{-1} with UV detection at 270 nm.The extraction performance of the sorbent was assessed by measuring the detector response (peak area of OPPs extracted).

2.5 Characterization of Sol–gel Sorbent

The prepared sol-gel SiO$_2$-NPs-CNPrTEOS was characterized for functional groups using KBr pellet method on a Perkin Elmer 1600 Series Fourier transform infared spectroscopy (FT-IR) (MA, USA) in the range of 400-4000 cm^{-1}. The surface morphology of the sol-gel sorbent was evaluated using a field emission scanning electron microscopy (FESEM) model JSM-6710F from JEOL (Tokyo, Japan). The surface area and pore size of the sol-gel material were determined by using nitrogen adsorption with an ASAP 2010 Micromeritics surface analyzer from Delta Analytical Instrument Inc. (PA, USA) at 77 K. The thermogravimetric analysis (TGA) was performed with TGA 7 Perkin-Elmer thermogravimetric analyzer at heating rate of 10˚C min^{-1}under nitrogen atmosphere.

## 3. RESULTS AND DISCUSSION

In this work, sol-gel chemistry was used to chemically bind highly polar cyanopropyl moieties to an evolving sol-gel network structure and sol-gel material

as a sorbent in SPE to provide efficient extraction of organophosphorus pesticides from aqueous solution. The sol-gel sorbent was prepared by using four main materials, namely cyanopropyltriethoxysilane, tetraethoxysilane as sol-gel precursor, ammonium hydroxide as a base catalyst and ethanol to obtain a homogeneous reaction mixture. The CNPrTEOS was chosen due to its potential for use as solid phase extraction sorbent of polar compounds.This sorbent not only can extract polar compounds but also can extract non-polar and mid-polar compounds simultaneously. The SiO_2-NPs-CNPrTEOS possess cyano functional groups (polar group) which is able to attract polar analytes thorough H-bonding. The applicability of the synthesized material as sorbent for solid phase extraction (SPE) was assessed based on the OPPs extracted.

3.1 Mechanism of SynthesisProcess

Silica nanoparticles(SiO_2-NPs) were synthesized using sol-gel method. The sol–gel process involved hydrolysis and polycondensation of a sol–gel precursor and polycondensation of its hydrolysis products between themselves to an evolving sol-gel network structure. The sol-gel process corresponds to the generation of colloidal suspensions (sol) which are later converted to viscous gel and the solid material. The synthesis of silica nanoparticles is based on the hydrolysis and condensation of silicon alkoxides[8]. The production of SiO_2-NPsundergoes two steps. The first step is synthesis of SiO_2-NPs by hydrolysis of the precursor (TEOS)using ethanol, waterand NH_4OH as catalyst at room temperature for four hours(**Figure 1**).In the hydrolysis step, reactive silanol group and ethanol are produced and in the polycondensation step, the hydrolyzed product produces a three-dimensional silica network with the elimination of water.In the second step, the prepared SiO_2-NPs were coated using (CNPrTEOS) in the presence of toluene as solvent under nitrogen gas by means of refluxing at 100 ºC for 24 h(**Figure 2**).
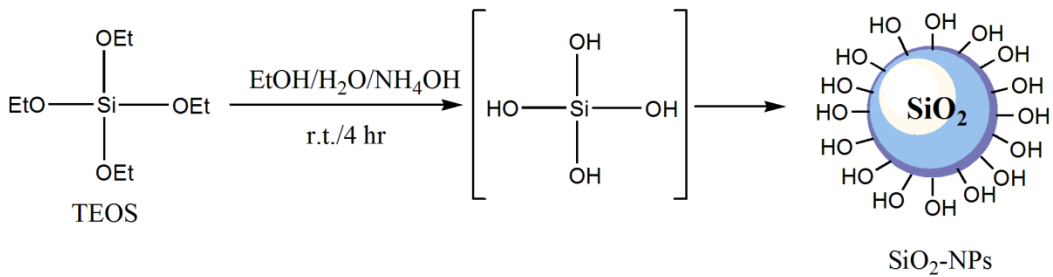
**Figure 1:** Synthesis of silica nanoparticles(SiO$_2$-NPs).
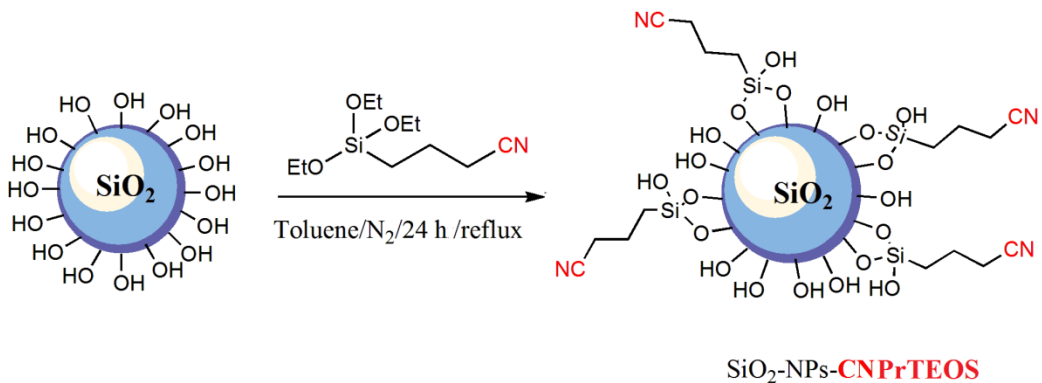
Figure 2: Coating of silica nanoparticles (SiO$_2$-NPs) using CNPrTEOS.

3.2   Characterization of the SiO$_2$-NPs-CNPrTEOS

Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), nitrogen adsorption (BET) and thermogravimetric analysis (TGA) were used to characterize the in-house SiO$_2$-NPs-CNPrTEOS sorbent. The raw TEOS and CNPrTEOS and also synthesized SiO$_2$-NPs and SiO$_2$-CNPrTEOSwereshowed in the range of 4,000 cm^{-1} to 400 cm^{-1}. The spectrum of SiO$_2$-NPs-CNPrTEOS **(Figure 3)**shows absorption band at 3,390cm^{-1} and 1634 cm^{-1} which corresponds to O-H bond stretching and this suggests the presence of absorbed water in the silica network and probably related to O-H of surfaceSiO$_2$-NPs-CNPrTEOS. There is the existence of methyl stretching bond (C-H) at 2,930 cm^{-1} in raw TEOS and CNPrTEOS. The Si-O-Si network stretching band is around 1,100cm^{-1}. The C≡N groups are at 2,246 cm^{-1} in raw CNPrTEOS and alsothe C≡N groupsare presentin SiO$_2$-CNPrTEOS(**Figure 3**). This indicates that

the coating of SiO₂-NPs-CNPrTEOS using precursor (CNPrTEOS) was successful.
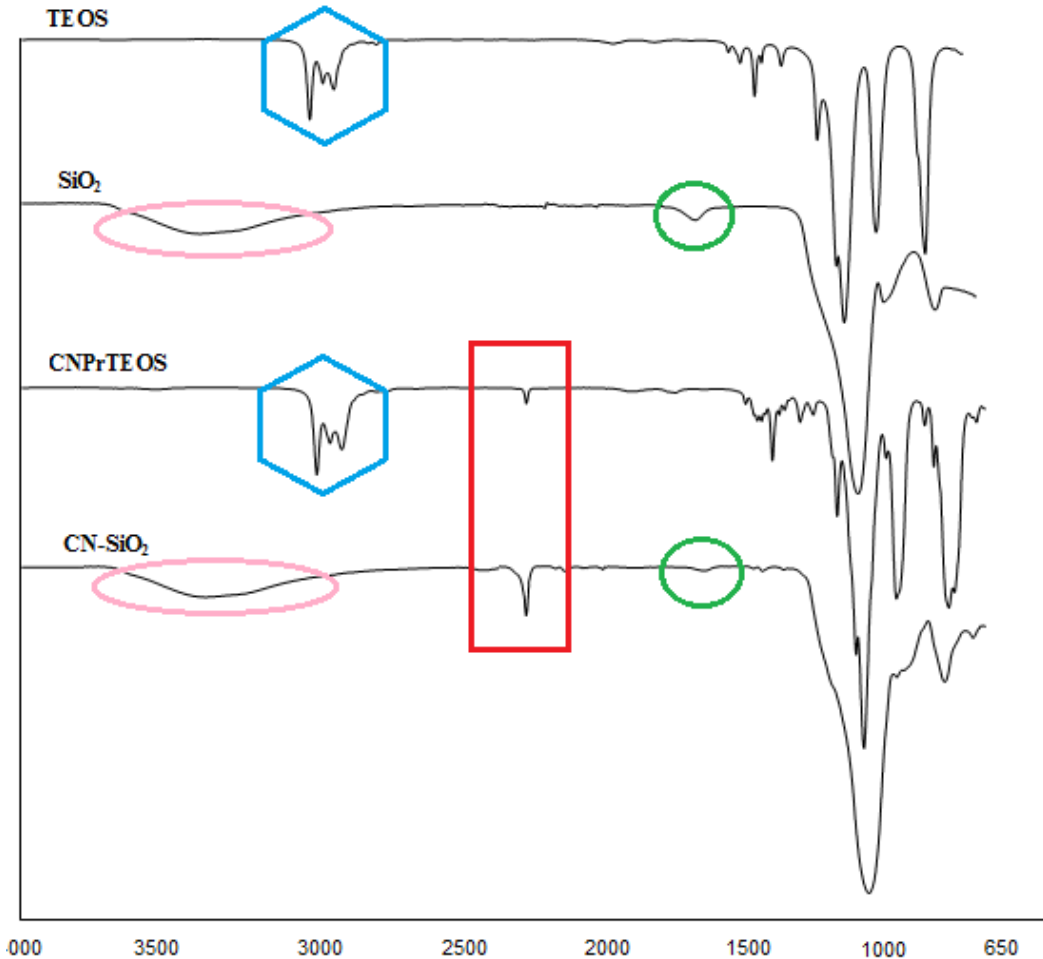
Figure 3: FT-IR spectrum of raw TEOS, raw CNPrTEOS, SiO₂-NPs and SiO₂-NPs-CNPrTEOS.

The surface morphology of SiO₂-NPs-CNPrTEOS was analyzed using FESEM **(Figure 4)**. The FESEM image shows that the synthesized SiO₂-NPs-CNPrTEOS is spherical particles. The average particle size of SiO₂-NPs-CNPrTEOS is 54 nm. The BET surface area of the synthesized SiO₂-NPs-CNPrTEOS was measured to be 570 m^{2}g^{-1} and the average pore diameter is 31Å (mesoporous). Based on the Brunauer-Emmet-Teller (BET) classification, the SiO₂-NPs-CNPrTEOS is in the class of type IV isotherm.
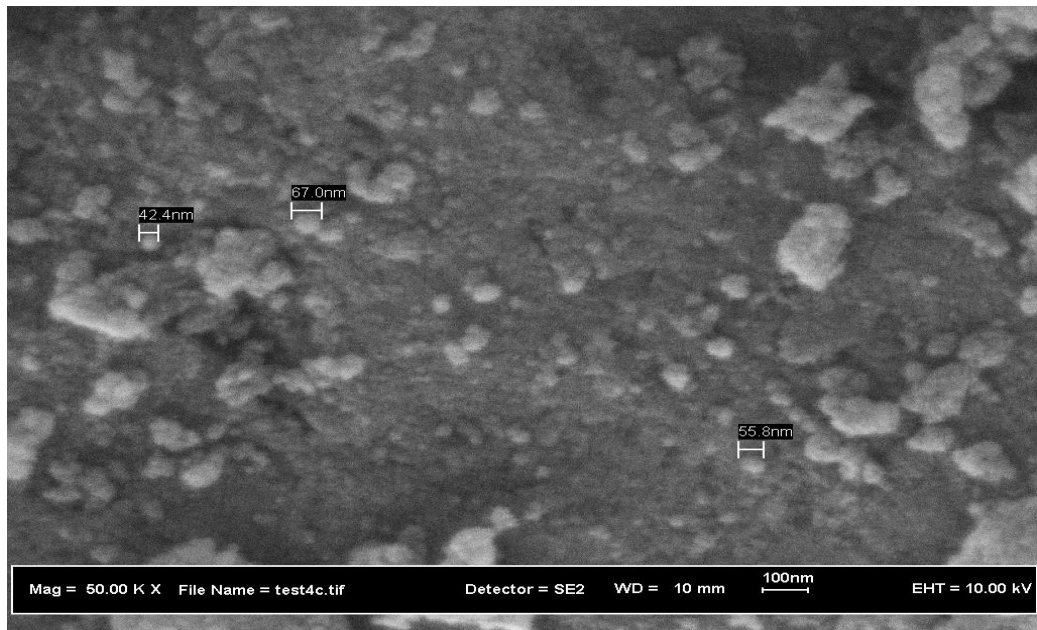
Figure 4:FESEM micrographs of SiO_2-NPs-CNPrTEOS sorbent at ×50K magnifications.

The results of thermogravimetricanalysis of SiO_2-NPs-CNPrTEOS sorbent and SiO_2-NPsin the 50–800ºC temperaturerange in air are shown in Figure5.The SiO_2-NPs materialand the SiO_2-NPs-CNPrTEOS sorbentexhibited high thermal stability (100ºC-800ºC)and (100ºC-450ºC) respectively. According to the SiO_2-NPs material thermal degradation, one weight loss stage is detected, below 100ºC and based on theSiO_2-NPs-CNPrTEOS sorbent thermal degradation,two weight loss stages were observed, below 100ºCand between 450 and 600ºC but theSiO_2-NPs-CNPrTEOS is stable after 600ºC **(Figure 5)**. The weight loss below 100ºC could be due to the evaporation of small amount of adsorbed water and the volatilization and thermal decomposition of the remnant of organic solvents. Between 450 and 600ºC, the weight loss could be attributed to the carbonization or the combustion of organic compounds. i.e. the loss of carbon, hydrogen and oxygen. Between 400 and 600ºC, the weight losses could be probably isascribed to the further combustion of organic moieties.
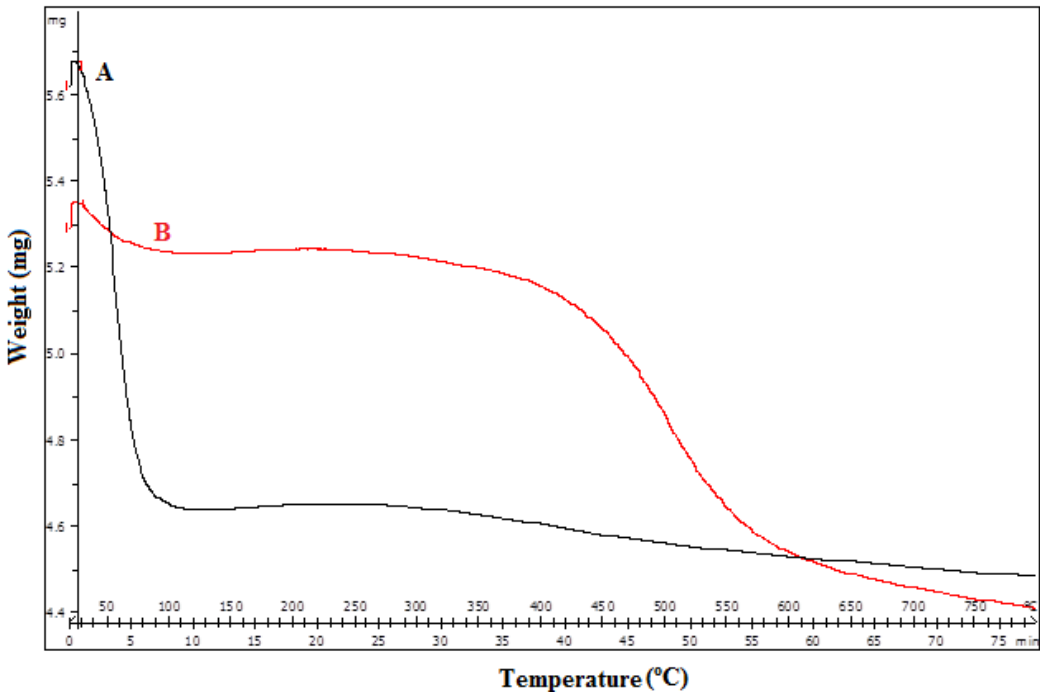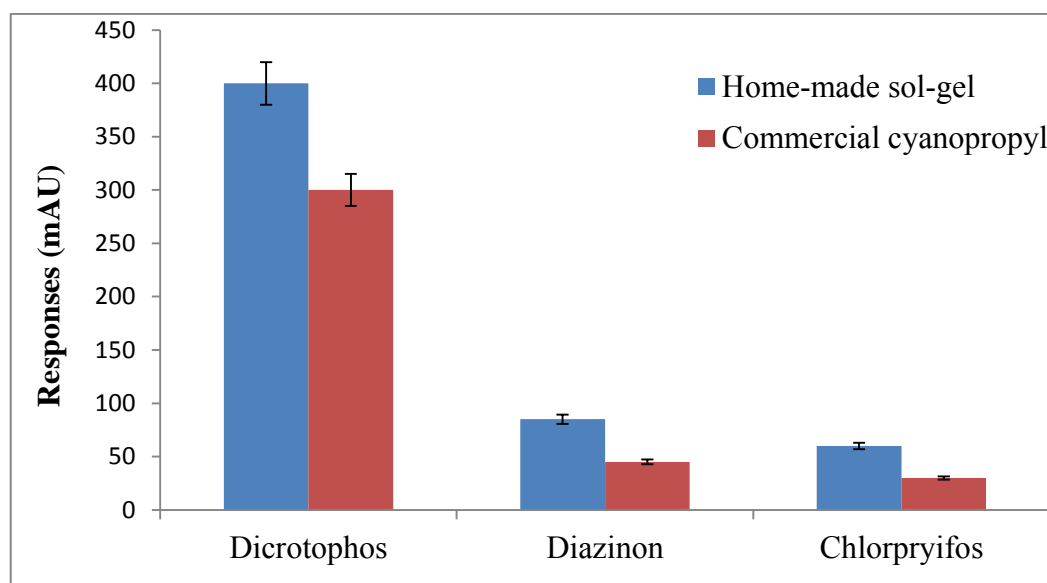
Figure 5:TGA profiles of (A)SiO_2-NPs and (B) sol-gel SiO_2-NPs-CNPrTEOS

3.3   Extraction Performance of the SiO_2-NPs-CNPrTEOS

The extraction performance of the SiO_2-NPs-CNPrTEOS produced as sorbent for SPE of three OPPs (polar dicrotophos, mid-polar diazinon and non-polar chlorpyrifos)was compared with commercial CN SPE from Supelco. The OPPs concentration used for both SPE was 1 µg mL^{-1}of each OPPs and used as mixture. The extraction abilities of the SiO_2-NPs-CNPrTEOS is presented and compared by plotting graphs of OPPs response for each OPPs(**Figure 6**). A high response reflects the good ability of the SiO_2-NPs-CNPrTEOS as SPE sorbent for the OPPs studied.

Figure 6 shows that the SiO_2-NPs-CNPrTEOS was capable of extracting polar dicrotophos better than the mid-polar diazinon and non-polar chlorpyrifos. It has a very high selectivity for the polar dicrotophos. This is most probably due to

the combination of high surface area and polar interaction between sorbent and analyte due to introduction of the polar CN moiety. The much higher response for the polar dicrotophosmight also be due to the H-bonding formed between H from-OH groupspresent in the SiO_2-NPs-CNPrTEOS sorbent and the lone pair electron on N atom plus the$\pi - \pi$ interaction between the C≡N moiety and alkene double bond in dicrotophos. The sorbent is also able to extract the mid-polar diazinon and non-polar chlorpyrifos (interaction with the $-CH_2CH_2CH_2-$ moiety) simultaneously with higher response than the commercial CN SPE [6, 7].

Figure 6: Comparison of extraction performance of the home-made SiO_2-NPs-CNPrTEOSand commercial cyanopropyl for three OPPs. SPE conditions: 1mL sample volume (1 µg mL^{-1}), 2 mL ofdichloromethane as eluting solventat flow rate of 0.5 mL min^{-1}. HPLC conditions: the mobile phase usedmethanol: water(70:30) at flow rate of 1.0 mL min^{-1} with UV detection at 270 nm.

4. CONCLUSIONS

The SiO_2-NPs-CNPrTEOS sorbent was successfully synthesized using sol-gel process to produce mesoporous spherical particles with an average particle size of SiO_2-NPs-CNPrTEOS ~54 nm. The surface area and pore size of the SiO_2-NPs-

CNPrTEOS are 570 m^2g^{-1} and 31Å, respectively. It was successfully used as sorbent for SPE of three OPPs of various polarities. The sorbent showed great potential for simultaneous extraction of polar and non-polar organic compounds. The extraction performance of the in-house synthesized SiO_2-NPs-CNPrTEOS was superior for the three OPPs and highly selective for polar dicrotophos as compared to commercial CN SPE.

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