

Sol-Gel Hybrid Cyanopropyltriethoxysilane-methyltrimethoxysilane as Adsorbent for Dispersive-Micro Solid Phase Extraction of Selected Organophosphorus Pesticides in Water Samples

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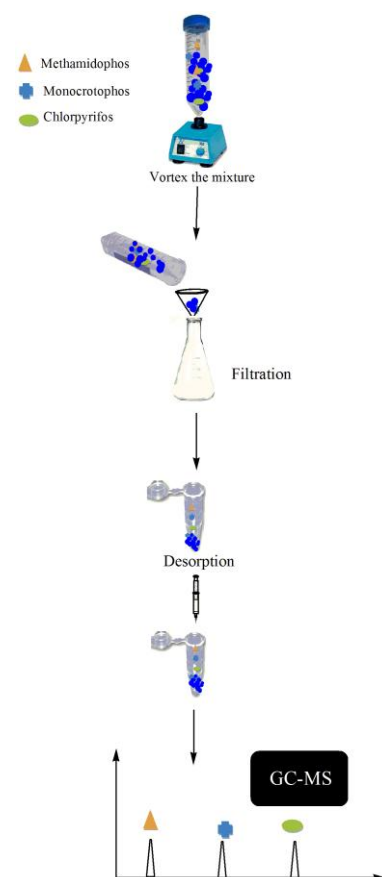
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Graphical abstract



Abstract

Commercial solid phase extraction (SPE) sorbents normally used for organophosphorus pesticides (OPPS) analysis is C18. However, it show low retention for polar compounds and is rather expensive. The limitations are overcome through the development of a new sol-gel hybrid material, cyanopropyltriethoxysilane-methyltrimethoxysilane (CNPrTEOS-MTMOS). Sol-gel hybrid CNPrTEOS-MTMOS was successfully synthesized and applied as an adsorbent for dispersive-micro-SPE (D- μ -SPE) of three selected OPPs from several water samples. Extracted analytes were analyzed using gas chromatography-mass spectrometry. Under the optimum conditions (100 mg CNPrTEOS-MTMOS as adsorbent, 10 mL water samples, 7 min extraction time, 300 μ L methanol as desorption solvent and 3 min desorption time), the method showed excellent detection limits (0.01-0.004 μ g L⁻¹ at S/N = 3) and linear range achieved were 0.01-10 μ g L⁻¹. The CNPrTEOS-MTMOS sorbent offers an alternative sorbent material for the extraction of OPPs of various polarity. The developed D- μ -SPE method was successfully applied for the simultaneous analysis of OPPs in several water samples and results were compared with published results. Sol-gel hybrid CNPrTEOS-MTMOS showed high potential as an alternative adsorbent for D- μ -SPE technique for OPPs.

Keywords: Sol-gel hybrid; Dispersive-Micro Solid phase Extraction; Organophosphorus Pesticides; Gas chromatography-mass spectrometry.

Abstrak

Pengekstrakan fasa pepejal (SPE) komersial yang biasa digunakan untuk analisis pestisid organofosforus (OPPs) adalah C18. Walau bagaimanapun, ia menunjukkan penahanan rendah untuk analit berkutub dan juga agak mahal. Kelemahan ini ditangani melalui penghasilan bahan baharu hibrid sol-gel sianopropiltriethoxysilana-metiltrimetoksilana (CNPrTEOS-MTMOS). Hibrid sol-gel CNPrTEOS-MTMOS telah berjaya disintesis dan diaplikasikan sebagai bahan penjerap untuk pengekstrakan mikro fasa pepejal serakan (D- μ -SPE) tiga OPPs terpilih daripada beberapa sampel sampel air. Analit yang telah diekstrak dianalisis menggunakan kromatografi gas-spektrometri jisim. Pada keadaan optimum (100 mg CNPrTEOS-MTMOS sebagai bahan penjerap, 10 mL sampel air, 7 min masa pengekstrakan, 300 μ L metanol sebagai pelarut penyaherapan dan 3 min masa penyaherapan), kaedah ini menawarkan had pengesanan yang cemerlang (0.01-0.004 μ g L⁻¹ pada S/N = 3) dan julat linear dicapai ialah 0.01-10 μ g L⁻¹. Bahan penjerap CNPrTEOS-MTMOS mempamerkan potensi tinggi sebagai bahan penjerap alternatif untuk pengekstrakan OPPs pelbagai kekutuban. Kaedah yang dibangunkan ini telah digunakan dengan jayanya untuk pengekstrakan secara serentak OPPs dalam beberapa sampel air dan dibandingkan dengan keputusan yang telah diterbitkan. Hibrid sol-gel CNPrTEOS-MTMOS menunjukkan potensi tinggi sebagai bahan penjerap alternatif untuk teknik D- μ -SPE untuk OPPs.

Kata kunci: Hibrid sol-gel; pengekstrakan mikro fasa pepejal serakan; pestisid organofosforus; kromatografi gas-spektrometri jisim

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1.0 INTRODUCTION

In the 1930s, the insecticidal properties of organophosphorus pesticides (OPPs) and carbamate compounds were found and the compounds were developed for pesticides use in 1940s. They have been extensively used since 1970s when the environmentally persistent organochlorine pesticides were banned for use in United States¹. Although OPPs compounds are considered less dangerous than organochlorine, there are still highly neurotoxic to humans and in some cases their degradation products have the potential to be more toxic with chronic exposure.

Since OPPs are neurotoxic and harmful to human, therefore there is an increasing concern with regard to the determination of these compounds. The direct determination of OPPs into instrument is limited due to presence of matrix interference and low concentration level of the analytes. Therefore sample preparation step is needed to isolate the analytes from the matrices or to preconcentrate them in order to improve their sensitivities and to increase the detection limit.

There are many sample preparation methods available and one of them is dispersive micro-solid phase extraction (D- μ -SPE). D- μ -SPE is a variation of dispersive solid phase extraction (DSPE) which is originally used as sample clean up method. In D- μ -SPE technique, the adsorbents can be applied in the dispersive mode with the purpose of trapping the target analytes. This microextraction technique was developed to overcome the limitation and simplify the traditional SPE which is a long procedure and need for complex equipment^{2,3}.

Several sorbents that are commercially available and commonly used in DSPE and D- μ -SPE include octadecyl (C18) bonded silica³, multi-walled carbon nanotubes⁴, primary secondary amine⁵ and activated carbon⁶. However, these conventional sorbents showed low retention for polar compounds⁷. The advancement of new sorbent materials for D- μ -SPE is not much emphasized and only a few works on sorbent materials have been reported to date^{8,9}.

Sol-gel technology offers a method of producing tailor-made sorbent for extraction purposes. There is a steady growth in the use of sol-gel process in the extraction of analytes of interest. Several methods have been reported for the application of sol-gel process e.g., SPE^{10,11}, solid phase microextraction¹²⁻¹⁴ and stir bar sorptive extraction¹⁵⁻¹⁶. To the best of our knowledge, the application of sol-gel hybrid material in DSPE and D- μ -SPE is still new. Previous successful work¹⁷ on the use of sol-gel hybrid sorbent as a new clean-up material for DSPE of acrylamide has prompted us to produce further sol-gel hybrid D- μ -SPE sorbent for OPPs application. In the current work, silica-based sol-gel hybrid sorbent was successfully prepared as a new adsorbent for D- μ -SPE where it was being applied in the dispersive mode with the aim of trapping the analyte/s of interest. The adsorbent is based on the use of two silica-based precursors, cyanopropyltriethoxysilane (CNPrTEOS) and methyltrimethoxysilane (MTMOS). This silica-based adsorbent was able to successfully extract simultaneously polar OPPs (methamidophos, monocrotophos) and also the non-polar OPPs (chlorpyrifos) and with higher extraction efficiency than commercial C18 sorbent.

2.0 MATERIALS AND METHODS

2.1 Pesticide Standards and Solvents

Standard pesticides of methamidophos, monocrotophos and chlorpyrifos were purchased from Fluka Sigma-Aldrich (St. Louis, USA). Standard solutions of 100 $\mu\text{g mL}^{-1}$ of each pesticide

were prepared in HPLC grade methanol from J. T. Baker Inc (Phillipsburg, USA). It was stored at 4°C when not in use.

2.2 Preparation of Sol-Gel Hybrid CNPrTEOS-MTMOS

The conditions for the preparation of sol-gel hybrid CNPrTEOS-MTMOS was adopted from the method of Wan Ismail¹⁸. Initially, 0.36 mL of water and 0.85 mL of ammonium hydroxide (NH_4OH) was put in a 5 mL beaker followed by drop wise addition of cyanopropyltriethoxysilane (CNPrTEOS) in water (CNPrTEOS 0.48 mL and 0.54 mL water). Then, methyltrimethoxysilane (MTMOS) solution (0.28 mL and water 0.54 mL) was added drop wise into the mixture. All the sol-gel materials were purchased from Sigma Aldrich Co. (USA). The mixture was stirred for 30 min at 28°C. The resulting particles were washed with deionized water (2×5 mL) to remove any residual catalyst. The washed particles were dried at 100°C for a day and finally ground using a pestle and mortar before use.

2.3 Characterization of Sol-Gel Hybrid CNPrTEOS-MTMOS

The raw CNPrTEOS, MTMOS and prepared sol-gel hybrid CNPrTEOS-MTMOS were characterized using Fourier transform infrared spectroscopy (FTIR) using ATR method on a Perkin Elmer FTIR spectrum 100 (MA, USA) fitted with ATR (Ge/Ge) accessory in the range of 600–4000 cm^{-1} . The surface morphology of the sol-gel hybrid CNPrTEOS-MTMOS was determined using a JSM-6701F field emission-scanning electron microscope (FE-SEM) from JEOL (Tokyo, Japan). The surface area and pore size of the sol gel hybrid CNPrTEOS-MTMOS were collected using a surface analyzer model ASAP 2010 Micromeritics from Delta Analytical Instruments Inc. (PA, USA).

2.4 D- μ -SPE and SPE Process

In D- μ -SPE process, the ground sol-gel hybrid CNPrTEOS-MTMOS (100 mg) was dispersed into 10 mL of sample solution containing 0.1 ng mL^{-1} of each OPP in a centrifuge tube. Optimum conditions (obtained by varying one parameter at a time) were used in the D- μ -SPE process. The mixture was vortexed for 7 min to assist extraction process followed by centrifugation at 3 000 rpm for 8 min. Adsorbent was filtered and dried by blowing with a gentle nitrogen flow. The collected adsorbent was then sonicated for 3 min in 300 μL of methanol. The resulting solution was filtered through 0.45 μm nylon membrane from Millipore (MA, USA) before subjected to GC-MS analysis. Commercial C18 SPE sorbent obtained from Supelco (Bellefonte, PA, USA) was used for comparison purpose. C18 SPE results from Wan Ibrahim *et al.*¹¹ were used for comparison.

2.5 GC-MS Analysis

Analysis of extracts of methamidophos, monocrotophos and chlorpyrifos were performed using a Hewlett Packard 6890N Gas Chromatograph (Santa Clara, CA, USA) equipped with a Hewlett Packard Model 6890N Mass Spectrometer (Santa Clara, CA, USA). An Ultra 2 column (25×0.20 mm i.d, 0.33 μm film thickness) was used in the analysis. Purified helium was used as carrier gas at flow rate of 1 mL min^{-1} . The oven temperature used was as follows: 70°C and ramp to 280°C at 20°C min^{-1} and hold for 10 min. The injector and detector temperatures were set at 260°C and 230°C, respectively. SIM mode was used for the OPPs analysis.

2.6 Real Sample Analysis

Method calibration graph was constructed by plotting peak area of the extracted analytes versus its concentration added to validate D- μ -SPE-GC-MS method towards the three selected OPPs using optimum D- μ -SPE conditions (100 mg of CNPrTEOS-MTMOS adsorbent, 10 mL sample volume, 7 min extraction time, 300 μ L methanol as desorption solvent). Linearity range, coefficient of determination and limit of detection (LOD at 3 S/N) was determined from the graph. For real sample analysis, tap water sample was taken from our laboratory, lake water sample was collected from the university lake and drinking water sample was purchased from a local shop in Skudai. Each of the water samples were filtered using 0.45 μ m nylon membrane filter from Whatmann (NJ, USA). For recovery analysis, all samples were spiked with 0.1 ng mL⁻¹ (European Union Maximum residue limit) of each methamidophos, monocrotophos and chlorpyrifos¹⁹.

3.0 RESULTS AND DISCUSSION

3.1 Preparation of Sol-gel hybrid CNPrTEOS-MTMOS

In this study, sol-gel chemistry was used to chemically bind highly polar CNPrTEOS and non-polar MTMOS to an evolving sol-gel network structure, and to use such a hybrid organic-inorganic material as a surface-bonded sorbent to provide efficient extraction of OPPs from a wide range of polarity. The material CNPrTEOS was selected in this study because extraction medium containing cyano functional group are known to be extremely polar and may proved to be highly effective in the extraction of polar analyte from aqueous sample²⁰. The MTMOS was selected as co-precursor because it yields narrow and uniform pores with higher surface²¹. Besides, MTMOS can also overcome undesirable effects such as cracking and shrinkage during the drying process of the sol-gel process²⁰. Basic catalyst, NH₄OH was used to prepare sol-gel in this study. Under base catalysis it is easy to form uniform network particles in the sol. Besides that, it also produced quite large pore volume and the If hydrolysis rate is faster than condensation rate, the silica unit

will build up at the ends of the developing chains, thereby yielding linear and closely packed with microporous interstitial species²².

3.2 Characterization of Sol-Gel Hybrid CNPrTEOS-MTMOS

Physical characterization methods used were Fourier transform infra red spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM) and nitrogen adsorption. FTIR was used to confirm that the sol-gel hybrid was successfully synthesized by the formation of siloxane linkages, Si-O-Si.

The spectrum of raw CNPrTEOS, MTMOS and sol-gel hybrid CNPrTEOS-MTMOS are shown in Figure 1. All the spectrum shows a broad peak around 3400 cm⁻¹ with indicates the peak of OH bond stretching and is attributed to non-condensed silanol and residual water. The spectrum of CNPrTEOS shows absorption band of Si-O-Si at 1248.66 cm⁻¹ and 1145.17 cm⁻¹ and C-H stretching at 2888.28 cm⁻¹. The spectrum also shows absorption band of C \equiv N at 2246.46 cm⁻¹. While for MTMOS, the spectrum shows medium absorption bands of C-H stretching at 2946.81 cm⁻¹ and 2842.16 cm⁻¹ and weak absorption bands of Si-O-Si at 1268.95 cm⁻¹, 1193.28 cm⁻¹ and 1092.59 cm⁻¹. This indicates that the hybridization process between CNPrTEOS and MTMOS was successful.

The morphology of the sol-gel hybrid CNPrTEOS-MTMOS was analyzed using FE-SEM (Figure 2). The micrograph showed irregular shaped particles with average particle sizes of 170-230 nm.

Brunner, Emmet and Teller (BET) surface area, pore volume and pore size distribution were performed for the sol-gel hybrid CNPrTEOS-MTMOS. The surface area of CNPrTEOS-MTMOS obtained was 9.00 m² g⁻¹, average pore size of 183.76 Å (mesoporous material) and pore volume of 0.00130 cm³ g⁻¹. Even though the surface area is low, it did not affect the extraction performance of the adsorbent for the OPPs probably due to the porous nature of the adsorbent. Low surface area (3.04 m² g⁻¹) of sol-gel titanium(IV) butoxide cyanopropyltriethoxysilane was also observed by Miskam et al.²³.

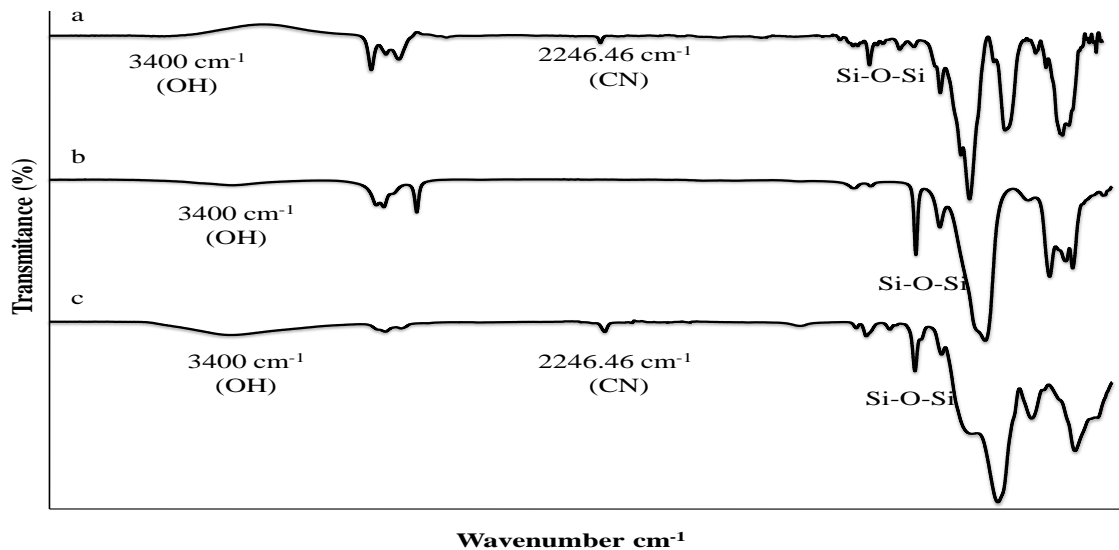


Figure 1 FTIR spectrum of (a) raw CNPrTEOS, (b) raw MTMOS and (c) sol-gel hybrid CNPrTEOS-MTMOS

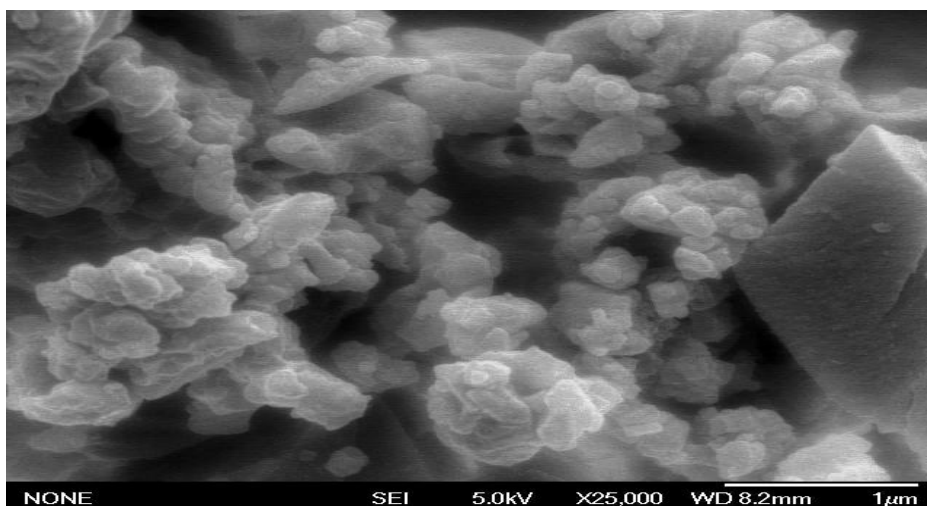


Figure 2 FE-SEM morphology of sol-gel hybrid CNPrTEOS-MTMOS at 25 000× magnification

3.3 Method Validation

Calibration graph of amount of analyte peak area versus its concentration was performed to validate the D- μ -SPE-GC-MS method towards methamidophos, monocrotophos and chlorpyrifos. The optimum D- μ -SPE conditions were applied to the extraction of the three selected OPPs from deionized water at varying concentration (0.05 - $10 \mu\text{g L}^{-1}$) for methamidophos and monocrotophos and (0.01 - $10 \mu\text{g L}^{-1}$) for chlorpyrifos. Good correlation between peak areas and analyte concentrations was obtained ($R^2 > 0.994$). The limit of detection (LOD) at $S/N = 3$ obtained was $0.03 \mu\text{g L}^{-1}$, $0.02 \mu\text{g L}^{-1}$ and $0.004 \mu\text{g L}^{-1}$ for methamidophos, monocrotophos and chlorpyrifos, respectively. The LOD obtained was 5 - $10\times$ lower than the maximum residue limit (MRL) set by the European Union (EU) [19] and is comparable with the result obtained from previous study by Wan Ibrahim *et al* [11] where CNPrTEOS-MTMOS was used as sorbent for SPE of methamidophos, dicrotophos, diazinon, malathion, methidathion and chlorpyrifos from several water samples.

The developed method was also compared with C18 SPE

method by Wan Ibrahim *et al.*¹¹ in terms of recoveries of the OPPs studied at the spiking levels used. Comparable recoveries (93-103%) were achieved for CNPrTEOS-MTMOS-D- μ -SPE method compared to recoveries (92-99%) obtained by C18 SPE method. The D- μ -SPE method using sol-gel hybrid CNPrTEOS-MTMOS is suitable for the analysis of OPPs at trace levels in water samples.

3.4 Real Sample Analysis

None of the analytes analysed were detected in the water samples under study. Thus, the three water samples were each spiked with 0.1 ng mL^{-1} (MRL) of each OPP studied in order to determine the accuracy and precision of the CNPrTEOS-MTMOS D- μ -SPE method. Good recoveries (90-108%) with good RSD (0.30-5.16%, $n = 3$) (Table 1) were obtained using the developed sol-gel hybrid CNPrTEOS-MTMOS. Figure 3 shows a typical GC-MS chromatogram of real sample analysis of OPPs from tap water.

Table 1 Average recoveries (%) and precision (RSD) of three selected OPPs from three types of water samples analyzed (each OPPs spiked at 0.1 ng mL^{-1}) using CNPrTEOS-MTMOS-D- μ -SPE

Sample	OPPs	Average recovery (%)	RSD (% , $n = 3$)
Tap water	Methamidophos	103	1.56
	Monocrotophos	90	3.10
	Chlorpyrifos	100	1.39
Drinking water	Methamidophos	97	1.41
	Monocrotophos	99	5.16
	Chlorpyrifos	99	0.67
Lake water	Methamidophos	108	1.93
	Monocrotophos	96	0.82
	Chlorpyrifos	102	0.30

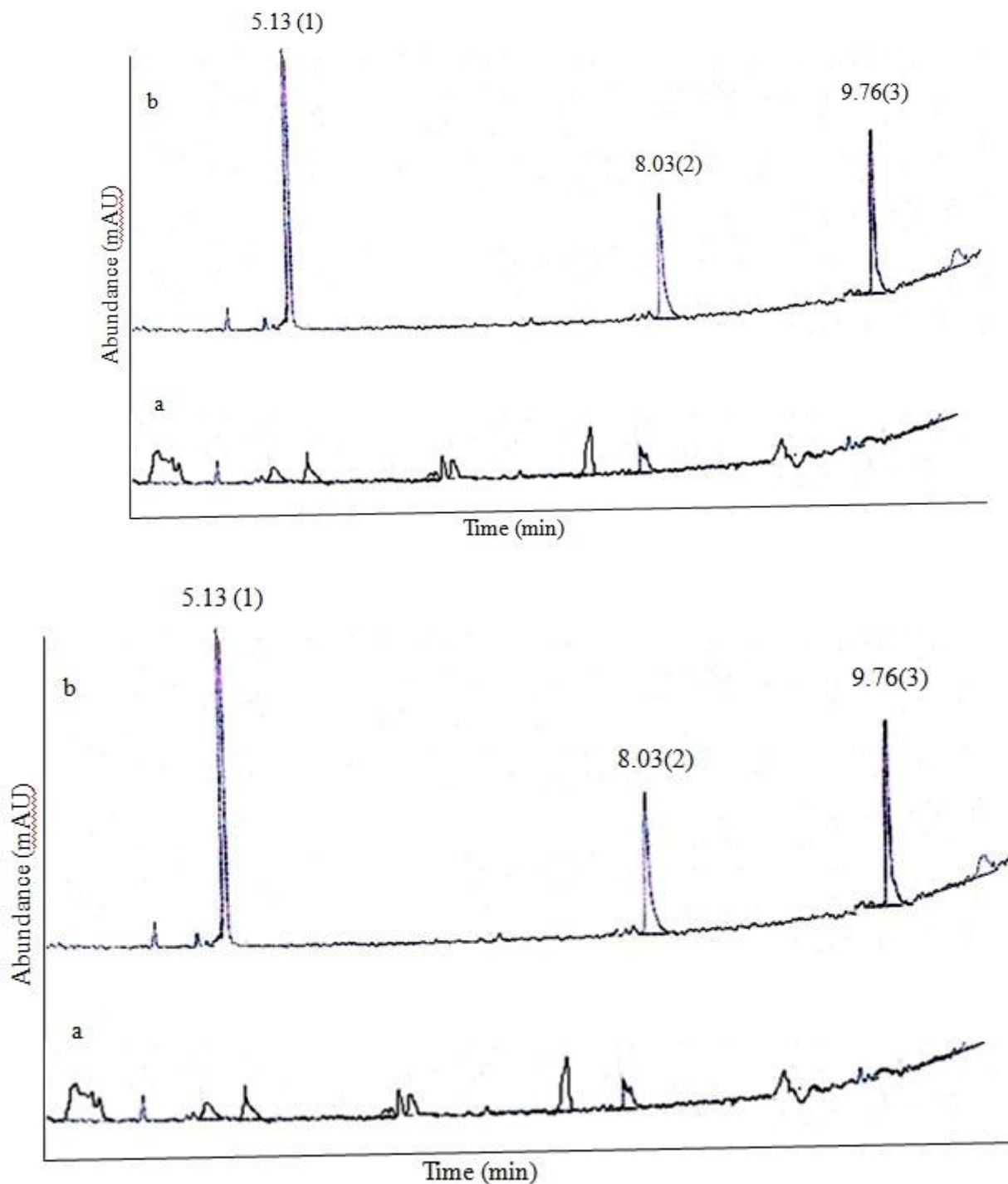


Figure 3 GC-MS chromatogram of (a) blank and (b) spiked (0.1 ng mL^{-1} each OPPs) tap water sample (b). GC conditions: Ultra 2 column ($25 \times 0.20 \text{ mm}$ i.d, $0.33 \mu\text{m}$ film thickness), column temperature: 70°C and ramp to 280°C at $20^\circ\text{C min}^{-1}$ and hold for 10 min, carrier gas: Helium gas at a flow rate of 1 mL min^{-1} , injection port temperature: 260°C , detection temperature: 230°C . Peaks: 1 metamidophos 2 monocrotophos 3 chlorpyrifos

4.0 CONCLUSION

The current work demonstrated the first report on the application of sol-gel hybrid CNPrTEOS-MTMOS as adsorbent for D- μ -SPE for simultaneous extraction of three selected OPPs of varying polarity namely methamidophos, monocrotophos and chlorpyrifos

from tap water, drinking water and lake water sample. The introduction of CNPrTEOS to MTMOS has helped to increase the polarity of the material produced and promote the interaction between both polar and non-polar OPPs with the hybrid sorbent simultaneously. The CNPrTEOS-MTMOS-D-u-SPE method is economical, environmental friendly, safer to the operator and

showed promising alternative adsorbent for simultaneous OPPs extraction of various polarities from various aqueous matrices, thus saving time.

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