Malaysian Journal of Analytical Sciences (MJAS)
Published by Malaysian Analytical Sciences Society

IN-SYRINGE DISPERSIVE SOLID PHASE MICROEXTRACTION FOR THE DETERMINATION OF ORGANOPHOSPHORUS PESTICIDE RESIDUES IN VEGETABLES

(Pengestrakan Mikro Fasa Pepejal Secara Penyerakan dalam Picagari bagi Penentuan Sisa Racun Jenis Organofosforus dalam Sayur-Sayuran)

Hairul Nizwan Manap[1], Faizah Binti Mohammad Yunus[1], Nur Nadhirah Mohamad Zain[2], Noorfatimah Yahaya[2], Hemavathy Surikumaran[3], Kumuthini Chandrasekaram[4,6], Kavirajaa Pandian Sambasevam[5,7], Muggundha Raoov[1,4*]

[1]Department of Chemistry, Faculty of Science,
University of Malaya, 50603 Kuala Lumpur, Malaysia.
[2]Department of Toxicology, Advanced Medical & Dental Institute,
Universiti Sains Malaysia, 13200 Kepala Batas, Pulau Pinang, Malaysia
[3]Faculty of Bioeconomic and Health Sciences,
Universiti Geomatika Malaysia, 54200 Kuala Lumpur, Malaysia
[4]Universiti Malaya Centre for Ionic Liquids (UMCIL), Department of Chemistry,
Faculty of Science, Universiti Malaya, Kuala Lumpur, Malaysia
[5]Advanced Materials for Environmental Remediation (AMER), Faculty of Applied Sciences,
Universiti Teknologi MARA, Negeri Sembilan Branch, Kuala Pilah Campus, Kuala Pilah, Malaysia
[6]Research Services Division (BPP, Institute of Research Management & Services (IPPP),
University of Malaya, 50603 Kuala Lumpur, Malaysia
[7]Electrochemical Materi and Sensor (EMaS) Research Group,
Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

**Corresponding author: muggundha@um.edu.my*

Received: 29 December 2022; Accepted: 20 May 2023; Published: 23 June 2023

Abstract

In-syringe dispersive solid-phase microextraction with activated carbon as adsorbent was successfully developed to determine organophosphorus pesticide (OPP) residues in vegetable samples and the analytes were detected using gas chromatography-flame photometric detector (GC-FPD). Under optimized conditions (6 mg of activated carbon in 10 mL sample volume with 3 min extraction time and desorption with 300 µL of acetone), activated carbon was proven to be an effective adsorbent for the organophosphorus pesticide residues in vegetable samples with a satisfactory percentage recovery achieved from 81.46 to 108.93%. All the studied analytes showed good linearity in the range of 10 to 500 µg kg^{-1} and the correlation of determination (R^2) was from 0.9962 to 0.9985. The LODs obtained were from 0.39 to 0.84 µg kg^{-1}, and LOQs were from 1.18 to 2.56 µg kg^{-1}. This method gives precision values for both intra- and inter-day within accepted variable limits (<15 % of RSD). The in-syringe dispersive solid-phase microextraction managed to eliminate the centrifugation process, reduce chemical consumption during extraction, and additionally speed up the extraction process, making it more efficient. This developed method can be applied to real samples such as vegetables and fruit juices as well as tap, river, or ground water analysis for the determination of OPPs.

Keywords: organophosphorus pesticide, in-syringe dispersive solid phase microextraction, gas chromatography-flame photometric detector

Abstrak

Pengekstrakan mikro fasa pepejal dalam picagari dengan menggunakan karbon aktif sebagai penyerap telah berjaya dibangunkan untuk menentukan sisa racun perosak jenis organofosforus (OPP) dalam sampel sayur-sayuran dan analisis telah dikesan dengan menggunakan peralatan analisis kromatografi gas – pengesan fotometrik nyalaan (GC-FPD). Di bawah keadaan yang dioptimumkan (6 mg karbon aktif dalam isipadu sampel 10 mL dengan masa pengekstrakan selama 3 minit dan diserap dengan 300 µL aseton), karbon aktif terbukti sebagai penyerap berkesan bagi sisa racun perosak organofosforus dalam sampel sayur-sayuran berdasarkan peratusan pengesanan semula yang dicapai dari 81.5 hingga 108.9%. Semua analit yang dikaji menunjukkan garis lurus yang baik dalam julat 10 hingga 500 µg kg^{-1} dan memberikan korelasi penentuan (R^2) dari 0.9962 hingga 0.9985. Had pengesanan yang di dapati adalah dari 0.39 hingga 0.84 µg kg^{-1}, dan had pengkuantitian adalah dari 1.18 hingga 2.56 µg kg^{-1}. Kaedah ini memberi nilai ketepatan pada kedua-dua intra dan antara hari dalam sisihan piawai relatif (RSD) yang diterima (<15% daripada RSD). Pengestrakan mikro fasa pepejal secara penyerakan dalam picagari berjaya mengelakkan proses pengemparan, mengurangkan penggunaan bahan kimia dalam proses pengekstrakan dan juga proses pengekstrakan menjadi lebih pantas dan lebih cekap. Kaedah yang dibangunkan ini boleh digunakan untuk sampel sebenar seperti sayur-sayuran, jus buah-buahan dan juga sesuai untuk analisis air paip, air sungai dan air tanah untuk penentuan sisa racun perosak organofosforus.

Kata kunci: perosak jenis organofosforus, pengekstrakan mikro fasa pepejal dalam picagari, kromatografi gas – pengesan fotometrik nyalaan

Introduction

The presence of a significant amount of nutrients and minerals in fresh vegetables, fruits, and pulses makes them important healthy diet food. Unfortunately, they too can turn out to be the source of toxic substances such as pesticides [1]. Pesticides are toxic substances with mixtures of chemical or biological ingredients designed to kill, reduce, or repel insects, weeds, rodents, fungi, and other organisms that threaten public health and the economy. They have numerous beneficial effects but risks as well. Pesticides are used by farmers to protect their fruits and vegetables from diseases and pests while at the same time providing high yields [2]. More than 1100 pesticides are currently registered, according to the status list of all active pesticide chemicals on the European Union market [3]. Pesticides are also commonly utilized in agricultural activities because of their low cost and high effectiveness in controlling pests, weeds, and illnesses.

The increased manufacturing of pesticides for agricultural and non-agricultural applications has resulted in pollution of soil, air, surface, and groundwater posing a major threat to the environment and human health through direct exposure or residues in food and drinking water [4]. Table 1 lists common pesticides group based on their controlling pests. Organophosphorus pesticides (OPPs) are a class of phosphate or phosphorothioate molecules that is one of the world's ten most well-known pesticides [4]. OPPs, on the other hand, are very toxic even at low levels, and can be transmitted to humans, birds, and mammals through contaminated water, air, and food. They are usually absorbed by the lungs, mouth, or skin, and accumulate in the salivary glands, kidneys, fat, and liver [5]. Trace-level OPPs in various types of sample matrices are difficult to detect due to interference such as sugar, plant pigments, and fats.

Vegetables and fruits, which are good sources of minerals, vitamins, antioxidants, and fiber, make up 30% of a consumer's diet, according to a 2003 report by the World Health Organization (WHO). Since Cameron Highlands is one of Malaysia's major vegetable producers, it is important to examine the risk of pesticide residues in these extensively produced vegetables that are grown there for human consumption. According to studies, certain fruits, and vegetables with greater pesticide residue levels and over the maximum residue limit (MRL) may be harmful to consumers' health. Maximum Residue Limits (MRLs), which limit the concentration level of commodities, promote food safety measures as they should not exceed 0.01-0.05 mg kg^{-1}. Unfortunately, as proven by previous research, among all the vegetables, cabbage has a higher contaminant value compared to others such as spinach, tomato, and celery. While mustard show the lowest one that has been contaminated by OPPs. The observed trend in the concentration of studied OPPs was dimethoate (36.8%) > diazinon (14.3%) > parathion methyl (12.3%) >parathion ethyl (20.3%) > chlorpyriphos (14.0%) >

malathion (9.9%). The EU order of percentages of OPPs above MRLs is as; cabbage (24.8%) > cauliflower (13.6%) > broccoli (11%) 17 > cauliflower (13.6%) > lettuce (4.0%) > spinach (3.7%) > celery (1.8%) > mustard (1.8%) [6, 7].

Table 1. Common pesticide groups based on their controlling pests

Insecticides	Fungicides	Herbicides	Rodenticides	Fumigants	Insect repellents
Pyrethroids	Thiocarbamates	Bipyridyls	Warfarines	Aluminium and zinc phosphate	Diethyltoluamide
Organophosphorus	Dithiocarbamates	Chlorophenoxy	Indanodiones	Methyl bromide	
Carbamates	Cupric salts	Glyphosate		Ethylene dibromide	
Organochlorine	Tiabendazoles	Acetanilides			
Manganese compounds	Triazoles	Triazines			

The determination of OPPs in complex matrices, such as environmental, food, and biological samples, usually requires extensive sample pre-treatment [8]. Preconcentration procedures must be included in the sample preparation steps because of the high sensitivity needed for OPP testing . OPP residues persist in environmental waters, fruits, and vegetables because of inappropriate and widespread OPP application [9]. Their broad applications in agriculture or insect control in public spaces result in OPPs and their metabolites being frequently detected in vegetables, fruits, water, soil, and other environmental matrices [10]. Regular sample clean-up to pre-concentrate the OPPs uses evaporation which may cause the OPPs to degrade thus lowering the detection or recovery of OPPs.

The common extraction technique used for the analysis of pesticides is conventional liquid-liquid extraction (LLE), solid-phase extraction (SPE), and solid-phase microextraction (SPME). Lately, many researchers have modified common extraction methods such as magnetic dispersive solid phase extraction (MD-SPE), reverse micelle-supramolecular solvent micro-extraction framework with dispersive solid phase extraction (MOF-DSPE), and magnetic solvent bar-liquid phase microextraction (MSB-LPME). However, these procedures have downsides, such as using a lot of toxic and expensive organic solvents, being tedious, and taking a long time [9, 11-14]. Dispersive solid phase microextraction (DSPME) is a technique that has been recently used for the extraction, clean-up, and pre-concentration of different analytes in real samples. DSPME is an easy, fast, and cost-effective SPME procedure that can be applied to complex matrices with high extraction efficiency, high enrichment factor, and reduced usage of sample solution and chemical solvents [15].

Thus, in this study, our focus is to develop a new, simple, and rapid method for the analysis of OPPs residues in vegetables and fruits by in-syringe DSPME using activated charcoal as an adsorbent to enhance the sensitivity of the method, to eliminate the centrifugation process and to reduce the use of chemicals in the extraction.

Materials and Methods

Chemicals and reagents

The selected OPPs used in this research namely Parathion-methyl (98.5%), Fenchlorphos (99.0%), and Chlorpyrifos (99.8%) purchased from Dr. Ehrenstorfer GmbH (Germany) as shown in Figure 1. Activated charcoal was purchased from Merck (Germany). Acetonitrile and methanol were purchased from Fisher Scientific (Korea). Acetone was purchased from Friendemann Schmidt Chemical (Australia). Ultrapure

deionized water (resistivity, 18.2 MΩ cm^{-1}) was produced by a Sartorius Milli-Q system (Germany) and was used during this study for the preparation of the solution.

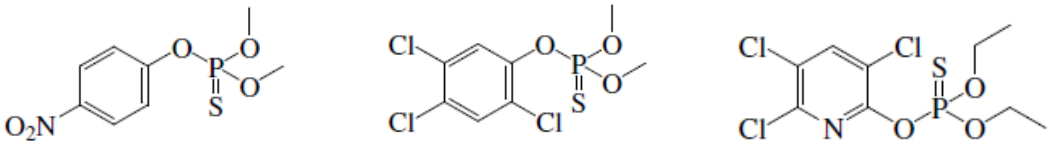

Figure 1. Structures of selected organophosphorus pesticides

GC-FPD conditions

All analysis was done using a GC-2010 Plus gas chromatography-flame photometric detector (GC-FPD) (Shimadzu, Japan) and this GC was equipped with auto-injector AOC-20i. The capillary column SGE-BP1 (30 m 0.25 mm I.D. 0.25 µm film thickness) was used to quantify OPPs. Helium gas was used as the carrier gas with a linear velocity flow mode. The pressure was 100 kPa with the total flow and column flow at 50.00 and 1.0 mL/min, respectively. The temperature of the injector and FPD detector was maintained at 260 ºC and 300 ºC, respectively. The injection was performed using splitless mode and the injection volume was set at 1 µL. The column temperature was programmed as follows: initial temperature of 100 ºC and held for 1 min, then increased to 200 ºC at the rate of 20 ºC min^{-1} and held for 8 min. The final temperature was increased to 220 ºC at the rate of 15 ºC min^{-1} and held for 2 min. The total run time for the GC analysis was 17.33 min.

In-syringe DSPME procedure

The schematic of the in-syringe DSPME procedure is shown in Figure 2. The prepared sample solution was added with 6 mg of activated charcoal and was vortexed for 3 min. Then, the mixed solution was transferred into a 10 mL syringe with a 0.45 µm syringe filter. At this time, OPPs were bonded with activated charcoal and remained inside the syringe filter. Then, the OPPs were desorbed using 300 µL acetone and the extracted OPPs were injected into GC-FPD for the quantitative analysis.

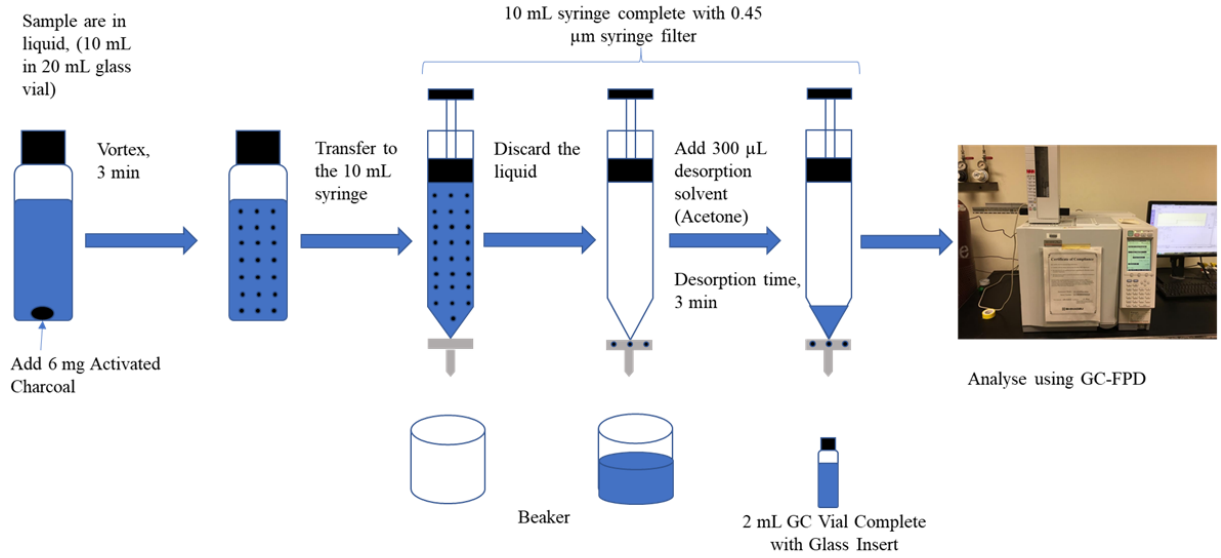

Figure 2. Schematic of in-syringe DSPME procedure

Sample collection and pre-treatment

Mustard, kale, cabbage, tomato, and strawberry were purchased from three different markets in Cameron Highland, Pahang. The representative sample (500 g) was chopped, and the sample was homogenized using the food processor. Then, sample juice was extracted using a juice extractor. The sample solution was filtered, and the suspended solid was discarded. Then, 10 mL of filtered solution was put in the 20 mL glass vial and kept in the refrigerator at 40°C till the extraction using the DSPME procedure.

Optimization of extraction conditions

To optimize the DLLME of OPPs from water samples, analytical factors that potentially affect the sample were studied. The parameters involved were tabulated in Table 2 below.

Table 2. Optimization condition

Parameters	Level
Mass of Activated carbon (mg)	2, 4, 6, 8 and 10
Extraction time (min)	1, 3, 5, 7 and 10
Desorption Solvent	Acetone, Acetonitrile and Methanol
Desorption volume (μL)	100, 300, 500, 700 and 1000
Desorption time (min)	0, 3, 5, 7 and 10
pH	5, 6, 7, 8 and 9

Method validation

Method validation (linearity, limits of detection (LOD) and quantitation (LOQ), pre-concentration factor, and recovery was performed using the proposed in-syringe DSPME method. Linearity was investigated over the range of 10 to 500 μg kg^{-1}. The LOD and LOQ values were calculated based on the standard deviation of the response of the standard blank and the slope of the calibration curve. The pre-concentration factor was calculated from the spiked peak. While recovery studies were carried out using spikes at three concentration levels (30, 50, and 100 μg kg^{-1}). All spiked samples were extracted in triplicates. All the formula is shown below;

$$\text{RSD} = \frac{\text{standard deviation}}{\text{mean}} \times 100\% \quad (1)$$

$$\text{LOD} = \frac{\text{standard deviation}}{\text{slope}} \times 3.3 \quad (2)$$

$$\text{LOQ} = \frac{\text{standard deviation}}{\text{slope}} \times 10 \quad (3)$$

$$\% \text{ Recovery} = \frac{C_{ext}}{C_{int}} \times 100 \quad (4)$$

where C_{ext} is the concentration of analyte in extractant phase; while C_{int} is the initial concentration of OPPs.

Results and Discussion

Assignment and identification of OPPs peak

The mixed OPPs standard solution (1 mg L^{-1}) was injected into GC-FPD in a splitless mode where the technical parameter such as injection volume, gas flow, and temperature gradient were optimized to get a better resolution. The peak was assigned and identified by retention time based on molecular weight and OPPs

structure as shown in Figure 3. The first peak at 12.312 min is parathion-methyl (PM), followed by fenchlorphos (FE) at 13.154 min and chlorpyrifos (CH) at 14.583 min.

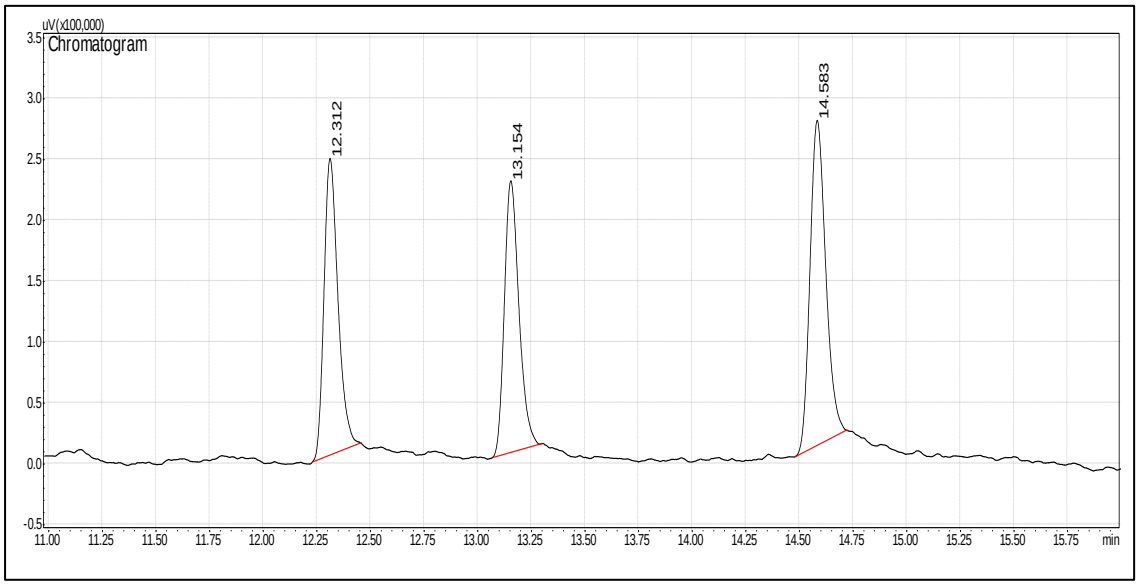

Figure 3. Chromatogram of OPPs a) parathion-methyl b) fenchlorphos c) chlorpyrifos

Optimization of extraction conditions

In this study, the effects of six critical parameters such as the mass of activated carbon, extraction times, volume, time, pH, and solvent were investigated. The optimization process is the process of changing one parameter while at the same time, keeping all other parameters of the same condition to monitor the responses. The optimization was carried out in triplicates using water as a sample matrix with a concentration of 250 µg L^{-1} each.

Effect of mass of activated carbon

The mass of adsorbent used in the extraction has a significant effect on the extraction efficiency. In this study, commercially available activated carbon was used as an adsorbent and the mass of activated carbon was studied in the range of 2-10 mg. Based on Figure 4(a), 6 mg of activated carbon gave a higher peak area as compared to below 6 mg and there is no obvious increase observed in the peak area when the mass of activated carbon is more than 6 mg. The reduced reaction could be because the saturation of active sites on the adsorbent has been exceeding. Hence, 6 mg of activated carbon was selected as the optimal adsorbent amount [9].

Effect of extraction time

Extraction time is an important factor that can influence extraction efficiency because there is a need for a short period for the binding of target compounds with the adsorbent. The effect of extraction time was studied in the range of 1-10 min. It was observed that the peak area for all OPPs increased as the extraction time increased up to 3 min and dropped thereafter when it reached more than 5 min maybe because of the desorption of analyte from the adsorbent [16]. Thus, 3 min was chosen as an optimal time for the extraction of vegetable samples as shown in Figure 4(b).

Effect of desorption solvent

Types of solvent used also play a vital role and give a significant effect on the extraction efficiency to ensure high recovery and sensitivity toward the performance [17]. Referring to Figure 4(f), acetone gave a higher peak area than methanol. To produce a very high quantity of contact area and quick migration of analytes from the aqueous sample into the extraction phase, the

extractant solvent must be disseminated into the aqueous sample as very small droplets. In comparison to the other two solvents, acetone has the lowest viscosity. The reaction decreases as the desorption solvent's viscosity rises (acetone, acetonitrile, and methanol respectively, 0.32, 0.37, and 0.55 centipoise at 20 °C). The likelihood that a reaction will occur increases with polar solvent viscosity. As a result, acetone was selected as an optimal solvent and this result was agreed with another researcher. As a result, acetone was selected as an optimal solvent and this result was agreed with another researcher [18].

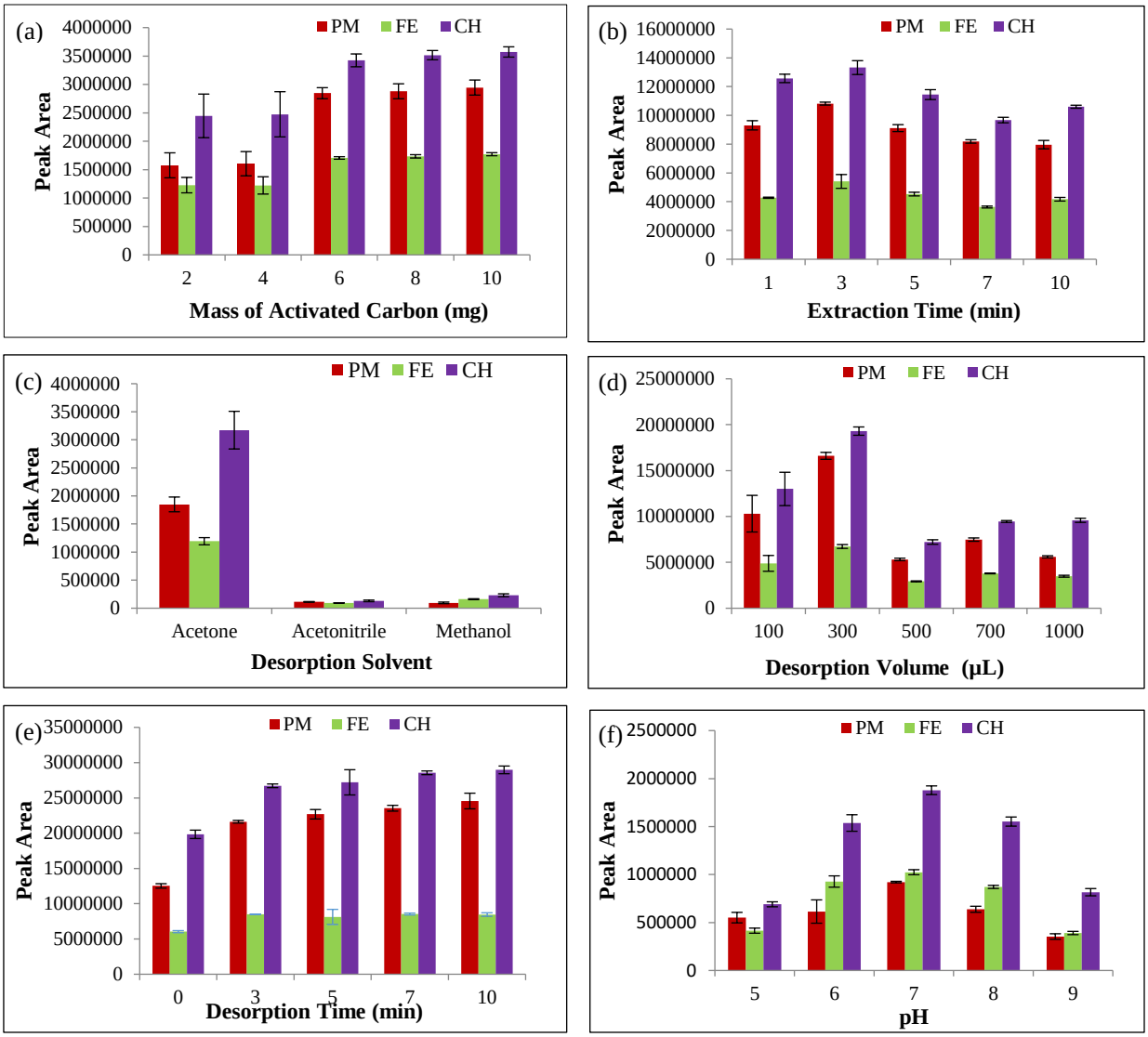

Figure 4. (a) Effect of mass of activated carbon (Extraction condition: extraction time, 5 min; desorption volume, 500 µL of acetone; desorption time, 3 min and without pH adjustment (b) Extraction time (Extraction conditions: mass activated carbon, 6 mg; desorption volume, 500 µL acetone; desorption time, 3 min); (c) Desorption volume (Extraction conditions: mass activated carbon, 6 mg; extraction time, 3 min; desorption time, 3 min); (d) Desorption time (Extraction conditions: mass activated carbon, 6 mg; extraction time, 3 min; desorption volume, 300 µL acetone); (e) pH (Extraction conditions: mass activated carbon, 6 mg; extraction time, 3 min; desorption time, 3 min; desorption volume, 300 µL acetone); (f) Desorption solvent: (Extraction conditions: mass activated carbon, 6 mg; extraction time, 5 min; desorption time, 3 min; desorption volume, 300 µL acetone) on the extraction efficiency.

Effect of desorption volume

In Figure 4(c) effect of desorption volume was studied in the range of 100 to 1000 µL. Among the studied volumes, 300 µL gives the highest peak area and this low volume fits the title micro-extraction. It was observed, that when the volume increases more than 300 µL, the peak area becomes smaller compared to those of 100 µL and 300 µL. This is probably due to the increasing dilution factor and the solubility of analytes in the aqueous phase the extraction step was increased which will lead to a decrease in the extraction efficiency. Thus, the smaller the volume is, the more concentrated the solvent becomes. Hence, an eluent volume of 300 µL was selected for further analysis as it gave the highest peak area ratio response for all four OPPs [19].

Effect of desorption time

The effect of time in the range of 0-10 min on the extraction efficiency of the targeted OPPs was investigated using acetone as the solvent. Figure 4(d) shows the peak area increases significantly between 0-3 min before decreasing when increasing the desorption time to 10 min [20]. Increase in peak area due to the response of analyte from sorbent to solution while the constant result after 5 min because of re-adsorption of analyte onto the sorbent. Hence, 3 min was selected as the optimal time in the subsequent extractions.

Effect of pH

Solution pH plays an imperative role in separation science as it controls both the degree of ionization of the materials present in the solution and the dissociation of functional groups of the analyte [21]. In this study, the pH of the sample solution was adjusted in the range of pH 5 to 9. The initial pH for the sample solution was between pH 6 to 8. Based on the graph in Figure 4(e), the optimal pH value was around pH 6-8 because of increasing in the OPPs stability between 4.5-7. When approaching pH 9 the peak area was decreasing because of OPPs start to hydrolyze as the higher the pH the faster the hydrolysis process of OPPs will be. Since the obtained pH is like the pKa value of the analyte, no pH adjustment is needed for further experiments.

Method validation

A series of spiked samples that ranged from 10 to 500 µg kg^{-1} were applied to plot the matrix match calibration curves (n=3). The method validation was done under optimized conditions (6 mg of activated carbon in 10 sample volumes with 3 min extraction time and with 300 µL of acetone). The linearity shows the correlation of determination (R^2) ranging from 0.9962 to 0.9985. The optimized method was determined by measuring the (repeatability) and inter-day (intermediate) at a spiking level of 100 µg kg^{-1} in vegetable samples. Precision was determined on the same day with five duplicates while inter-day precision was calculated with five replicates on three different days. Relative standard deviation (RSD) ranged between 0.89% to 2.17% while inter-day ranged between 1.27% to 3.13%. The assessed values on precision were found to be within the known variable limits (<15 %) [12]. Table 3 displays the linear performance, LOD, LOQ, PF, and inter-day results. In-syringe DSPME can detect and quantify the OPPs at concentrations as low as 1.18 µg kg^{-1}. The pre-concentration factor is described as enrichment factor times with theoretical volume. Based on the calculation, it was found that the pre-concentration factor for parathion-methyl, fenchlorphos, and chlorpyrifos are 5548, 1216, and 3833 respectively at the concentration of 250 µg kg^{-1}.

Table 3. Linearity, LOD, LOQ, PF, intra-day and inter-day performance for in-syringe DSPME procedure

Analyte	Linearity Range (µgL^{-1})	R^2	LOD (µgL^{-1})	LOQ (µgL^{-1})	Intra-day RSD%(n=5) at 100 (µgL^{-1})	Inter-day RSD% (n=3) at 100 (µgL^{-1})	Pre-concentration Factor at 250 (µgL^{-1})
Parathion-methyl	10-500	0.9985	0.53	1.60	2.16	0.89	5548
Fenchlorphos	10-500	0.9962	0.39	1.18	3.13	1.61	1216
Chlorpyrifos	10-500	0.9966	0.84	2.56	1.27	2.17	3833

Recovery

The recovery study was done with three different spiked levels (30, 50, and 100 µg kg^{-1}) in blank vegetable samples. Table 4 displays the relative recovery data obtained from the experiment where the recovery for parathion-methyl, fenchlorphos, and chlorpyrifos are within 81.46 to 108.85%, 97.73 to 108.93%, and 92.71 to 106.14% respectively.

Table 4. Relative Recovery for OPPs Extracted by in-syringe DSPME

Analytes	Relative Recovery (%) ± %RSD (n=3)		
	30 µg kg^{-1}	**50 µg kg^{-1}**	**100 µg kg^{-1}**
Parathion-methyl	108.85 ± 1.98	93.31 ± 3.68	81.46 ± 4.66
Fenchlorphos	108.93 ± 4.79	106.04 ± 2.21	97.73 ± 4.72
Chlorpyrifos	105.04 ± 3.59	106.14 ± 3.40	92.71 ± 2.46

Real sample analysis

The developed in-syringe DSPME method was applied to real sample analysis to determine OPPs in vegetable samples of mustard, kale, cabbage, tomato, and strawberry. All 15 vegetable samples were purchased from three different market locations in Cameron Highland, Pahang. This analysis was run in optimized in-syringe DSPME conditions. This indicates that most farmers at Cameron Highland, Pahang are following the rules and regulations set up by the Agricultural Department during farming, harvesting, and preserving the vegetables.

Conclusion

In-syringe solid phase microextraction using activated carbon as an adsorbent was successfully developed to determine the pesticide residues in vegetable samples and then were detected using GC-FPD. Under optimized conditions (6 mg of activated carbon in 10 volumes of the sample with 3 min extraction time and 300 µL of acetone), activated carbon was proven to be an effective adsorbent for pesticide residues in vegetable samples based on higher percentage recoveries achieved from 81.5 to 108.9 %. All the studied parameters showed good linearity in the range of 10 to 500 µg kg^{-1} and gives a correlation of determination (R^2) from 0.9962 to 0.9985. This method gives precision values on both and inter-day within accepted variable limits (<15 % of RSD). The in-syringe solid-phase microextraction method managed to reduce the use of chemicals in the extraction. Additionally, this method proves to be faster and more efficient than other conventional extraction methods. Table 5 shows the comparison between this project with previous studies. This developed method can be applied to real samples such as vegetables and fruit juices as well as tap, river, and groundwater analysis for the determination of OPPs.

Table 5. Comparison of current study on the analysis of pesticides

Analysis Method	Type of Sample	Linear Range (µg L^{-1})	LOD (µg L^{-1})	LOQ (µg L^{-1})	Recovery (%)	Ref.
Zinc-Base MOFs-DSPE – GC-FID	Water & fruit juice	0.1-100	0.03-0.21	0.06-0.65	92-100	[9]
QuEChERS-DLLME – GC-FID	Fruits & Vegetables	1.6-5000	0.27-0.48	0.97-1.6	84-103	[12]
SPME – GC-FPD	Vegetables	0.1-100	0.01-0.14	0.03-0.42	75-117	[16]
PDMS/MOFs-SBSE – GC-FPD	Water	0.2-100	0.043-0.085	0.06-0.22	80-115	[18]

PV in-syringe DLMPE-GC-MS	Vegetables	10-200	4.8-7.1	5.1-8.2	90.2-92.2	[20]
MWA-DLLME-GC-FID	Water	3-40000	0.65-1.3	0.77-1.92	80-99.7	[21]
SBSE-GC-FID	Vegetables and fruit juices	0.6-1000	1.7-5.6	2.0-6.4	73-104	[22]
MD-μ-SPE-GC-IMS	Water	2-1000	0.46-1.0	0.56-2.0	70-81	[23]
LLME	Water and fruit juices	0.5-400	0.1-0.35	0.18-0.66	92.2-110.5	[24]
C_{18}	Water	0.01-5.00	0.003-0.0004	0.007-0.0022	88-100	[25]
Activated carbon in-syringe DSPME	Vegetables	10-500	0.39-0.84	1.18-2.56	81.46-108.9	Current work

Acknowledgment

The authors would like to seize this opportunity to express their gratitude to the Ministry of Higher Education for the assistance and financial support under the Fundamental Research Grant Scheme (FRGS/1/2020/ STG04/UM/02/9). The authors acknowledge the Department of Chemistry, Faculty of Science, and the University of Malaya for providing the facilities. The authors also would like to acknowledge Universiti Sains Malaysia for research collaboration.

References

1. Sharma, D., Nagpal, A., Pakade, Y. B. and Katnoria, J. K. (2010). Analytical methods for estimation of organophosphorus pesticide residues in fruits and vegetables: A review. *Talanta,* 82(4): 1077-1089.
2. Samsidar, A., Siddiquee, S., & Shaarani, S. M. (2018). A review of extraction, analytical and advanced methods for determination of pesticides in environment and foodstuffs. Trends in Food Science & Technology, 71, 188-201.
3. Mukwevho, N., Fosso-Kankeu, E., Waanders, F., Kumar, N., Ray, S. S. and Yangkou Mbianda, X. (2019). Photocatalytic activity of $Gd_2O_2CO_3$·ZnO·CuO nanocomposite used for the degradation of phenanthrene. *SN Applied Sciences,* 1: 1-11.
4. Mohd, M. S., Siti, U. M., Mazidatul, A. M. and Wan, A. W. I. (2011). Determination of organophosphorus pesticides by dispersive liquid-liquid micro extraction coupled with gas chromatography-electron capture detection. *Malaysian Journal of Analytical Sciences*, 15(2): 232-239.
5. Dozein, S. V., Masrournia, M., Es' haghi, Z. and Bozorgmehr, M. R. (2021). Development of a new magnetic dispersive solid-phase microextraction coupled with GC-MS for the determination of five organophosphorus pesticides from vegetable samples. *Food Analytical Methods,* 14(4): 674-686.
6. Chambers, A. G. S. (2020). Food (Amendment) (No3) Regulations 2020.
7. Farina, Y., Abdullah, M. P., Bibi, N. and Khalik, W. M. A. W. M. (2016). Pesticides residues in agricultural soils and its health assessment for humans in Cameron Highlands, Malaysia. *Malaysian Journal of Analytical Science,* 20(6): 1346-1358.
8. Chen, J., Duan, C. and Guan, Y. (2010). Sorptive extraction techniques in sample preparation for organophosphorus pesticides in complex matrices. *Journal of Chromatography B,* 878(17-18): 1216-1225.
9. Amiri, A., Tayebee, R., Abdar, A. and Sani, F. N. (2019). Synthesis of a zinc-based metal-organic framework with histamine as an organic linker for

the dispersive solid-phase extraction of organophosphorus pesticides in water and fruit juice samples. *Journal of Chromatography A*, 1597: 39-45.

10. Wang, P., Luo, M., Liu, D., Zhan, J., Liu, X., Wang, F. and Zhou, Z. (2018). Application of a magnetic graphene nanocomposite for organophosphorus pesticide extraction in environmental water samples. *Journal of Chromatography A,* 1535: 9-16
11. Wu, L., Song, Y., Hu, M., Zhang, H., Yu, A., Yu, C., ... and Wang, Z. (2015). Application of magnetic solvent bar liquid-phase microextraction for determination of organophosphorus pesticides in fruit juice samples by gas chromatography mass spectrometry. F*ood Chemistry*, 176: 197-204.
12. Farajzadeh, M. A., Sohrabi, H. and Mohebbi, A. (2019). Combination of modified QuEChERS extraction method and dispersive liquid–liquid microextraction as an efficient sample preparation approach for extraction and preconcentration of pesticides from fruit and vegetable samples. *Food Analytical Methods*, 12: 534-543.
13. Gorji, S., Biparva, P., Bahram, M. and Nematzadeh, G. (2019). Rapid and direct microextraction of pesticide residues from rice and vegetable samples by supramolecular solvent in combination with chemometrical data processing. *Food Analytical Methods*, 12: 394-408.
14. Fernandes, V. C., Freitas, M., Pacheco, J. P., Oliveira, J. M., Domingues, V. F. and Delerue-Matos, C. (2018). Magnetic dispersive micro solid-phase extraction and gas chromatography determination of organophosphorus pesticides in strawberries. *Journal of chromatography A,* 1566: 1-12.
15. Ghorbani, M., Aghamohammadhassan, M., Chamsaz, M., Akhlaghi, H., and Pedramrad, T. (2019). Dispersive solid phase microextraction. *TrAC Trends in Analytical Chemistry*, 118: 793-809.
16. Sapahin, H. A., Makahleh, A. and Saad, B. (2019). Determination of organophosphorus pesticide residues in vegetables using solid phase micro-extraction coupled with gas chromatography–flame photometric detector. *Arabian Journal of Chemistry*, 12(8): 1934-1944.
17. Markus, A., Gbadamosi, A. O., Yusuff, A. S., Agi, A. and Oseh, J. (2018). Magnetite-sporopollenin/graphene oxide as new preconcentration adsorbent for removal of polar organophosphorus pesticides in vegetables. *Environmental Science and Pollution Research*, 25: 35130-35142.
18. Xiao, Z., He, M., Chen, B. and Hu, B. (2016). Polydimethylsiloxane/metal-organic frameworks coated stir bar sorptive extraction coupled to gas chromatography-flame photometric detection for the determination of organophosphorus pesticides in environmental water samples. *Talanta*, 156: 126-133.
19. Nodeh, H. R., Ibrahim, W. A. W., Kamboh, M. A. and Sanagi, M. M. (2017). New magnetic graphene-based inorganic–organic sol-gel hybrid nanocomposite for simultaneous analysis of polar and non-polar organophosphorus pesticides from water samples using solid-phase extraction. *Chemosphere*, 166: 21-30.
20. Amri, F., Niazi, A. and Yazdanipour, A. (2022). Three-pesticide residue analysis in tomato using a fast pressure variation in-syringe dispersive liquid-phase microextraction technique coupled with gas chromatography-mass spectrometry by assisting experimental design. *International Journal of Environmental Analytical Chemistry*, 102(3): 615-632.
21. Ayazi, Z., Jaafarzadeh, R. and Matin, A. A. (2017). Montmorillonite/polyaniline/polyamide nanocomposite as a novel stir bar coating for sorptive extraction of organophosphorous pesticides in fruit juices and vegetables applying response surface methodology. *Analytical Methods*, 9(31): 4547-4557.
22. de Souza Pinheiro, A. and de Andrade, J. B. (2009). Development, validation and application of a SDME/GC-FID methodology for the multiresidue determination of organophosphate and pyrethroid pesticides in water. *Talanta*, 79(5): 1354-1359.
23. Kermani, M., Jafari, M. T. and Saraji, M. (2019). Porous magnetized carbon sheet nanocomposites for dispersive solid-phase microextraction of organophosphorus pesticides prior to analysis by

gas chromatography-ion mobility spectrometry. *Microchimica Acta*, 186: 1-11.

24. Zohrabi, P., Shamsipur, M., Hashemi, M. and Hashemi, B. (2016). Liquid-phase microextraction of organophosphorus pesticides using supramolecular solvent as a carrier for ferrofluid. *Talanta*, 160: 340-346.
25. Hadjmohammadi, M. R., Peyrovi, M. and Biparva, P. (2010). Comparison of C_{18} silica and multi-walled carbon nanotubes as the adsorbents for the solid-phase extraction of Chlorpyrifos and Phosalone in water samples using HPLC. *Journal of Separation Science*, 33(8): 1044-1051.