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## Trace Level Quantification of Organophosphorus Pesticides from Fleshy Fruit Samples by Magnetic Solid-phase Extraction Using Fabricated SBA-15/Fe<sub>3</sub>O<sub>4</sub> Coupled with HPLC/UV

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A mesoporous silica SBA-15/iron oxide (Fe<sub>3</sub>O<sub>4</sub>-SBA-15) nanocomposite was fabricated and employed as a magnetic solid-phase extraction (MSPE) sorbent to determine three types of organophosphorus pesticides (OPPs) in fruit samples. The fabricated nanocomposite was analysed by high-performance liquid chromatography using ultraviolet detector (HPLC-UV). Meanwhile, the optimisation of extraction efficiency on three OPPs analyses used three different parameters, *viz.* desorption conditions, extraction time, and sorbent amount. The experimental results showed that the Fe<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposite achieved high analyte recoveries ranging from 89-118% with a relative deviation of less than 8.0%. By combining the optimised MSPE conditions with HPLC-UV, a suitable method for determining three OPPs was developed. This study revealed that the proposed method exhibits good coefficients of determination varying from 0.9942 to 0.9980, with low limit detection (LODs) ranging from 0.03-0.08 mg l<sup>-1</sup> and low limit quantifications (LOQs) of 0.10-0.24 mg l<sup>-1</sup>. Based on these findings, the fabricated Fe<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposite is a suitable sorbent with excellent adsorption capacity for the selected OPPs from fruit matrices.

**Keywords:** Magnetic solid-phase extraction, Mesoporous silica nanocomposite, Magnetite, Organophosphorus pesticides, Fruit samples

### INTRODUCTION

Analyte preconcentration, a sample treatment for removing impurities, has evolved over the last two decades to improve analytical chemistry development. However, there is a concern that hazardous substances in the analytical process pollute the environment [1]. Sample preparation is required due to the complexity of the matrices

and the low level of the analyte [2]. Due to these circumstances, scientists are determined to develop green chemical sample treatment methods that are compatible with sustainable development practices and achieve higher merit in analytical chemistry. Reduction of the pollution problem, environmentally friendly procedures, and green analytical chemistry have been implemented into research with the common goal to decrease consumption of toxic substances [3].

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Solid-phase extraction (SPE) has been widely used in

recent decades due to its low analysis cost and simple operation with the possibility of automation [4]. Despite its ease of use and applicability, the conventional SPE method has several drawbacks, including cartridge clogging, high backpressure, and engagement in multi-stage procedures [5]. In recent years, microextraction has excellent attention, particularly in green analytical chemistry, which develops more environmentally friendly routes using less organic solvent and natural material as extraction tools [6].

The magnetic MSPE method is a practical approach that has overcome the challenges of the typical SPE [7]. The universality of this approach indicates that the extraction potential is growing globally by the adoption of magnetic sorbents. The key strengths of the MSPE method are its large surface area and fast diffusion process, which have the capabilities to attain high extraction capacity (98.6-103.5%) and good extraction efficiency [8]. Besides, the ability of magnetic sorbents to quickly isolate from samples through the external magnetic field offers fast and easy separation. Comparative studies have shown that MSPE methods outperform traditional SPE due to their excellent extraction efficiency and elimination of time-consuming and labour-intensive extraction measures, which are mainly required for large samples [9].

A significant feature of the MSPE method is the utilisation of sorbents to establish an analyte extraction. Several sequences of magnetic particles are employed for pesticide extraction. One of the most widely used is iron oxide ( $\text{Fe}_3\text{O}_4$ ) since it is comparatively cheap, harmless, and easy to synthesise and modify [8]. Unfortunately, the deficiencies in  $\text{Fe}_3\text{O}_4$  particles are unstable and quickly oxidised [10]. Surfaces of magnetic particles are functionalised with inorganic or organic materials to prevent oxidation and improve robustness and sorption capabilities. Silica and alumina are the two commonly employed inorganic materials to prepare functionalised  $\text{Fe}_3\text{O}_4$  particles [11]. Between the two, silica/magnetite is the most frequently used because the silica shell improves the stability of the  $\text{Fe}_3\text{O}_4$  cores in the solution. It could also prevent the dipolar magnetite between its particles and the silica from evenly dispersing the particles [12,13]. Besides, silica/magnetite offers versatility in surface modification, physicochemical stability, and biocompatibility [14].

SBA-15 is a mesoporous silica-based material with rectangular, hexagonal pores with large holes supporting a

significant amount of bioactive molecules coverage [15]. SBA-15 possesses a series of desirable features, including a high specific surface area ( $600\text{-}1000\text{ m}^2\text{ g}^{-1}$ ), chemical stability, narrow pore distribution, and thermodynamic stability [16]. Furthermore, the massive active site on the pore wall enables several specific chemical groups to be grafted [17]. In light of these benefits, it is convenient in a variety of applications, including catalysis [18], sensing [19], drug distribution [20], and organic pollutant adsorption [21]. Consequently, a description of the specification for silica/magnetite composite has been extensively used in environmental research. For instance, amino-functionalised SBA-15 derivatised  $\text{Fe}_3\text{O}_4$  for herbicide extraction from water samples [22],  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{KIT-6}$  composite materials for pyrethroid pesticides extraction [23],  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  composite for methylene blue enrichment [24], and SBA-15 coated particles for cerium removal in aqueous samples [25].

The determination and extraction of pesticide residues in fruits are of great significance and require the development of pre-treatment and sampling steps to enhance sensitivity. Since strawberries and grapes are nutritional plants with high economic value, they are harvested for industrial processing and direct consumption on food crops. However, insect pests are continuously reducing the quality and yield of both fruits. Pesticide residues accumulated in strawberries and grapes during harvesting may be harmful to consumers [26, 27]. Because of the thinner surfaces that do not form an impenetrable wall, pesticides permeate fruit tissue. Some of it could be absorbed by fresh fruit tissue to protect it from pests that enter through the skin and absorb the liquid inside [28].

OPPs are one of the potential pesticides found in high concentrations in fruits. They are the most extensively used category of agricultural pesticides [29]. Although this pesticide is environmentally friendly, it has caused harm to mammals [30]. In such circumstances, several health issues arise due to the toxicity of contaminants through ingestion, inhalation, or absorption of the skin. Recent studies have indicated that the extreme neurotoxicity of OPPs has inhibited the effective functioning of the nervous system [31,32]. Extensive usage suggests a risk to human health and welfare as it is already detectable in certain food items, even a small concentration of OPPs. In view of the increasing prevalence of adverse effects, an efficient

analytical methodology is essential.

The available data indicate that the MSPE techniques adopted by magnetic particle sorbents have been extensively studied. There are currently a few studies that can inherently provide the potential of magnetic-based mesoporous silica as a sorbent for MSPE of pesticides in food crops. Therefore, the primary goal of this work is to assess the feasibility of preparing the mesoporous nanocomposite Fe<sub>3</sub>O<sub>4</sub>-SBA-15 as a viable sorbent for OPPs extraction using MSPE techniques. It is necessary to recognise three OPPs, namely chlorpyrifos, diazinon, and parathion methyl in grape and strawberry matrices, followed by an HPLC-UV to evaluate the sorbent extraction efficiency. The efficiency influences the recovery of the extraction, and corresponding optimised values have been obtained to demonstrate this study.

## EXPERIMENTAL

### Standards and Reagents

All the pesticides analytical standards (chlorpyrifos, diazinon, and parathion methyl (purity ≥ 98%), tetraethyl orthosilicate (TEOS), and poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (Pluronic P-123, MW = 5800 g mol<sup>-1</sup>) used in this study were obtained from Sigma Aldrich (USA). HPLC grade solvents (acetonitrile, acetone, methanol, ethyl-acetate, and n-hexane), iron(III) chloride (FeCl<sub>3</sub>), iron(II) chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O), sodium hydroxide (NaOH), and potassium dihydrogen phosphate were purchased from Merck (Darmstadt, Germany). QRec (Selangor, Malaysia) supplied hydrochloric acid (37%), ammonia solution (28%), and phosphoric acid, while the Milli-Q Gradient water system from Millipore provided ultrapure water (Massachusetts, USA).

### Instrumentation

The adsorption bands of the synthesised nanocomposite (Fe<sub>3</sub>O<sub>4</sub>-SBA-15) were measured using a Perkin Elmer 8300 FTIR spectrophotometer (Massachusetts, USA) in the wavelength range from 400-4000 cm<sup>-1</sup>. The morphology of sorbent was observed using a field emission scanning electron microscope (FESEM) (Model: JEM-2300, Tokyo, Japan). Transmission Electron Microscopes (TEM) analyses

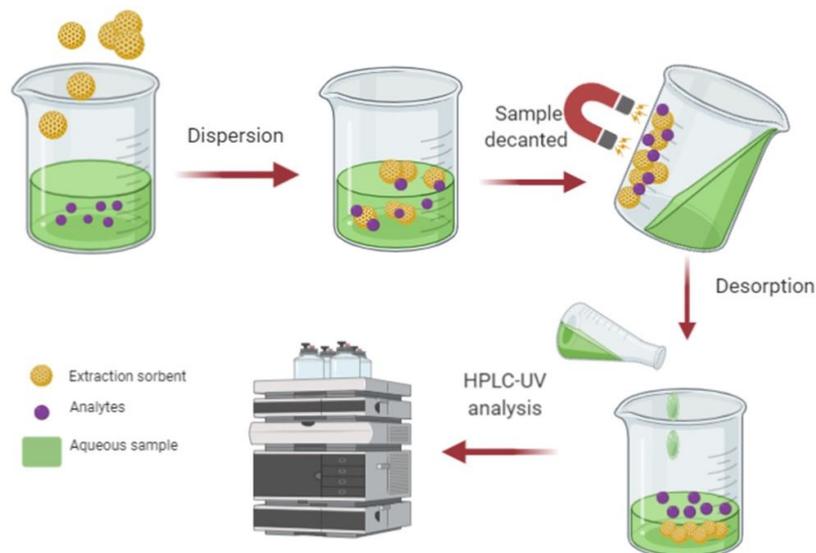
were carried out using a JOEL JEM-2001 electron microscope at 200 kV (UK). X-Ray Diffraction (XRD) pattern investigation was determined using a Rigaku Miniflex II X-ray diffractometer (Japan) with a stationary X-ray source Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ , 30 Kv, 15 mA).

A vibrating sample magnetometer (VSM) from Lake Shore Cryotronics, Inc. (Westerville, OH, USA) was used to monitor the magnetic properties of sorbent. The Agilent ZORBAX Eclipse C18 column (5  $\mu\text{m}$  x 2.1 x 100 mm) was used for the chromatographic separation (Agilent Technologies, USA). At 0.2 ml min<sup>-1</sup> (flow rate), the mobile phase was acetonitrile:phosphate buffer (pH 4.5) (60:40% v/v). Peaks in the analytes were detected using a UV detector set to 210 nm. The sample injection volume was 5  $\mu\text{l}$  using a microsyringe (Hamilton, California, USA).

### Preparation of Sorbents

Synthesis of mesoporous SBA-15 silica. With minor modifications, mesoporous SBA-15 silica was synthesised using a technique developed in the literature [33]. A solution of distilled water (30 ml), HCl (2 M, 120 ml), and Pluronic P123 (4.0 g) was stirred at 35 °C for 20 h. Subsequently, 8.5 g of tetraethyl orthosilicate (TEOS) was added with water and stirring vigorously for 15 min. The mixture was maintained under static conditions for 20 h at the same temperature (35 °C). The white silica solution was then transferred to a 90 °C oven for the additional 24 h before filtration and drying at 45 °C for 72 h. Finally, the dried powder was calcined for 6 h at 500 °C and stored in a container for future use to remove the template.

Synthesis of mesoporous silica nanocomposite SBA-15/iron oxide (Fe<sub>3</sub>O<sub>4</sub>-SBA-15). In this study, a modification of magnetic-based on mesoporous silica (Fe<sub>3</sub>O<sub>4</sub>-SBA-15) was introduced with minor amendments [34]. Initially, 1 mmol of FeCl<sub>2</sub>·4H<sub>2</sub>O and 2 mmol of FeCl<sub>3</sub> were mixed in 100 ml of doubled distilled water with 0.5 g of synthesized SBA-15. The mixture was then stirred vigorously with the nitrogen degassing. A 10 ml aqueous NH<sub>3</sub> solution was added dropwise during the process. The solution mixture was continuously stirred for one hour until it turned black. Next, the solution was centrifuged with double distilled water until the pH reached neutral. The synthesized Fe<sub>3</sub>O<sub>4</sub>-



**Fig. 1.** Schematic illustration of the MSPE using  $\text{Fe}_3\text{O}_4\text{-SBA-15}$  sorbent.

SBA-15 was later dried at room temperature in a vacuum desiccator.

### Sample Collection and Preparation

Grapes and strawberries were chosen as true models since both can be directly eaten. Hence, pesticide particles that potentially adsorbed on their surface could be identified. The sample was prepared following the documented procedure [35]. Firstly, the grape and strawberry samples were sliced into tiny pieces. Next, 1000  $\mu\text{l}$  of the standard solution of selected pesticides ( $1 \text{ mg l}^{-1}$ ) were spiked onto 10 g samples and left at room temperature for one hour. Then, 10 ml of distilled water and methanol were added and pounded with a laboratory mixer for 5 min, followed by homogenisation with an ultrasonicator (4000 rpm). The supernatants were collected after centrifugation of the solid sediment. Both supernatants (from the grape and strawberry samples) were eventually purified twice with filter paper. The same technique was applied to unspiked samples without the addition of the standard pesticide solution.

### Magnetic Solid-Phase Extraction (MSPE)

In the preliminary stage, the addition of 50 mg of  $\text{Fe}_3\text{O}_4\text{-SBA-15}$  to 10 ml of spiked samples with an established concentration of OPP pesticides was performed. The

extraction process was carried out using an orbital shaker for 15 min, 250 rpm rotational speed, and room temperature to achieve a homogenous dispersion solution [36]. The stirring rate could minimise the mass transfer resistance. However, a higher stirring rate will result in a backextraction of the analyte from the sorbent to the solution, possibly due to an increase in the temperature of the applied high kinetic force [37].

The sample solution was then decanted using an external magnet, and the trapped analytes were eluted with 500  $\mu\text{l}$  of acetone under ultrasonication for 5 min. Next, the magnet was once again put to the vial, and the supernatant was drained using gentle nitrogen flow before the residual was enriched with 0.1 ml of acetone. Finally, 5  $\mu\text{l}$  of an aliquot portion of finally concentrated samples were injected in HPLC-UV. Figure 1 illustrates a diagram of the MSPE procedure.

## RESULTS AND DISCUSSION

### Characterisation of $\text{Fe}_3\text{O}_4\text{-SBA-15}$ Nanocomposite

FTIR was used to determine the type of functional groups present in pure SBA-15 and  $\text{Fe}_3\text{O}_4\text{-SBA-15}$  sorbents. There are three major identical bands of SBA-15 observed at  $1090 \text{ cm}^{-1}$  (asymmetric Si-O-Si stretching),  $960 \text{ cm}^{-1}$  (symmetric Si-O-Si stretching), and  $799 \text{ cm}^{-1}$  (Si-OH

**Table 1.** FTIR Absorption Bands for SBA-15 and Fe<sub>3</sub>O<sub>4</sub>-SBA-15

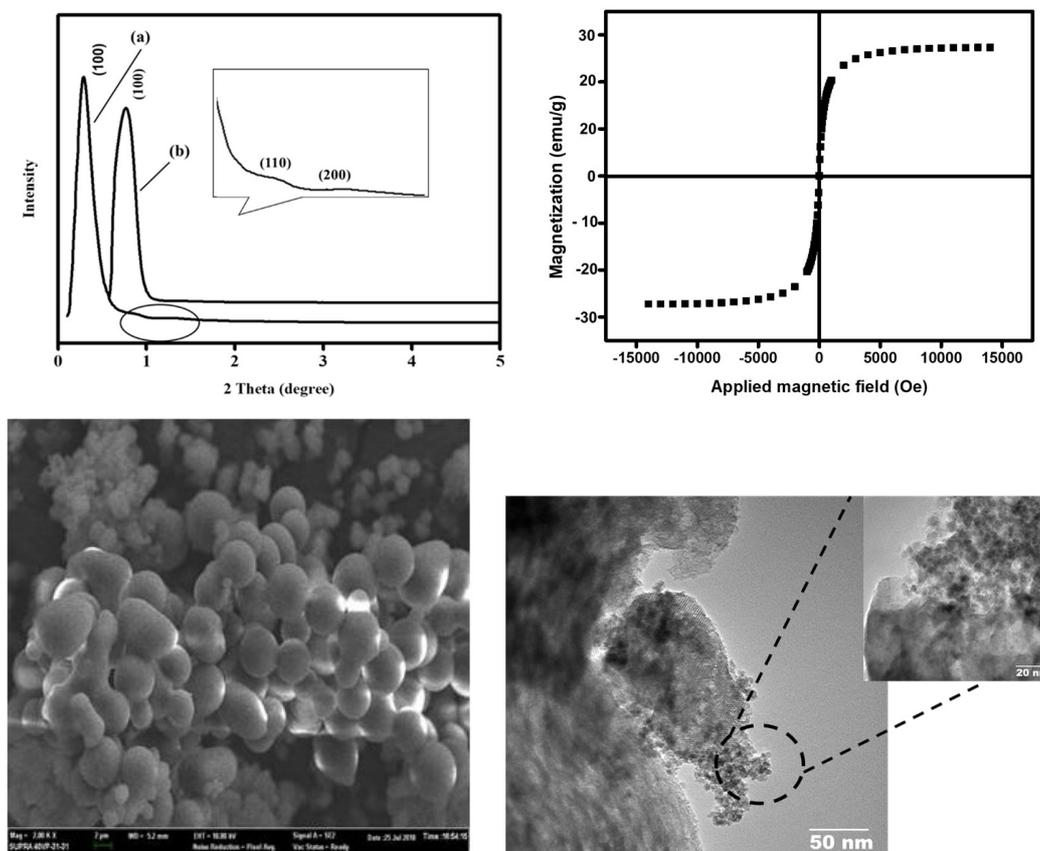
Vibrational modes	Samples/Wavenumber (cm <sup>-1</sup> )	
	SBA-15	Fe <sub>3</sub> O <sub>4</sub> -SBA-15
Adsorbed H <sub>2</sub> O	3455	3450
C-H Stretching	2850-3000	-
C-H bending	1372	1370
Asymmetric Si-O-Si	1084	1090
Symmetric Si-O-Si	957	960
Si-OH stretching	799	799

vibrations) (Table 1) [38,33]. This data was supported by XRD diffractograms, as shown in Fig. 2a.

The Bragg diffraction intensities of the sample

shifted and decreased after being modified with magnetite particles (Fe<sub>3</sub>O<sub>4</sub>). In contrast, the (1 0 0) diffraction peaks are retained, indicating that the organic group is grafted onto the SBA-15 pore structure [39]. The peak intensity of the Fe<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposite decreases due to the contraction of the support framework. The contraction is caused by the incorporation of the magnetite phase on the pore structure of silica channels. It is also demonstrated that the textural properties of SBA-15 were not destroyed, indicating that the mesoporosity was preserved following the silica coating step [40].

At room temperature, the magnetic strengths of Fe<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposite were measured using the VSM technique. Figure 2b depicts the materials' magnetic hysteresis loop with S-like curves. The curve then passes through a zero magnetisation point without remanence and



**Fig. 2.** Characterisation of sorbent *via* (A) XRD diffractogram of: a - SBA-15, b - Fe<sub>3</sub>O<sub>4</sub>-SBA-15; (B) VSM magnetisation curve of Fe<sub>3</sub>O<sub>4</sub>-SBA-15; (C) FESEM image of SBA-15; (D) TEM image of Fe<sub>3</sub>O<sub>4</sub>-SBA-15.

coercivity, demonstrating its superparamagnetic properties [41]. The saturation magnetisation amount of  $30.72 \text{ emu g}^{-1}$  for  $\text{Fe}_3\text{O}_4$ -SBA-15 sorbent is displayed, indicating its suitable magnetic property.

As reported in a previous study [42], the sorbent saturation magnetisation was lower than the  $\text{Fe}_3\text{O}_4$  particles ( $81.9 \text{ emu g}^{-1}$ ). The pattern was due to the contribution of the inorganic materials SBA-15 to the total magnetisation. A magnetisation value of  $16.3 \text{ emu g}^{-1}$  has also been reported to be sufficient for magnetic separation from the solution [43]. Therefore, the  $\text{Fe}_3\text{O}_4$ -SBA-15 nanocomposite is favourable for magnetic adsorbents with suitable saturation magnetisation values to determine OPPs in fruit matrices.

A morphology study using FESEM (Fig. 2c) shows that due to magnetic interactions between particles,  $\text{Fe}_3\text{O}_4$  particles in spherical-like shape are agglomerated and deposited unevenly onto the exterior surface of SBA-15 [12]. TEM analysed the particle size range between 6 and 7 nm. The TEM image (Fig. 2d) shows a honey-comb-like hexagonal array, and the accumulation appears as a dark dot on the surface of mesopores [44]. Based on FESEM and TEM analysis, the fabrication process does not alter the texture and preserves the mesoporous SBA-15 structure [45].

### Optimisation of Extraction Conditions

The extraction and elution processes of the MSPE method play a significant role in achieving satisfactory analyte recovery. Various experimental parameters such as extraction time, desorption solvent, desorption time, and sorbent amount were studied and optimised the conditions to achieve a higher recovery of  $\text{Fe}_3\text{O}_4$ -SBA-15.

### Extraction Time

One of the primary factors determining the time after which equilibrium is achieved in the system is the extraction time profile of target analytes. A sufficient contact time between analyte and sorbent is generally required to reach adsorption equilibrium [46]. The extraction performance analyses the impact of the parameter within 5 to 20 min. The extractions were carried out using the proposed method. The solutions were agitated with an orbital shaker to aid in the analyte's mass transfer to the

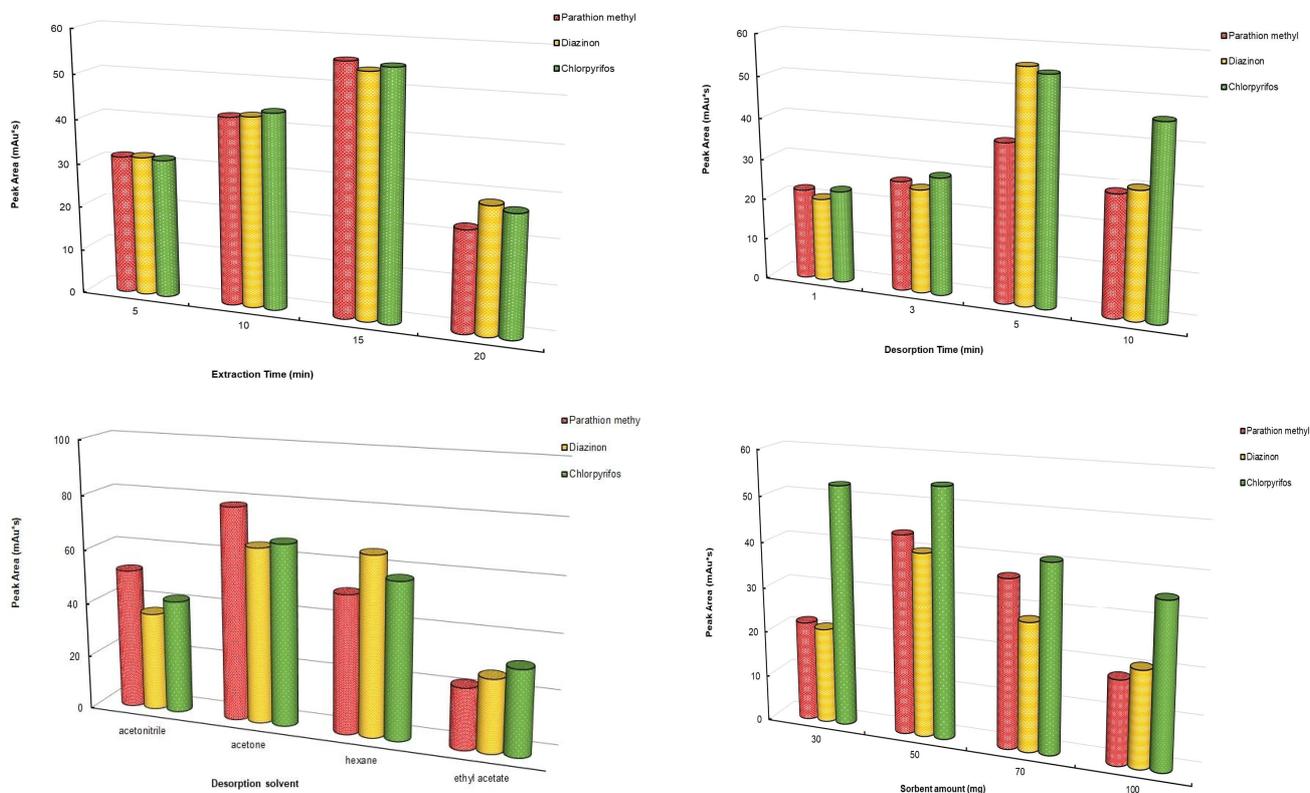
sorbent [47]. The experimental conditions were mass of sorbent (50 mg), desorption solvent (500  $\mu\text{l}$  acetone), and desorption time (5 min).

The peak area ratio for all OPPs reached equilibrium within 15 min, as shown in Fig. 3a. The trend indicates that the OPPs and sorbent reached a rapid distribution equilibrium in few minutes. The sorbent's large contact surface area with the samples allows for swift mass transfer of analytes from the aqueous phase to the sorbent [48]. Within 20 min, the peak area signal has significantly decreased. The decrease could be attributed to analyte decomposition caused by extending the extraction time that increased the temperature [49].

### Desorption Conditions

Desorption is one of the fundamental processes affecting the ultimate fate of contaminants in solids to achieve high recovery and sensitivity on the method's performance [50]. Generally, solvent's desorption and polarity and the analytes' solubility, which depends on their compatibility with the analytical instrument, should all be considered. Hence, four organic solvents with decreasing polarity order, viz. acetonitrile, acetone, ethyl acetate, and hexane, with relative polarities of 0.46, 0.36, 0.23, and 0.01, respectively, were used. The resulting efficiencies were compared using the analyte's chromatographic peak area. 10 ml of a sample solution containing  $1 \text{ mg l}^{-1}$  of OPPs and 500  $\mu\text{l}$  of the organic solvents were used to assess the efficiency.

Acetone was chosen as an elution solvent among the desorption solvents investigated since it has the highest desorption ability (Fig. 3b). Acetone is used to elute all polar and non-polar OPPs from the sorbent effectively. Furthermore, the polar properties of acetone are similar to the polarity of the selected OPPs [51]. Hence, acetone was used throughout the entire study as a desorption solvent. Fig. 3c shows the effect of desorption time between 1 to 10 min. The pattern indicated that as the desorption time increased from 1 to 5 min, the peak area ratio increases significantly. However, the desorption time decreases as the time is prolonged to 10 min. A longer desorption time could lead to re-adsorption of analyte onto the sorbent and solvent evaporation [37]. Therefore, 5 min were selected as an optimum desorption time and applied in subsequent



**Fig. 3.** Effect of (a) extraction time, (b) desorption solvents, (c) desorption time, and (d) sorbent dosage on OPPs pesticide extraction efficiency.

extractions.

### Sorbent Amount

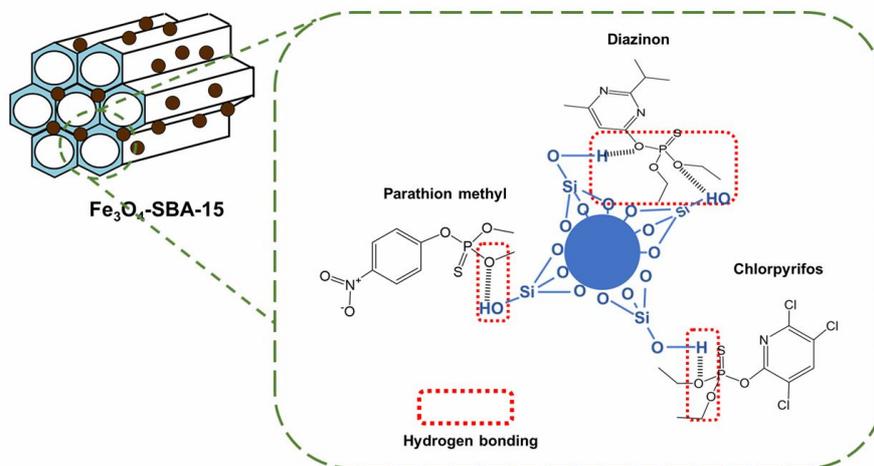
One of the critical factors in investigating the effect of sorbent quantity on extracting the selected OPPs from the solution is sorbent mass. During the loading process, each sorbent particle has a limited capacity to retain the target analyte and contaminants. A good sorbent mass is vital as an insufficient amount of sorbent leads to column overload or irreproducible recoveries, while an excess of it increases solvent requirement [52]. Hence, the effect of sorbent mass was investigated using different amounts ranging from 30 mg to 100 mg at 15 min of extraction time, 5 min of desorption time, and acetone as an elution solvent. Figure 3d shows that as the sorbent dosage increased to 50 mg, the peak area of OPPs increases significantly.

Moreover, the results show that there is no further

increment when 70 mg of the sorbent is used. The decrease in response could be attributed to the saturation of active sites on the sorbent, which was more significant than expected [53]. Thus, 50 mg of sorbent mass was chosen as an optimal mass for further analysis. The increased concentration of the binding site on the sorbent could explain the significantly improved OPPs' peak area performance [54].

### Proposed Molecular Interaction

Several interactions could occur between sorbent and sorbate, either attractive or repulsive, such as electrostatic interaction, hydrogen bonding, and hydrophobic interaction. They are strongly influenced by the charge densities of the material, the adsorptive molecules, and the ionic strength of the solution [55]. The sorbent synthesised in this study is hydrophilic and could interact with the sorbate *via* hydrogen



**Fig. 4.** Schematic representation showing the possible interaction mechanism for Fe<sub>3</sub>O<sub>4</sub>-SBA-15.

**Table 2.** Comparison of the Sorbent Amount and Recoveries Obtained of DSPE and MSPE Method

Properties	DSPE	MSPE
Recoveries (%)	81-110	89-119
Enrichment factor (%)	72	83
The sorbent amount (mg)	100	50
Nature of method	Simple and fast with filtration and centrifugation process	Simple and fast without filtration and centrifugation process

bonding under ideal conditions. Figure 4 illustrates the possible interactions between the synthesised sorbent and OPPs. The sorbent structure contains a silanol group on mesoporous silica materials, whereas the selected OPPs have different anionic sites (O, N, S, and Cl). Through a strong hydrogen bonding, the hydrogen of the hydroxyl group binds to the anionic groups at the silanol surface. As a result, the selected OPPs are extracted from all synthesised sorbents.

### Comparison Extraction Performance between DSPE and MSPE

A preliminary study on dispersive solid-phase extraction (DSPE) with similar MSPE parameters was carried out separately. Their performance was compared based on recovery range, sorbent amount, and operation efficiency. As shown in Table 2, the DSPE gains pesticide recoveries ranging from 81-110%, whereas the MSPE recoveries range

from 89-119%. In terms of extraction sorbent dosage, magnetic particles have a large surface area and unique magnetic properties. As a result, 50 mg of sorbent was sufficient for MSPE sample preparation, whereas 100 mg of sorbent was required for the DSPE method to deal with a 10 ml sample.

In terms of sorbent amount, MSPE and DSPE were compared to SPE [56]. According to previous studies, our developed methods used a comparable amount of sorbent with SPE (100 mg). The developed methods are better in LOD and LOQ and can be recycled to extract OPPs in complex matrices. Furthermore, the MSPE method is dispersed directly into the sample solution. An external magnetic field simply recovers the sorbent collection, whereas the DSPE method requires centrifugation and filtration steps. The MSPE method demonstrates its benefits in improving operational efficiency by avoiding time-consuming column and filtration steps after extraction and

**Table 3.** Analytical Features of the Proposed Method (MSPE)

Parameter	Strawberry			Grape		
	Chlorpyrifos	Diazinon	Parathion methyl	Chlorpyrifos	Diazinon	Parathion methyl
Linear range <sup>a</sup>	0.10-5.00	0.10-5.00	0.10-5.00	0.10-5.00	0.10-5.00	0.10-5.00
Correlation coefficient	0.9942	0.9964	0.9971	0.9984	0.9977	0.9980
LOD <sup>b</sup>	0.05	0.08	0.05	0.04	0.03	0.07
LOQ <sup>c</sup>	0.16	0.24	0.15	0.16	0.10	0.21

<sup>a</sup>All concentration based on mg l<sup>-1</sup>. <sup>b</sup>Limit of detection. <sup>c</sup>Limit of quantification.

**Table 4.** The Precision of the MSPE Method

Compound	Repeatability (RSD%, n = 3)		Reproducibility (RSD%, n = 3)	
	0.1 (mg l <sup>-1</sup> )	5.0 (mg l <sup>-1</sup> )	0.1 (mg l <sup>-1</sup> )	5.0 (mg l <sup>-1</sup> )
	Strawberry			
Chlorpyrifos	107.1 (0.1)	96.1 (1.2)	80.9 (0.63)	85.3 (2.7)
Diazinon	88.7 (2.2)	83.8 (2.9)	82.0 (6.3)	108.0 (2.1)
Parathion methyl	112.5 (3.3)	109.3 (1.2)	104.1 (1.3)	93.3 (7.4)
Grape				
Chlorpyrifos	109.9 (1.4)	117.2 (0.4)	105.7 (0.1)	117.1 (1.2)
Diazinon	115.5 (2.1)	93.6 (3.8)	95.7 (2.1)	109.4 (1.0)
Parathion methyl	81.7 (2.1)	95.0 (3.7)	114.7 (2.1)	118.4 (0.5)

simplifying sample preparation procedures.

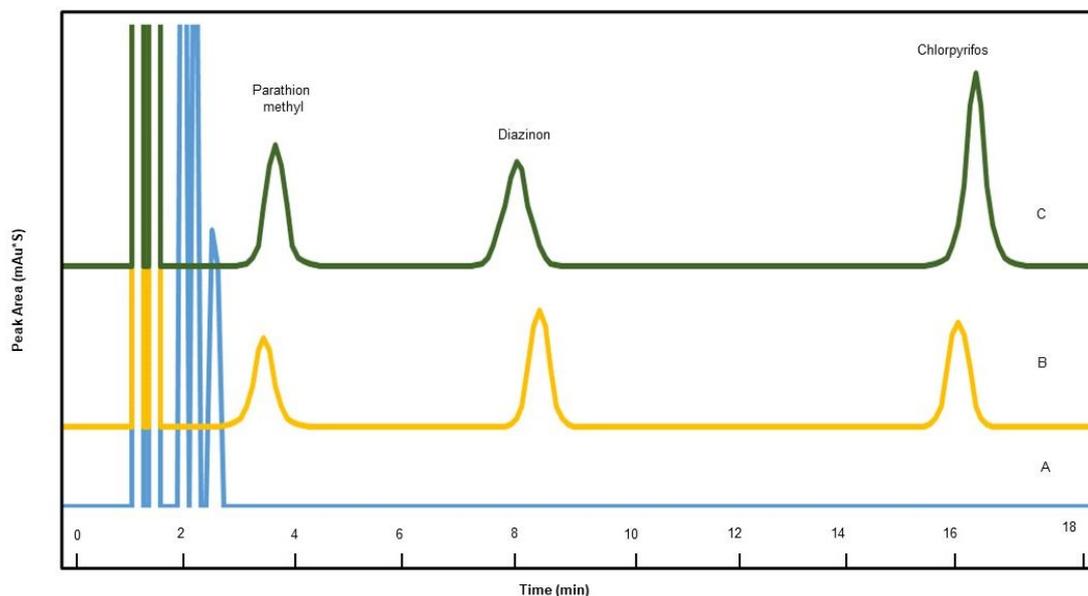
### Method Performance Validation

Figures of merit validated the applicability of the MSPE method under the optimised experimental conditions (15 min extraction time, 5 min desorption time, 50 mg of sorbent, and acetone as desorption solvent). The analytical parameters of linearity, the LOD, LOQ, precision, and accuracy were evaluated for method verification. Table 3 shows the analytical characteristics of the proposed method. Matrix match calibration was used in this study because of the expected complexity of the fruit samples. It may contribute to the analytical signal; comparing the signal between the sample and the analyte becomes impossible [57].

This method was using strawberry and grape samples at

various concentrations of the selected pesticides. For all analytes tested at their corresponding detection wavelengths, good linearities were obtained with an appropriate determination coefficient ( $R^2 \geq 0.9990$ ). The LOD and LOQ for each targeted analyte were estimated to have signal-to-noise (S/N) ratios of 3 and 10, respectively. The LOD and LOQ of three analytes were 0.03 mg l<sup>-1</sup> to 0.08 mg l<sup>-1</sup> and 0.10 mg l<sup>-1</sup> to 0.24 mg l<sup>-1</sup>, respectively, indicating that the analytical approach was well developed.

Triplicate analysis of three selected analytes at two concentration levels (0.1 and 5.0 mg l<sup>-1</sup>) was measured both for repeatability and reproducibility (n = 3, consecutive day) to assess method precision (%RSD). The resulting %RSD was below 8%, indicating that the method is sufficiently repeatable (Table 4).



**Fig. 5.** HPLC-UV chromatogram for the (A) unspiked and spiked actual samples with 1 mg l<sup>-1</sup> of strawberry (B) and grape (C).

**Table 5.** Results Obtained for Fruit Samples Analysis

OPPs	Spiked level (mg l <sup>-1</sup> )	Strawberry		Grape	
		Recovery (%)	RSD <sup>a</sup>	Recovery (%)	RSD <sup>a</sup>
Chlorpyrifos	0	ND	ND	ND	ND
	1	101.7	2.1	92.6	0.9
Diazinon	0	ND	ND	ND	ND
	1	100.0	5.5	89.2	2.9
Parathion methyl	0	ND	ND	ND	ND
	1	118.0	6.1	91.1	1.9

<sup>a</sup>%, n = 3. ND = not detected.

### Analysis of Real Samples

The proposed method was used in this study to assess the efficacy and feasibility of using pesticide residues in grape and strawberry samples. Figure 5 depicts the HPLC-UV chromatograms of the unspiked and spiked curves with 1 mg l<sup>-1</sup> fruit samples. The obtained results show no trace of all analytes since the OPPs traces in both fruits are in trillions and could not be detected by HPLC-UV [58]. The recoveries were carried out and measured from the spiked

fruit samples to assess the method's reliability. As shown in Table 5, the method recoveries for three OPPs ranged from 89-118%, with RSDs of less than 8%.

### Comparison with Other MSPE Methods

Table 6 compares the properties of the proposed MSPE method in various samples to determine OPPs pesticides. As can be seen, the LODs in this work were lower than C<sub>18</sub>-Fe<sub>3</sub>O<sub>4</sub>@MSiO<sub>2</sub> [59] but higher than Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/C<sub>18</sub>

**Table 6.** Comparison of the Presented Method with other Reported MSPE Methods for the Determination of OPPs

Method	Sorbent	Mass sorbent (mg)	Matrices	Extraction time (min)	LOD (mg l <sup>-1</sup> )	RSD (%)	Recovery (%)	Enrichment factor	Reusability	Ref.
MSPE-GC-MS <sup>a</sup>	<sup>c</sup> C <sub>18</sub> -Fe <sub>3</sub> O <sub>4</sub> @MSiO <sub>2</sub>	10	Water	20	0.03	<10.7	N/A	N/A	N/A	[59]
MSPE-GC/MS	<sup>d</sup> Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> /C <sub>18</sub>	15	Water	30	5 × 10 <sup>-6</sup> - 2.5 × 10 <sup>-5</sup>	<9.6	62.2-86.4	1015	N/A	[60]
MSPE-HPLC-UV <sup>b</sup>	<sup>e</sup> G-CNT-Fe <sub>3</sub> O <sub>4</sub>	80	Water	20	1.4 × 10 <sup>-6</sup> - 1.1 × 10 <sup>-5</sup>	<8.8	75.6-102.5	930-1510	15	[61]
MSPE/HPLC-UV	<sup>f</sup> Fe <sub>3</sub> O <sub>4</sub> @TiO <sub>2</sub> /CTAB	100	Water	20	2.6 × 10 <sup>-5</sup> - 3.0 × 10 <sup>-5</sup>	<8.7	88.5-96.7	~1,000	5	[42]
MSPE-HPLC-UV	Fe <sub>3</sub> O <sub>4</sub> -SBA-15	50	Fruits	15	0.03-0.08	<8.0	89-118	83	3	This work

<sup>a</sup>GC-MS-gas chromatography-mass spectrometry. <sup>b</sup>HPLC-UV-high-performance liquid chromatography-ultraviolet detector. <sup>c</sup>C<sub>18</sub>-Fe<sub>3</sub>O<sub>4</sub>@MSiO<sub>2</sub>-C18-functionalised Fe<sub>3</sub>O<sub>4</sub>@mSiO<sub>2</sub> Microspheres. <sup>d</sup>Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/C<sub>18</sub>-magnetic core-shell silica nanoparticles with C<sub>18</sub>. <sup>e</sup>G-CNT-Fe<sub>3</sub>O<sub>4</sub>-graphene-carbon nanotube-Fe<sub>3</sub>O<sub>4</sub> nanocomposite. <sup>f</sup>Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub>/CTAB-magnetic titanium dioxide modified with cetyltrimethylammonium bromide. \*mg l<sup>-1</sup>.

[60], G-CNT-Fe<sub>3</sub>O<sub>4</sub> [61], and Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub>/CTAB [42]. The methods' relatively low detection limit is partly attributed to the high sensitivity of the ultraviolet detector. Furthermore, the proposed method has the shortest extraction time. In some cases, there is a noticeable difference. For instance, the methods developed by Xiong 2012, required 30 min to extract the analytes.

In contrast, MSPE-HPLC-UV takes 15 min to reach extraction equilibrium, indicating the proposed method's rapid and effective mass transfer [60]. The addition of magnetism properties simplifies and accelerates the phase separation process. The proposed method is simple, sensitive, and efficient. The LODs could meet the EU regulation on the maximum concentration of OPPs in fruit samples while also having good potential for analysing three targets OPPs in fruit samples.

## CONCLUSIONS

A simple, fast, and user-friendly MSPE method has been developed to determine three selected OPPs in fruit

samples. The proposed sorbent was a Fe<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposite based on mesoporous silica SBA-15 nanoparticles modified with Fe<sub>3</sub>O<sub>4</sub> particles. Due to its magnetic properties, the sorbent is easy to handle and time effective since filtration and centrifugation steps were neglected. This study demonstrated a remarkable relative recovery of 89-118% and low LOD (0.03 to 0.08 mg l<sup>-1</sup>) with a %RSD of 0.1-7.4 for selected OPPs in actual samples. To conclude, the Fe<sub>3</sub>O<sub>4</sub>-SBA-15 nanocomposite is a versatile sorbent for alternative green MSPE to preconcentrate OPP pesticides.

## DECLARATION OF CONFLICT INTEREST

The authors declare that they have no conflict of interest.

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