

NEW SOL-GEL SILICA-BASED HYBRID MATERIALS AND THEIR
APPLICATIONS IN THE ANALYSIS OF ORGANOPHOSPHORUS
PESTICIDES IN VARIOUS MATRICES

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In the name of ALLAH, the Most Merciful and the Most Beneficent.

Peace be upon our prophet Muhammad SAW.

This thesis is dedicated to my late father, beloved mother, husband and family.

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ABSTRAK

Bahan pengerap komersial adalah berasaskan bahan polimer dan biasanya direkabentuk untuk mengekstrak analit berkutub atau tidak berkutub secara berasingan dan pengerap ini mahal. Dalam kajian ini, masalah tersebut ditangani melalui pembangunan tiga bahan baharu buatan sendiri hibrid sol-gel organik-inorganik yang telah menjadi bahan penting untuk analisis residu pencemar organik. Dua daripada bahan baharu hibrid sol-gel organik-inorganik telah disintesis, dicirikan dan diguna sebagai pengerap untuk dua teknik penyediaan sampel iaitu pengekstrakan bar berputar (SBSE) dan pengekstrakan fasa pepejal (SPE). Prestasi pengekstrakannya dinilai untuk pengekstrakan beberapa pestisid organofosforus (OPPs) terpilih dalam sampel air, buah-buahan dan sayur-sayuran. Bahan pertama iaitu 3-(2-aminoetilamino) propiltrimetoksisilana-polidimetilsiloksana telah disintesis sebagai pengerap SBSE dan digabungkan dengan kromatografi cecair berprestasi tinggi dengan pengesan ultraungu. Kedua-dua OPPs berkutub dan tidak berkutub telah diekstrak serentak menggunakan pengerap baharu ini dan menunjukkan kepilihan tinggi terhadap OPPs berkenaan berbanding pengerap komersial polidimetilsiloksana (PDMS) Twister™ SBSE. Hibrid sol-gel baharu kedua ialah metiltrimetoksisilana-sianopropiltrioksisilana (MTMOS-CNPrTEOS) yang digunakan sebagai pengerap SPE untuk pengekstrakan OPPs sebelum analisis dengan kromatografi gas spektrometri jisim. Pengerap baharu ini menunjukkan had pengesanan lebih rendah ($10\text{-}70\text{ pg mL}^{-1}$) dan perolehan semula yang sangat baik (94.93-99.98%) berbanding pengerap komersial C_{18} SPE ($0.05\text{-}1.23\text{ ng mL}^{-1}$). Faktor yang mempengaruhi proses sol-gel telah dioptimumkan bagi setiap pengerap untuk mendapatkan pengerap tercekap dan untuk meningkatkan pengekstrakan sebatian yang lebih berkutub. Filem hibrid sol-gel baharu ketiga berasaskan kumpulan siano telah disintesis menggunakan cetakan molekul (MIP) dengan metamidofos untuk aplikasi penderia OPPs dalam analisis sampel sayur-sayuran dan buah-buahan. Pengeluaran besar tetapi berkos rendah, kaedah sintesis yang mudah dan pengkhususan yang boleh diramal melalui rekabentuk logik telah memberi kelebihan ekonomi yang menggalakkan penyelidik untuk membangunkan kaedah dan aplikasi MIP. Filem hibrid sol-gel berasaskan kumpulan siano bertindak sebagai monomer berfungsi menyediakan tapak pencaman lebih banyak melalui ikatan hidrogen dengan metamidofos sebagai templat pencaman. Tingkah laku elektrokimia metamidofos pada penderia sol-gel dicirikan dengan voltametri kitaran. Keputusan menunjukkan bahawa kaedah baharu ini mampu menyediakan pengesan metamidofos yang peka, anti-gangguan dan pantas dalam sampel sebenar.

ABSTRACT

Commercial sorbent materials are based on polymeric materials and are normally designed to extract polar or non-polar analytes separately and are expensive. In the current work, these problems were addressed through the development of three new in-house sol-gel hybrid organic-inorganic materials which have become important materials for the analysis of organic pollutants residues. Two of these new sol-gel hybrid organic-inorganic materials were synthesized, characterized and used as sorbents for two sample preparations techniques namely, stir bar sorptive extraction (SBSE) and solid phase extraction (SPE). Their extraction performances were evaluated for extraction of selected organophosphorus pesticides (OPPs) in water, fruit and vegetable samples. The first material, 3-(2-aminoethylamino) propyltrimethoxysilane-polydimethylsiloxane, was synthesized as SBSE sorbent and combined with high performance liquid chromatography with ultraviolet detector. Both polar and non-polar OPPs were extracted simultaneously using the new sorbent and it showed high selectivity for the OPPs as compared to commercial polydimethylsiloxane (PDMS) Twister™ SBSE sorbent. The second new sol-gel hybrid material synthesized, methyltrimethoxysilane-cyanopropyltriethoxysilane, was used as SPE sorbent for OPPs extractions prior to gas chromatography-mass spectrometry analysis. This new sol-gel hybrid sorbent showed lower detection limits (10-70 pg mL⁻¹) and excellent recoveries (94.93-99.98%) against commercial C₁₈ SPE sorbent (0.05-1.23 ng mL⁻¹). Parameters affecting sol-gel process were optimized for each sorbent material to obtain the most efficient sorbent materials and to improve the extraction of the more polar compounds. The third new cyano-based sol-gel hybrid film was synthesized using molecular imprinting (MIP) with methamidophos for sensing OPPs applications in the analysis of vegetable and fruit samples. Low-cost large-scale production, ease of synthesis, and the predictability of specificity by logical design, provide economic advantages which have encouraged researchers to further develop the methodology and applications of MIPs. Cyano-based sol-gel hybrid film act as functional monomers providing more recognition sites through hydrogen bonds with methamidophos for template recognition. The electrochemical behaviour of methamidophos at the sol-gel sensor was characterized by cyclic voltammetry. The results showed that the new method is able to provide a sensitive, anti-interferent and rapid detection of methamidophos in real samples.

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LIST OF ABBREVIATIONS

CAC	-	Codex Alimentarius Commission
DOA	-	Department of Agriculture
SEM	-	Scanning Electron Microscopy
FT-IR	-	Fourier Transform-Infrared Spectroscopy
GC	-	Gas Chromatography
HPLC	-	High Performance Liquid Chromatography
HSSE	-	Headspace Sorptive Extraction
LC	-	Liquid Chromatography
LLE	-	Liquid-liquid Extraction
LOD	-	Limit of Detection
LOQ	-	Limit of Quantification
LPME	-	Liquid-phase Microextraction
MASE	-	Membrane-assisted Solvent Extraction
MISPE	-	Molecularly-imprinted Solid Phase Extraction
MOA	-	Ministry of Agriculture and Agro-Based Industry
MRLs	-	Maximum Residue Limits
MTMOS	-	Methyltrimethoxysilane
OCPs	-	Organochlorinated Pesticides
PDMS	-	Polydimethylsiloxane
OPPs	-	Organophosphorus Pesticides
PAHs	-	Polycyclic Aromatic Hydrocarbons
PBS	-	Phosphate buffer solution
PCBs	-	Polychlorobiphenyl

PDMS	-	Polydimethylsiloxane
PMHS	-	Poly(methylhydroxysiloxane)
PVA	-	Poly(vinyl) alcohol
RSD	-	Relative Standard Deviation
SBSE	-	Stir Bar Sorptive Extraction
SFE	-	Supercritical Fluid Extraction
SPE	-	Solid Phase Extraction
SPME	-	Solid Phase Microextraction
TFA	-	Trifluoroacetic acid
TEOS	-	Tetraethoxysilane
TMOS	-	Tetramethoxysilane
UV	-	Ultra-violet

LIST OF SYMBOLS

μL	-	microliter
cm	-	centimeter
h	-	hour
kg	-	kilogram
$K_{o/w}$	-	octanol-water distribution coefficient
kV	-	kilovolt
M	-	molarity
mg	-	milligram
min	-	minutes
mL	-	milliliter
mm	-	millimeter
ng	-	nanogram
nm	-	nanometer
pg	-	pictogram
ppb	-	part per-billion
ppm	-	part per-million
R^2	-	coefficient of determination
t_R	-	retention time

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CHAPTER 1

INTRODUCTION

1.1 Background

Pesticides have been widely used to eliminate or control a variety of agricultural pests that can damage crops and livestock and thus reduce farm productivity (Han *et al.*, 2009; Zhang *et al.*, 2009; Silva *et al.*, 2011). From an agricultural industry perspective, pesticides are an important component of economic and effective pest control and their continued use is essential. Unfortunately, pesticide residues, which are left in the environment during their widespread uses in agricultural areas have posed a serious health and environmental problem due to their high toxicity as an inhibitor of acetylcholinesterase (nervous system enzyme) (Martínez-Huitle *et al.*, 2008; Gao *et al.*, 2012). Therefore, sample pre-treatment and also detection methods of pesticides are seen to lead a way to combat the abuse of them.

In recent years, sol-gel-derived products have been widely modified to enhance the efficiency of sample pre-treatment (de Moraes *et al.*, 2003; Liu *et al.*, 2004; da Costa Silva & Augusto, 2006; Mao *et al.*, 2012; Wan Ibrahim *et al.*, 2010; 2011a; 2011b; 2012) and also detection methods (Li *et al.*, 2005; Chen *et al.*, 2011; Huang *et al.*, 2011). Organic-inorganic hybrid materials are one of the most expanding material classes based on the sol-gel process. The synergistic combination of the various components in one material leads to properties and processing possibilities that cannot be reached by other materials. Particular advantages of hybrid materials are that they can be produced under mild reaction conditions.

Commercial sorbent materials for sample pretreatment methods are predominantly designed to separately extract polar and non-polar analytes. High cost and long analysis time are the major drawback. In this study, these problems were addressed through the preparation of new sol-gel hybrid organic-inorganic sorbent materials for the analysis of organophosphorus pesticides (OPPs) by stir bar sorptive extraction (SBSE) and solid phase extraction (SPE) methods. For this, new sol-gel hybrid 3-(2-aminoethylamino) propyltrimethoxysilane-polydimethylsiloxane (AEAPTMOs-PDMS) was used as new sorbent material in SBSE while methyltrimethoxysilane-cyanopropyltriethoxysilane (MTMOs-CNPrTEOS) was used as new sorbent material in SPE method. Both sorbents were found to provide excellent efficiency against commercial sorbents. They were very efficient in extracting polar and non-polar OPPs simultaneously.

Another problem highlighted in this study is the challenging demand for detection method to provide quick results to assist immediate action, high sensitivity and good detection limit to handle trace analysis of OPPs within a complicated sample matrix. For direct determination of selected OPP, a new cyano-based sol-gel hybrid film coated on indium tin oxide (ITO) glass was constructed and used as working electrode in cyclic voltammetry (CV) to assess the contamination of methamidophos in fruit and vegetable samples. Commercial working electrodes used in CV for OPPs analysis are not only expensive but also less sensitive and selective. The new prepared working electrode in this study is sufficiently stable and can be used repetitively up to 50 measurements which minimize the analysis cost. The new sol-gel hybrid film was molecularly imprinted with methamidophos to enhance the sensitivity and selectivity of methamidophos in complex real samples. Comprehensive studies on the applicability of the new developed sol-gel hybrid materials were conducted by analyzing selected OPP in a variety of real samples.

1.2 Summary

This study was conducted in three parts where three different new sol-gel hybrid materials have been synthesized and applied to the analysis of OPPs. The first part presented the study on synthesis, characterization and application of new sol-gel

hybrid, AEAPTMOs-PDMS coating for SBSE of six selected OPPs coupled to high performance liquid chromatography with ultraviolet detector (HPLC-UV). The second part of the study focused on the synthesis, characterization and application of a new sol-gel hybrid, MTMOs-CNPrTEOS as a SPE sorbent for analysis of six selected OPPs coupled to gas chromatography with mass spectrometry (GC-MS). Both methods were used to extract six selected OPPs of different polarity namely, chlorpyrifos, diazinon, dicofol, malathion, methamidophos and methidathion in water, fruit and vegetable samples. The last part of the study is on sensing application of a new cyano-based sol-gel hybrid film after being molecularly imprinted with methamidophos. The new developed film were coated on ITO glass and used as modified electrode in CV for the detection of methamidophos in fruit and vegetable samples. The problem statement, objectives, scopes and significance of this study are also covered.

Chapter 2 compiles the introduction to the selected pesticides studied and their classification, sol-gel technology, various extraction techniques, development of selected extraction technique using sol-gel technology, and last but not least the development of direct detection of analytes based on electrochemical sensor using sol-gel technology.

Chapter 3 describes the separation of the six selected pesticides using HPLC-UV as well as the synthesis, characterization and application of the sol-gel hybrid AEAPTMOs-PDMS as coating for use in SBSE technique for the determination of the six selected OPPs in water, fruit and vegetable samples. Several important sol-gel synthesis parameters such as mol ratio, drying time, solvent type, water volume, number of dipping and type of acid catalyst were optimized. The characterization of the optimum sol-gel hybrid sorbent was conducted using Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscope (SEM). Extraction temperature, extraction time, desorption temperature, type of desorption solvent and desorption time were optimized as the extraction parameters.

Chapter 4 describes the synthesis, characterization and application of the new sol-gel hybrid material, MTMOs-CNPrTEOS as SPE sorbent to determine the

selected OPPs in water, fruit and vegetable samples by using GC-MS. Three sol-gel synthesis parameters were selected to be studied including mol ratio, basic pH value and drying temperature. The optimum sol-gel hybrid sorbent was characterized using FTIR, SEM and nitrogen adsorption. Several important extraction parameters such as sample volume, type of elution solvent and elution solvent volume were optimized. Optimized SPE conditions were used in method validation and applied to the analysis of OPPs in water, fruit and vegetable samples.

Chapter 5 reports the synthesis, characterization and application of the new working electrode using molecular imprinted (MIP) sol-gel hybrid film as sensing material coated on ITO glass and its applicability in determination of a polar OPP namely methamidophos in fruit and vegetable sample by CV detection. Sol-gel synthesis parameters such as mol ratio, effect of TEOS addition, hydrolysis time and dip coating rate were optimized, while two parameters that affecting the CV detection including pre-concentration time and stirring rate were also optimized. For characterization, the optimum sol-gel hybrid sorbent was examined using CV (blocking/insulating study), Raman Spectroscopy, and SEM.

Finally, chapter 6 summarizes the overall conclusions and future directions for further studies. This chapter summarizes the overall results obtained such as the characterization of the synthesized materials, optimized conditions and the analytical performance of the developed methods. Future directions are presented and discussed for further improvement of the study.

1.3 Problem Statement

The liquid-liquid extraction (LLE) method, most widely used technique in controlling the analyte residues in food and environment, has its own inherent disadvantages. The disadvantages include the use of large quantity of organic solvents, which might be expensive to buy and dispose of, and cause environmental problem and potential health concerns, difficult to couple with any other instrumental

analysis systems, not easily automated, limited enrichment factor and for many sample types there are problems with emulsion formation and precipitation. Other extraction method is solid-phase microextraction (SPME) which uses low or no organic solvent but its sample capacity is low. High sample capacity can be obtained on SPE which use small amount of organic solvent, ease in operation, and low cost but in some cases the extraction solvent may not be compatible with an analytical system. To overcome this, the solvent is evaporated and the remaining residue is dissolved in a compatible solvent. Supercritical fluid extraction (SFE) requires high investment costs compared to traditional atmospheric pressure extraction techniques, difficult to use in routine analysis due to the tedious optimization procedure, requires high cost of pure liquid-like compressed CO₂ as the extraction medium and overall design of SFE makes the technique incompatible with field analyses.

SBSE using PDMS coated stir bar has been applied mainly to extract non-polar and weakly polar compounds, and it fails in the extraction of semi-polar and very polar compounds unless they have been previously derivatized. Moreover, PDMS do not allow displacement of analytes to occur because retaining capacity for PDMS is not influenced by the presence of large amount of water since all solutes have their own partitioning equilibrium into the PDMS phase (Baltussen *et al.*, 1999). Sol-gel technology has been one of the emerging technologies in the synthesis of organic-inorganic hybrid materials. The advantages of sol-gel technology will be covered in Chapter 2. However, only limited numbers of applications of sol-gel hybrid sorbent materials have been reported. Thus, in this study, sol-gel hybrid AEAPTMO₃-PDMS was used as the novel SBSE coating material for the extraction of non-polar, semi-polar and very polar OPPs from water, fruit and vegetable samples.

The most common and conventional extraction technique for the analysis of analytes of interest is SPE method, which is another highlighted extraction method in this study. In SPE, the most common and classic material used as sorbent media is chemically bonded silica, usually with a C₈ or C₁₈ organic group. Since the above materials presents low recoveries for the polar compounds or are too specific for a particular analyte, new materials have been developed in the last few years. The sol-

gel technology approach has brought new promises in providing new sorbent materials for use in SPE. More hybrid materials synthesized using sol-gel technology can be explored for its potential to be use in SPE method since the reaction is easy to carry out under mild conditions. For SPE method, the present study focused on the synthesis, characterization and application of new sol-gel hybrid sorbent based on MTMOS-CNPrTEOS for determination of OPP residues with wide polarity range in water, fruit and vegetable samples.

Another highlighted problem in this study is the drawbacks of traditional detection methods for compounds of interest. Many methods are available for pesticide detection. Chromatographic methods are used as reference methods, but they have strong drawbacks, such as complex and time consuming treatments of the samples, usually have to be performed in a specialized laboratory by skilled personnel and are not portable. These issues turn out to be a major problem when rapid and sensitive measurements are needed. The cholinesterase based biosensors are one of the best alternatives in the context of this strategy. These biosensors are simple to fabricate and low cost of the equipment also make possible in situ measurement of pesticides. However, electrochemical sensor has gained a great attention nowadays because when dealing with enzymes, the catalytic biosensor may be inhibited by substances in the sample, ambient conditions need to be controlled (pH and temperature) and they have limited shelf life. Electrochemical sensors for the trace level measurement of analytes of interest are ideally suited for various sample matrices due to their high sensitivity and selectivity, rapid response time and low cost. In this study, the electrochemical detection of selected OPP was carried out using CV with modified working electrode. The sensing materials formed using sol-gel technology has found numerous applications in various fields. Sensitive material can be generated by adding some recognition element in the sol-gel matrix during synthesis, which does not interact chemically with the surroundings. Thus, a new cyano-based sol-gel hybrid film was constructed and molecularly imprinted with methamidophos for sensing applications in vegetable and fruit samples.

1.4 Objectives of the Study

The aim of this research is to produce new and novel sol-gel hybrid organic-inorganic materials that can be applied in the analysis of OPPs from different types of sample matrices. The objectives of this research are as follows:

- 1) To develop and apply a new sol-gel hybrid AEPTMOS-PDMS coated SBSE coupled to HPLC-UV in the analysis of six selected OPPs in water, fruit and vegetable samples.
- 2) To develop and apply a new sol-gel hybrid MTMOS-CNPrTEOS based SPE coupled to GC-MS in the analysis of six selected OPPs in water, fruit and vegetable samples.
- 3) To develop and apply new cyano-based sol-gel hybrid film imprinted with methamidophos as sensing material coated on ITO glass as modified working electrode in CV for the detection of methamidophos in fruit and vegetable samples.

1.5 Scope of Study

Development and application of sol-gel hybrid organic-inorganic materials were studied. Several important sol-gel process parameters were optimized before used as extraction sorbent and also detection film. Several extraction and detection parameters were investigated and optimum conditions were applied to the analysis of selected OPPs from different sample matrices and compared with commercially available method.

The current work involves using sol-gel method to produce three new sol-gel hybrid materials namely, AEPTMOS-PDMS, MTMOS-CNPrTEOS and CNPrTEOS.

Synthesis parameters optimized for SBSE sorbent were effect of different mol ratios of precursors and stationary phase, drying time, types of solvent, number of dipping, types of acid catalysts and effect of water volume. Synthesis parameters optimized for SPE sorbent were effect of different mol ratios of precursors and stationary phase, pH value and drying temperature. Synthesis parameters optimized for electrochemical sensor sorbent were effect of mol ratio of precursor and water, percentage of added tetraethoxysilane (TEOS), hydrolysis time and dip coating rate. Extraction parameters optimized in SBSE including extraction temperature, extraction time, desorption temperature, type of desorption solvent and desorption time while extraction parameters optimized in SPE were sample volume, types of elution solvent and volume of elution solvent. Two CV parameters optimized were pre-concentration time and effect of stirring rate. Detections are performed using GC-MS for SPE, HPLC-UV for SBSE and CV for electrochemical sensor. Characterization of sol-gel hybrid AEAPTMOs-PDMS was performed using FT-IR and SEM while characterization of sol-gel hybrid MTMOs-CNPrTEOS was performed using FT-IR, SEM and nitrogen adsorption. Characterizations of sol-gel hybrid CNPrTEOS was performed using CV, Raman Spectroscopy and SEM. Samples used in the study of new developed SBSE and SPE methods were water (tap and lake water), vegetables (cucumber and long beans) and fruit (grapes and guava) samples while samples used in the study of new developed electrochemical sensor were vegetable (mustard and cabbage) and fruit (strawberry and apple) samples.

1.6 Significance of the Study

The use of SBSE may help to reduce the organic solvent and the sample amount. The new sol-gel hybrid sorbent synthesized is expected to improve the extraction performance for non-polar and semi-polar pesticides present in consumer products such as vegetables and fruits. SBSE is also simple, inexpensive and an environmentally friendly method. The optimization of sol-gel coating parameters help in obtaining stronger and more porous coating on glass surface as supporting material for sol-gel sorbent.

The use of SPE with sol-gel hybrid materials as sorbent is expected to reduce the use of organic solvent. The use of the bifunctional sol-gel hybrid sorbent materials is expected to reduce the analysis time as they are able to extract both polar and non-polar analytes simultaneously unlike the commercial SPE sorbents. SPE offers cleaner extracts and easy to automate. When using in-house sol-gel hybrid materials as SPE sorbents, it is expected to reduce the cost of SPE kits as the sorbents has high stability and repeatability. The sol-gel process used to synthesize the new SPE sorbents is simple and easy to carry out under mild conditions. The new developed method is also expected to give lower detection limit when combined with GC-MS.

Electrochemical sensor using CV with modified working electrode is expected to improve the performance of the conventional detection method and eliminate the use of expensive reagents which will provide low cost analytical tools. In addition, the new method is simple to operate, inexpensive, rapid response time and has long term stability. In this study, the use of MIP sol-gel hybrid film coated ITO-glass as working electrode has overcome the high cost, instability and less sensitivity and selectivity of commercial working electrodes. The sol-gel technology was chosen to synthesis the hybrid film as coating on the ITO-glass as it has the potential to produce highly innovative and sensitive materials according to the desired interest. Furthermore, the introduction of molecular imprinting in sol-gel science is expected to be very promising for the development of robust sensor materials as it has the ability to create optimized template sensitive cavities for analyte re-inclusion without interacting chemically with polymer system. The combination of these two strategies (sol-gel technology and molecular imprinting technique) in electrochemical sensor leads to the development of highly sensitive and robust materials that possess synergic effects.

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