



Dispersive solid-phase extraction using microporous metal-organic framework UiO-66: Improving the matrix compounds removal for assaying pesticide residues in organic and conventional vegetables

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ABSTRACT

An efficient dispersive solid-phase extraction method was developed to trace pesticide residues in commonly consumed vegetables. In this method, UiO-66 with uniform micropores was used as sorbent, and gas chromatography-mass spectrometry was applied to detect the pesticides. Thanks to the size sieving action of uniform micropores, UiO-66 directly extracted the target pesticides from vegetable matrices and excluded the relatively large matrix compounds. This well eliminated the matrix effect. The important experimental conditions were evaluated by orthogonal array experimental design. In optimized conditions, good linearity ($R^2 \geq 0.99$), detection limits (0.4–2.0 ng/g), recoveries (60.9–117.5%) and precision (relative standard deviations < 14.6%) were achieved. Moreover, the sorbent UiO-66 can be reused more than 20 times. These demonstrate a simple, reliable and robust method to screen the pesticide residues in vegetables. Furthermore, the validated method was applied to detect the pesticides in various organic and conventional vegetables.

1. Introduction

Vegetables are an essential class of foods for human beings. The rational consumption of vegetables brings great health benefits owing to their rich nutrients (Yu & Yang, 2017). During vegetable cultivation process, many pesticides were used to ensure the yield (Chen, Wang, Zhang, & He, 2018; Pang, Yang, & He, 2016). In these pesticides, organophosphorus (OPP) and pyrethroid pesticides (PYR) are widely utilized (Babina, Dollard, Pilotto, & Edwards, 2012). They can penetrate into the vegetables and usually not be metabolized completely in short time, resulting in the contamination of vegetables (Yu & Yang, 2017). Moreover, OPP and PYR are neurotoxin insecticides, which would threaten human health (Babina et al., 2012; Mao et al., 2020). To protect human health, the maximum residue limit (MRL) for OPP and PYR in foods have already been set by the legislatures of many countries

(Pirsaheb, Fattahi, & Shamsipur, 2013). Thus, there is highly demanded for detection of pesticide residues in vegetable.

The interfering compounds from vegetable matrix probably cause false quantified results and may result in potential damage to the apparatuses (Song et al., 2019). To accurately quantify the trace pesticides in vegetable, the crux is to develop efficient sample pretreatment technique (Liu et al., 2016). Till now, various reliable sample preparation techniques have been established for extraction and purification of vegetable samples. However, some limitations are still existed, such as requiring large amounts of solvents and demanding tedious and time-consuming operation (Liu et al., 2016). Therefore, there is still an urgent need to develop a simple, efficient and environmentally-friendly method of sample preparation for monitoring the pesticides in vegetables.

Dispersive solid-phase extraction (d-SPE) has been considered as an

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efficient technique to establish the easy, fast, and economical analysis method for its features of simple operating procedure and less solvent consumption (Li et al., 2015; Liu et al., 2016). In the d-SPE, the sorbents are commonly either used to adsorb interfering compounds (Anastassiades, Lehotay, Stajnbaher, & Schenck, 2003) or adsorb analytes in bulk samples (Li et al., 2015). Although significant progress has been achieved through the d-SPE technique, several issues still remain. For instances, the interfering compounds are hardly to be removed and obvious matrix effect is observed (Rutkowska, Lozowicka, & Kaczyński, 2019). In some cases, the elimination of interfering compounds is accompanied with the loss of analytes, resulting in poor recoveries (Mao et al., 2018). Thus, it is a great challenge to develop d-SPE based method that can effectively eliminate matrix effect while maintains superior recovery for assaying pesticide residues in foods.

To improve the performance and effect of d-SPE, the sorbents play the crucial roles. To date, various sorbents have been used in d-SPE, such as PSA, GCB, C18, multi-walled carbon nanotubes, fibers, porous silica, modified magnetic nanoparticles and metal-organic frameworks (MOFs) (Awual, Hasan, Islam, Asiri, & Rahman, 2020; Awual, Shenashen, Jyo, Shiwaku, & Yaita, 2014; Han et al., 2016; Li et al., 2015; Liu et al., 2016; Shahat et al., 2018; Song et al., 2019; Yu & Yang, 2017). In these sorbents, MOFs are a class of very well studied porous materials (Ma et al., 2018), due to its highly porous structures and superior adsorption affinity and capacity to organic compounds (Hasan & Jhung, 2015). These intrinsic natures of MOFs make them to be good sorbents for the d-SPE technique. However, the d-SPE based methods by using MOFs as the sorbents are less explored in monitoring food safety. One restraining factor is the low thermal and chemical stability of MOFs (Duo, Wang, Wang, Lu, & Liang, 2018). In recent years, a typical Zr-MOF UiO-66, which has been characterized with highly thermal and chemical stability, low cost and large surface area, has drawn great attentions (Cavka et al., 2008; Xiao et al., 2018). In addition, we noticed that UiO-66 contains abundant hydroxyl and aromatic groups, which provides lots of adsorption sites for pesticides via hydrogen bonding and π - π stacking interactions. And UiO-66 has uniform micropores with the apertures of ca. 0.7 and 1.0 nm (Han et al., 2015), and these uniform pores can effectively exclude the vegetable matrix compounds that are generally with large molecular size and allow the relative smaller pesticides to enter. It could significantly reduce the matrix interference. These imply that UiO-66 may be an ideal sorbent for developing the efficient d-SPE method for pesticide residues analysis in vegetables.

Herein, the aim of the current report was to develop and evaluate an efficient d-SPE technique for assaying OPP and PYR in commonly consumed vegetables. In this work, UiO-66 was synthesized in our lab and used to directly adsorb the OPP and PYR from crude vegetable extracts. The OPP and PYR were determined by gas chromatography-mass spectrometry (GC-MS). The condition optimization of the new proposed d-SPE procedure was carried out based on orthogonal array experimental design. The linearity, detection limits, recoveries, precision and matrix effect of the developed method was evaluated. Furthermore, the current established method was applied to analyze OPP and PYR residues in organic and conventional vegetables.

2. Materials and methods

2.1. Analytes and reagents

Six pesticide standards including parathion (purity 99.99%), isocarbophos (purity 99.99%), triazophos (purity 99.99%), bifenthrin (purity 99.99%), permethrin (purity 99.99%) and fenvalerate (purity 99.99%), were received from Sigma-Aldrich (St. Louis, MO, USA). The standard stock solutions of each pesticide were prepared with acetone. These stock solutions were used to prepare the different concentrations of mixed standard working solutions by stepwise dilution with *n*-hexane. The different concentrations of matrix-matched standards were made by dissolving the appropriate volumes of mixed standard working solutions

in blank matrix extracts. All solutions were placed at 4 °C in the fridge. Methanol, ethyl acetate, and acetonitrile were HPLC-grade and purchased from Anhui Fulltime Specialized Solvents & Reagents CO., LTD. (Anhui, China). HPLC-grade acetone and *n*-hexane were purchased from Fisher Scientific Company (Fair Lawn, NJ, USA). The terephthalic acid (H₂BDC), *N,N*-dimethylformamide (DMF), ammonia solution (NH₃·H₂O) and Zirconium chloride (ZrCl₄) were AR grade and obtained from Sinopharm chemical reagent Co., Ltd. (Shanghai, China).

2.2. Preparation of UiO-66

UiO-66 was prepared by the procedures reported in our previous publication (Mao, Yan, Wan, Luo, & Yang, 2019). In brief, 1.27 g of H₂BDC and 20 mL of DMF was mixed in a 100 mL beaker. After stirring for 15 min in a vortex mixer (VWR, Germany), 0.65 mL of NH₃·H₂O (2 mol/L) was added. In another 100 mL beaker, 20 mL DMF was used to dissolve ZrCl₄ (1.8 g) with stirring for 30 min. Subsequently, the prepared H₂BDC solution was slowly added into the ZrCl₄ solution and kept under stirring for 20 min. Then, 60 mL DMF was added into the above solution and kept under mixing for 15 min. Later, the final mixture was separately transferred into ten Teflon liner stainless steel autoclaves (15 mL) with equal volume solution and reacted at 120 °C for 24 h in an oven. Finally, the resulting product was separated via centrifuging (9000 × *g* for 10 min), washing with DMF, exchanging with methanol for three times (activation) and drying at 100 °C under vacuum overnight. The obtained powder was UiO-66.

2.3. Characterizations of UiO-66

Puxi XD-3 diffractometer using Cu K α radiation was used to perform the X-ray diffraction (XRD) experiments. The scan speed was set at 2°/min in the 2 θ range from 5 to 45°. Fourier transform-infrared spectrum (FT-IR) was performed on a Nicolet-5700 spectrophotometer via recording information within 4000–400 cm⁻¹ regions using KBr discs. Scanning electron microscope (SEM) image of the prepared UiO-66 was performed on a JEOL JSM-6701F field emission model. N₂ sorption-desorption isotherm was tested by Quantachrome Autosorb iQ2 analyzer at 77 K. the UiO-66 was activated at 200 °C for 12 h under higher vacuum before analysis. The multi-point Brunauer-Emmett-Teller (BET) equation was selected to estimate the surface area. Pore size distributions were derived from the nonlocal density functional theory model.

2.4. Sample preparation

Ten different conventional vegetables, which included lettuce, long bean, tomato, carrot, broccoli, cucumber, celery, spinach, cabbage, and mushroom, were obtained from Shengsong supermarkets in Singapore. The corresponding organic vegetables were obtained from Quanfa organic farm in Singapore. After being transported to laboratory, the vegetables were homogenized via a BL-1522 electric blender (AKIRA, Singapore). In the study, the organic lettuce sample without target pesticide was chosen as blank matrix sample to make matrix-matched standards, optimization experiments and recovery experiments. For the optimization experiments, 5.0 g homogenized organic lettuce was spiked with the target pesticides (50 ng/g) for the test. For the recovery experiment, 5.0 g of homogenized organic lettuce was spiked at three different volumes (100, 250, 500 μ L) of mixture standards (1 μ g/mL). The spiked samples were blended with vortex and stood for 2 h. Subsequently, the samples were used to test. 5 mL *n*-hexane was added into 5 g samples in the centrifuge tube. In order to ensure that *n*-hexane can interact well with vegetable matrix, the centrifuge tubes were vortex-mixed vigorously for 5 min at full speed mode. Subsequently, the mixture was centrifuged with 5810R centrifuge (Eppendorf, Singapore) at 4000 × *g* for 4 min. Finally, the supernatant extracts were collected.

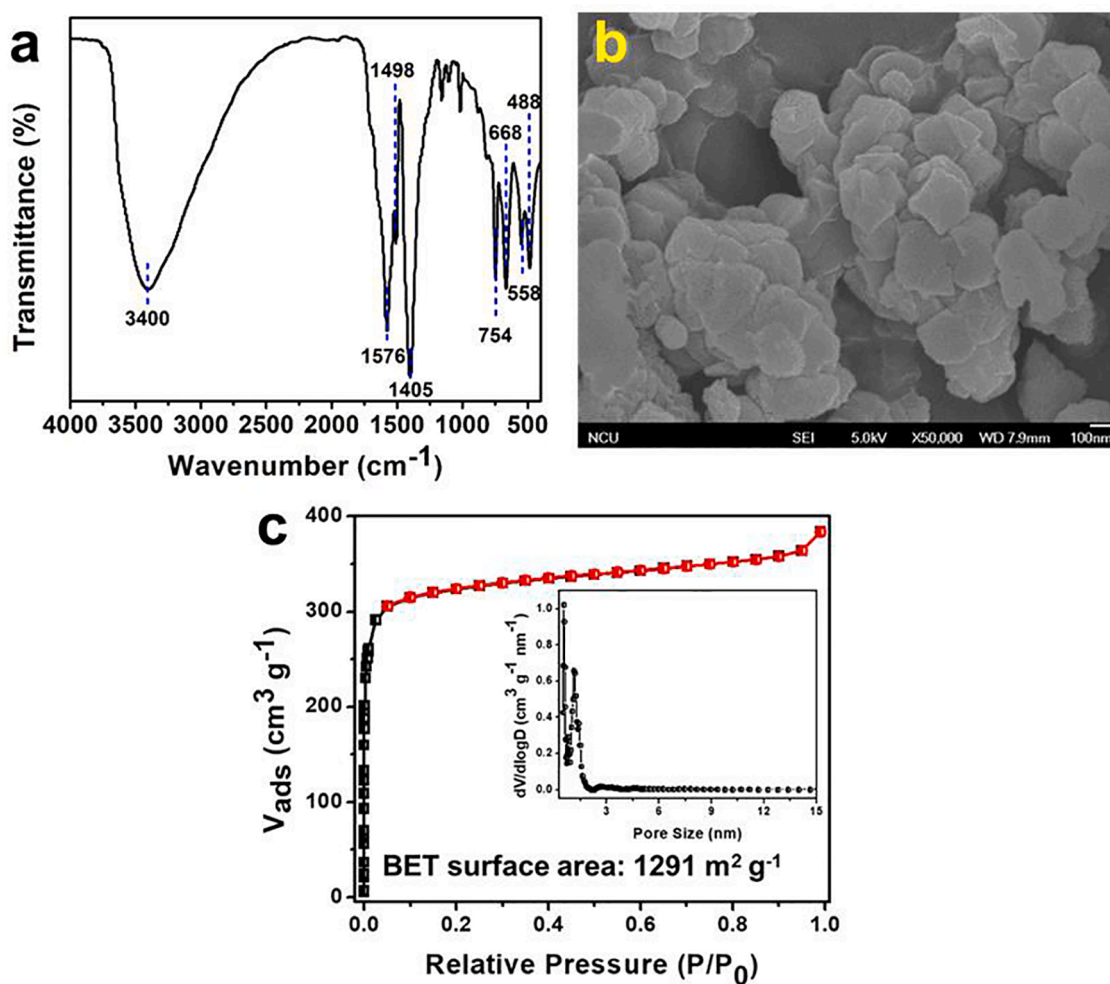


Fig. 1. Characterization of the synthesized UiO-66: (a) FT-IR spectra; (b) SEM image; (c) N_2 sorption isotherm and pore size distributions.

2.5. Procedure of d-SPE

The d-SPE procedure was performed with 15 mL centrifuge tube. Firstly, 1 mL above sample extraction solution and 50 mg UiO-66 were added into the tube. Then, the adsorption experiment was conducted under ultrasound-assisted extraction for 20 min. Subsequently, the sample solution was decanted by centrifugation at $4000 \times g$ for 4 min. Subsequently, the analytes were eluted from UiO-66 by 3 mL acetone for 10 min in an ultrasonic cleaner. The obtained eluate was collected through centrifugation and dried by a B-490 rotary vacuum evaporator (BÜCHI Labortechnik AG, Switzerland). The residue was redissolved with 300 μ L acetone using a vortex agitator, and then filtered for quantitative analysis.

2.6. GC-MS analysis

The analysis was performed by Shimadzu GC 2010 gas chromatography system integrated with Shimadzu AOC-5000 plus autosampler and mass selective detector Shimadzu GCMS-QP2010 Ultra. The target pesticides were detected through the following conditions: the injector was 260 °C and the injector volume was 1 μ L. The carrier gas was helium gas (purity 99.999%) with a constant flow rate (1.0 mL/min). The analytical column was BPX-5 fused silica capillary column (30 m, 0.25 mm i.d., 0.25 μ m film thickness). The programmed temperature was as below: initially at 140 °C, held for 2 min; then ramp to 220 °C at 20 °C/min, held for 4 min; finally increase to 280 °C at 10 °C/min, held for 6 min. The MS transfer-line temperature and ion source temperature were

both 280 °C. The electron impact mode at 70 eV was set. Solvent delay was 10 min. The target pesticides were analyzed with selected ion monitoring mode (SIM). Qualitative and quantitative ions in SIM programme were selected by injection of individual pesticide standard in full scan mode. The formulas, molecular weights, log K_{ow} , retention times, qualitative and quantitative ions of target pesticides were listed in Table S1.

2.7. Method validation

The developed method was evaluated for validation parameters in terms of linearity, calibration data, matrix effect (ME), detection limits (LOD), quantification limits (LOQ), accuracy and precision. Linearity was tested through different concentration levels in pure solvent standards and matrix-matched standards (10–500 ng/g). The LOD and LOQ were obtained through stepwise dilution of mixed standard working solutions (10 ng/g) with *n*-hexane to reach the ratio of signal to noise of 3 and 10, respectively. ME was assessed by the slopes in the two above-mentioned calibration data. The accuracy was assessed by recovery. The precision was evaluated in term of relative standard deviations (RSDs) of recovery experiments.

2.8. Statistical analysis

All the experiments were conducted in triplicate independently to obtain reliable results, and the average mean was chosen as the response. IBM SPSS software was used to perform the analysis of

Table 1
The factors and levels in L₉ (3⁴) Orthogonal Array Design, along with the results of optimization experiments.

Trial NO.	Factor(%) ± SD (n = 3)			Average recovery					
	A: sorbent amount (mg)	B: adsorption time (min)	C: desorption time (min)	Parathion	Isocarbophos	Triazophos	Bifenthrin	Permethrin	Fenvalerate
1	1 (10)	1 (5)	1 (10)	73.6 ± 2.6	80.1 ± 5.2	105.8 ± 14.6	43.8 ± 4.5	22.9 ± 0.5	60.3 ± 1.7
2	1 (10)	2 (10)	2 (20)	72.4 ± 3.5	80.5 ± 3.0	109.7 ± 5.1	52.4 ± 5.1	21.9 ± 0.1	56.3 ± 2.7
3	1 (10)	3 (20)	3 (30)	78.7 ± 1.9	85.8 ± 8.3	133.6 ± 12.7	58.6 ± 7.5	24.9 ± 2.2	54.0 ± 9.4
4	2 (30)	1 (5)	2 (20)	114.7 ± 8.8	37.4 ± 2.0	75.0 ± 5.9	42.4 ± 6.3	61.3 ± 5.4	38.1 ± 2.8
5	2 (30)	2 (10)	3 (30)	114.3 ± 14.1	43.2 ± 4.8	81.4 ± 10.8	46.8 ± 7.3	53.0 ± 7.1	33.8 ± 6.2
6	2 (30)	3 (20)	1 (10)	119.0 ± 9.5	38.8 ± 6.9	92.4 ± 16.7	50.0 ± 4.9	53.2 ± 2.9	31.2 ± 3.5
7	3 (50)	1 (5)	3 (30)	127.0 ± 12.6	51.2 ± 9.3	76.5 ± 9.0	60.8 ± 6.1	65.1 ± 1.9	66.2 ± 4.9
8	3 (50)	2 (10)	1 (10)	134.9 ± 4.8	74.0 ± 6.1	119.6 ± 12.1	69.3 ± 4.3	80.9 ± 3.3	87.5 ± 3.8
9	3 (50)	3 (20)	2 (20)	139.2 ± 5.4	61.4 ± 1.4	114.7 ± 1.8	65.6 ± 3.1	82.1 ± 2.5	77.6 ± 4.2
K ₁	405.1	400.7	445.8						
K ₂	375.3	444.0	434.2						
K ₃	517.9	453.6	418.3						
R	142.5	52.9	27.5						
Optimization level	A ₃	B ₃	C ₁						

Note: K_i = the mean effect in different level (i = 1, 2, 3) of each factor for all of pesticides

R = Max(K) – Min(K)

A₃: the optimization level for Factor A (sorbent amount) is level 3 (50 mg); B₃: the optimization level for Factor B (adsorption time) is level 3 (20 min); C₁: the optimization level for Factor C (desorption time) is level 1 (10 min).

variance (ANOVA). The experiment results were assessed with least significant difference (LSD). Different capital letters of each pesticide mean significantly different among different groups ($P < 0.05$) for the evaluation of sample analysis and reusability experiment.

3. Results and discussion

3.1. Material characterization

The XRD pattern of the lab prepared UiO-66 is shown in Fig. S1. The diffraction peaks was consistent with the published literature (Cavka et al., 2008; Han et al., 2015; Shahat, Hassan, Azzazy, Hosni, & Awual, 2018), suggesting the successful synthesis of UiO-66.

Fig. 1a depicts the FT-IR spectrum of as-prepared UiO-66. The peaks around 3400/488 cm⁻¹ and the peaks at 668/558 cm⁻¹ could be attributed to the vibrations of hydroxyl group and Zr-O bond of Zr₆O₄(OH)₄ clusters, respectively (Han et al., 2015; Shaik et al., 2019). The peaks at 1576/1405 cm⁻¹ and the peaks at 1498/754 cm⁻¹ could respectively be assigned to vibrations of coordination carboxylate group and benzene ring of terephthalic acid (Han et al., 2015; Yu, Li, Ng, Yang, & Wang, 2018). These further confirm the successful synthesis of UiO-66. Moreover, no significant absorption peaks related to -CH₃ group appeared in the range of 2750–3000 cm⁻¹ (Braun et al., 2011), indicating the complete removal of DMF and methanol in the pores of UiO-66.

The morphology of prepared UiO-66 was characterized by SEM. From the SEM image (Fig. 1b), as-prepared UiO-66 particles were uniform and possessed a mean size of 200 nm. The porous nature of the prepared UiO-66 was examined by N₂ sorption-desorption isotherm. As observed from Fig. 1c, the prepared UiO-66 displayed typical type-I isotherm with remarkable N₂ uptake at P/P₀ < 0.1, which proves that UiO-66 has microporous structure. The pore sizes in the UiO-66 were centered at 0.6 and 1.1 nm, the surface area was 1291 m² g⁻¹ and the pore volume was 0.594 cm³ g⁻¹, these were comparable to the previously reported data (Cavka et al., 2008; Han et al., 2015).

3.2. Optimization of sample preparation

To achieve a superior recovery in the d-SPE process, target pesticides should be easily adsorbed and desorbed completely from the adsorbent. Therefore, the experimental parameters that might impact the recovery, including desorption solvents and volumes, type of extraction, extraction temperature, sorbent amount, adsorption time, and elution time were examined in detail.

3.2.1. Effect of desorption solvent

The ability of desorption solvent significantly affects the recovery of analyte (Yu & Yang, 2017). As revealed by previous studies, UiO-66 shows sufficient stability in most of polar and nonpolar solvents (Cavka et al., 2008; Duo et al., 2018; Xiao et al., 2018). In this study, five commonly used solvents with different polarities including acetonitrile, methanol, acetone, dichloromethane, and ethyl acetate were examined as eluents. To assess their abilities of desorption, three replicate experiments were performed for each solvent. These results were plotted as line chart in Fig. S2a. The results showed that acetone exhibited the best elution ability in these studied solvents. The reason for this might be that acetone has stronger interaction with UiO-66 than target pesticides. Additionally, acetone is easier to evaporate to concentrate target analytes because of its low boiling point. Therefore, acetone was selected as desorption solvent.

3.2.2. Effect of desorption solvent volume

The effect of acetone volume was investigated range from 1 to 12 mL. As listed in Fig. S2b. The recoveries of pesticides increased when acetone increasing from 1 to 3 mL, and keep constant when acetone further increased. Therefore, 3 mL of acetone was chosen in subsequent experiments.

3.2.3. Effect of extraction type

Ultrasound assisted extraction (UAE) and vortex agitation are common and efficient techniques to enhance extraction performance (March & Cerdà, 2016). Thus, both techniques were investigated and compared. Comparable results for two techniques are obtained when the treatment time is longer than 10 min. In addition, UAE can process samples in

Table 2
Analytical performance of organophosphorus and pyrethroids in pure solvent and organic lettuce sample.

pesticide	Linear range (ng/g)	Pure standard calibration curves	R ²	matched-matrix standard calibration curves	R ²	LOD (ng/g)	LOQ (ng/g)	MRL ^a (ng/g)	MRL ^b (ng/g)	ME (%)
Parathion	10–500	y = 1085.7x + 4990	0.9981	y = 1092.7x + 18240	0.9956	1.2	4.1	500–700	–	0.6
Isocarbophos	10–500	y = 809.13x + 1012.7	0.9990	y = 871.82x + 5073.9	0.9950	1.9	6.5	–	–	7.8
Triazophos	10–500	y = 443.75x + 214.51	0.9980	y = 575.36x + 1569.6	0.9941	2.0	6.5	–	–	29.7
Bifenthrin	10–500	y = 2105.0x + 2745.7	0.9999	y = 2511.0x + 2500.3	0.9997	1.1	3.8	50–300	50–300	19.3
Permethrin	10–500	y = 2146.8x + 172.01	0.9980	y = 2310.0x + 67142	0.9961	0.6	2.1	50–5000	50–5000	7.6
Fenvalerate	10–500	y = 1494.6x + 545.71	0.9998	y = 1687.2x + 1590.5	0.9997	0.4	1.4	50–5000	50–3000	12.9

Note: ^a Source:SFA, Singapore Food Agency, Food with maximum amounts of pesticides.

^b Source:CAC, Codex Alimentarius Commission, Codex Alimentarius Commission Pesticide Residues in Food Online Database.

batches and achieve automatic processing, while vortex agitation is done manually and only process limited samples each time. Thus, UAE was selected in this study.

3.2.4. Effect of extraction temperature

Extraction temperature is one of parameters which may affect the extraction efficiency (Tian, Sun, Wang, Luo, & Feng, 2018). To assess the effect of extraction temperature for OPP and PYR pesticides, the temperature of the ultrasound water bath was investigated from room temperature (22 °C) to 50 °C. As revealed in Fig. S2c, obvious decrease in recoveries for all target analytes is observed as the temperature increase from 22 to 30 °C. For temperatures >30 °C, the recovery of isocarbophos is further decrease. This phenomenon may be explained by that adsorption process is exothermic (Tian et al., 2018; Zhang, Yang, Wang, Wang, & Wang, 2016). On the basis of the above test results, room temperature at about 22 °C was selected for the extraction procedure.

3.2.5. Orthogonal array experimental design

To obtain better efficiency, some important experimental conditions need to be carefully assessed and evaluated. In this study, the effect of

sorbent amount, adsorption time and desorption time on recovery were optimized through a cost-effective statistical tactic, orthogonal array experimental design (Mao et al., 2019). Table 1 displays the factor and level in the L₉ (3⁴) orthogonal matrix. The factor A, B, and C express as sorbent amount, adsorption time, and desorption time, respectively. The three different levels of factor were expressed with the number of 1, 2 and 3.

For each trial, three parallel samples were implemented, thus the recovery results of the six pesticides in each trial are the means of three parallel tests (shown in Table 1). The mean effects for each factor at three different levels were calculated and expressed as K₁, K₂, and K₃. The importance of the factor is assessed using range value (R value) (Mao et al., 2019). Greater R value means that the factor is more significant to recovery. As shown in Table 1, the R value of factor A is 142.5, much greater than 52.9, and 27.5 resulted from B, and C, respectively. That means that the sorbent amount is the most significant effect to recovery. The optimum experimental parameters deduced from the results of orthogonal array experimental design were as follows: sorbent amount: 50 mg; adsorption time: 20 min; and desorption time: 10 min.

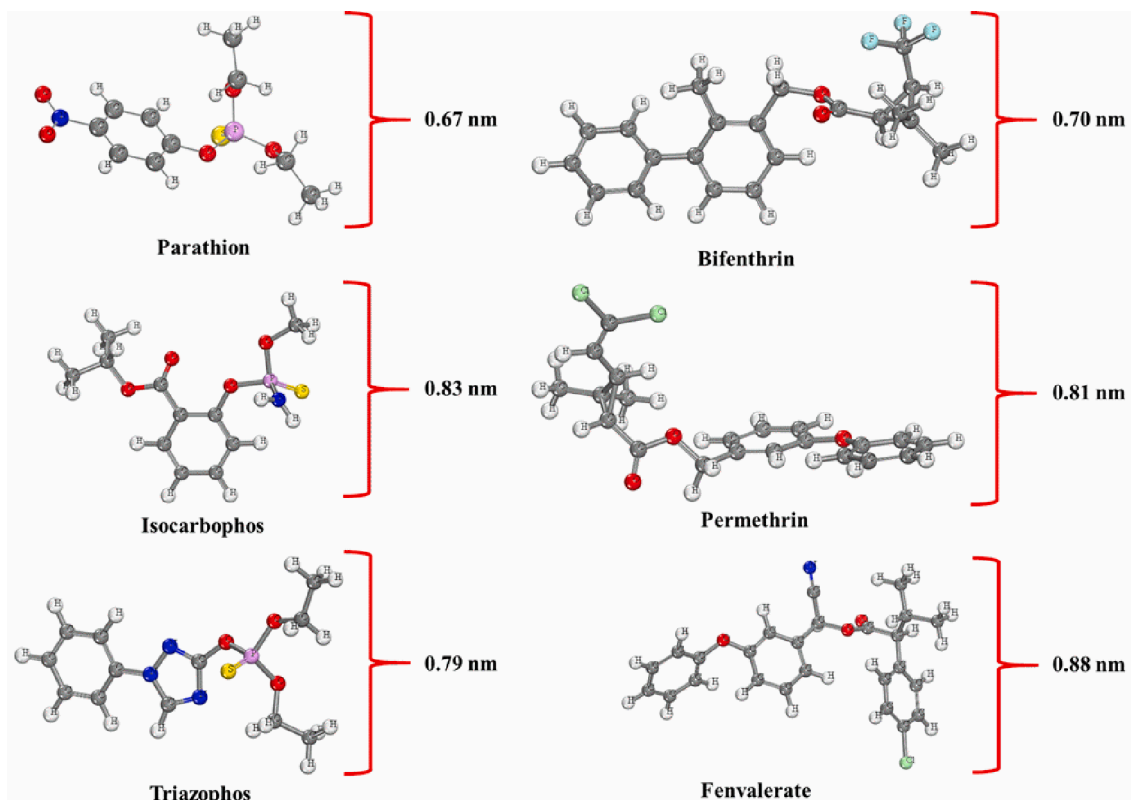


Fig. 2. The structure and size of pesticide optimized with Gaussian 09 W program package and Gview 5.0.

3.3. Reusability of UiO-66

Reusability of adsorbent is a key parameter influencing the practical application and cost of analytical method (Awual et al., 2020; Awual, 2019). Thus, the reusability of UiO-66 was inspected in this work. In order to make sure no pesticide residue in UiO-66 before the next d-SPE process, the used UiO-66 was washed again according to the elution step in the section of "2.5. Procedure of d-SPE". Then, UiO-66 was collected by drying at 100 °C for 1 h and subsequently used in the next d-SPE experiment. As demonstrated in Fig. S3, the recoveries of most of pesticides remain and have no significant difference even after 20 runs, which indicated the excellent reusability and stability of UiO-66.

3.4. Matrix effect

Chromatographic analysis is widespread adopted technique in pesticide analysis. However, the matrix effect (ME) is one of fundamental problem and has been usually encountered in the chromatographic analysis methods (Mao et al., 2019; Rutkowska et al., 2019). It will result in adversely affect for quantitative analysis, especially on determining trace amount of pesticide residue in complex samples (Rutkowska et al., 2019). Thus, the ME of the present method was evaluated. Two sets of standard solutions containing the six target pesticides were made according to the description in the section "2.1. Chemicals and reagents". The ME is calculated with the slopes in pure standard calibration curves and matrix-matched standard calibration curves with the equation (Lozano et al., 2014).

$$ME(\%) = \left(\left(\frac{\text{Slope of calibration curve in matrix}}{\text{Slope of calibration curve in solvent}} \right) - 1 \right) \times 100$$

The calculated MEs are listed in Table 2. It can be seen that the MEs for the studied pesticides were among ca. $\pm 20\%$, which reveals that the matrix effect can be neglected in the present method (Song et al., 2018). Based on this result, pure standard calibration curves and matrix-matched standard calibration curves both can be applied to quantification. The latter were used to quantitative analysis in this work.

3.5. Adsorption pesticides from crude vegetable extract

The structures of studied pesticides were evaluated with Gaussian 09 W program package and Gview 5.0. The detailed calculation method for the sizes of pesticides was described in Supplementary material. As illustrated in Fig. 2, the sizes of targeted pesticides were all smaller than the pore window of UiO-66 (1.1 nm). It means that these studied pesticides in the extracts of vegetables could enter to the pores of UiO-66 and be absorbed via weak interaction such as Van der Waals interaction, π - π stacking or hydrogen bonding (Mao et al., 2019), while the relatively large matrix compounds (polysaccharides, proteins, pigments, vitamins, etc.) were effectively excluded by the pores of UiO-66. This size sieving action of UiO-66 could well purify the analytes and effectively reduce the interference of matrix compounds. It is the possible reason for the unremarkable matrix effect in the current method.

3.6. Performance evaluation of the method

Under optimum conditions, the prepared standard solutions were detected by GC-MS. Each concentration level run three times. The calibration data are summarized in Table 2. As shown in Table 2, excellent linearity was achieved, with correlation coefficient (R^2) ranged from 0.9941 to 0.9999 (Table 2). The LODs and LOQs of the target pesticides were 0.4–2.0 ng/g, and 1.4–6.5 ng/g, respectively. The LOQ values were lower than MRLs set by Singapore Food Agency and Codex Alimentarius Commission (listed in Table 2). These results prove that the developed method is sufficiently sensitive to test pesticide residue in food samples.

Table 3

The recovery and precision of recovery validation experiment in the spiked sample.

Pesticides	Spiked level (ng/g)	Intra-day (n = 6)		Inter-day (n = 36)	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Parathion	20.0	93.5	13.4	97.0	12.6
	50.0	97.8	6.5	103.3	10.7
	100.0	87.6	6.8	91.3	9.6
Isocarbophos	20.0	105.5	7.9	113.2	9.9
	50.0	90.2	5.6	105.7	13.5
	100.0	72.0	6.5	78.6	9.4
Triazophos	20.0	111.3	11.5	116.8	10.4
	50.0	107.0	7.3	117.5	10.0
	100.0	88.9	6.7	96.2	9.0
Bifenthrin	20.0	81.4	9.8	88.2	11.4
	50.0	63.6	5.7	75.3	12.6
	100.0	60.9	8.4	64.9	8.3
Permethrin	20.0	111.7	10.7	112.1	10.8
	50.0	80.5	7.9	84.6	11.3
	100.0	74.5	5.8	80.9	9.2
Fenvalerate	20.0	102.6	14.2	104.5	13.1
	50.0	77.4	11.5	82.5	14.6
	100.0	81.3	5.9	87.1	9.4

Recovery validation experiment was implemented for analyzing accuracy and precision. Table 3 shows the recoveries and RSDs of recovery experiment. Most of pesticides recoveries were 70–120%, which were in agreement with requirements of European Commission, Health & Consumer Protection Directorate-General (European Commission, 2013). The RSDs of the intra-day and inter-day experiments were 5.6–14.2 and 8.3–14.6%, respectively, which fulfilled the mentioned standard of RSD $\leq 20\%$ (European Commission, 2013). According to these results, the developed method is reliable to detect OPP and PYR residues in vegetables.

3.7. Comparison to previous reported methods

To evaluate the proposed method, the present method was compared to several reported methods for pesticide analysis in vegetables. Important parameters such as the method procedures, solvent amount, sorbent amount, sorbent reusability, LOD, LOQ, ME, recovery and RSD are taken into account.

The data are shown in Table S3. From Table S3, the LODs and LOQs of the proposed method in this work are lower than or comparable to most of published methods (Anastassiades et al., 2003; Han et al., 2016; Ling & Huang, 1995; Sang, Wang, Tsoi, & Leung, 2013; Wang, Chow, Leung, & Chang, 2012; Zawiyah et al., 2007; Zhou et al., 2015). Meanwhile, good recovery and deviation are also achieved as the reported pretreatment technique. This revealed that the method is sensitive, accurate and precise. The ME of pesticides was well eliminated in this designed d-SPE procedure. This is superior to that of published methods (Han et al., 2016; Wang et al., 2012; Zhou et al., 2015).

Moreover, Table S3 also reveals that the current method consumes less solvent and sorbent. And the sorbent UiO-66 shows perfect performance and can be easily recycled. The sorbents are usually disposable in previous methods, adding the extra cost (Anastassiades et al., 2003; Han et al., 2016; Ling & Huang, 1995; Sang et al., 2013; Wang et al., 2012; Zawiyah et al., 2007; Zhou et al., 2015). These suggest that the developed method is also an environmentally-friendly and economical method for the detection of OPP and PYR in vegetables.

3.8. Analysis of organic and conventional vegetables samples

To verify the applicability and feasibility, ten commonly consumed

Table 4
The analytical results of organic and conventional vegetable sample.

Pesticide	Organic Lettuce		Conventional Lettuce		Organic Long bean		Conventional Long bean	
	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)
Parathion	ND ^A	102.2 ± 6.3	ND ^A	99.7 ± 12.6	ND ^B	88.9 ± 5.9	9.7 ± 0.7 ^A	100.5 ± 7.9
Isocarbophos	ND ^A	93.7 ± 5.3	ND ^A	93.7 ± 7.5	ND ^B	73.6 ± 6.3	5.4 ± 0.5 ^A	115.6 ± 6.0
Triazophos	ND ^A	112.0 ± 8.2	ND ^A	114.2 ± 11.0	ND ^A	86.4 ± 2.2	ND ^A	105.1 ± 14.1
Bifenthrin	ND ^A	66.3 ± 3.1	ND ^A	68.8 ± 7.0	ND ^A	64.3 ± 5.0	ND ^A	60.4 ± 1.1
Permethrin	ND ^A	83.7 ± 7.8	ND ^A	80.0 ± 9.2	ND ^A	86.4 ± 6.2	ND ^A	79.1 ± 1.5
Fenvalerate	ND ^A	82.4 ± 9.8	ND ^A	76.4 ± 6.7	ND ^A	92.6 ± 7.4	ND ^A	79.2 ± 5.8
Pesticide	Organic Tomato		Conventional Tomato		Organic Carrot		Conventional Carrot	
	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)
Parathion	ND ^A	100.1 ± 4.2	ND ^A	121.4 ± 3.0	ND ^A	74.1 ± 5.3	ND ^A	84.3 ± 5.9
Isocarbophos	ND ^A	77.9 ± 9.3	ND ^A	93.6 ± 4.1	ND ^A	75.4 ± 3.9	23.9 ± 2.1 ^A	85.0 ± 10.2
Triazophos	ND ^A	103.0 ± 9.7	ND ^A	122.9 ± 5.1	ND ^A	75.0 ± 7.1	ND ^A	79.8 ± 8.3
Bifenthrin	ND ^A	65.6 ± 4.2	ND ^A	69.9 ± 2.2	ND ^A	63.5 ± 2.8	ND ^A	63.2 ± 8.7
Permethrin	6.0 ± 0.5 ^B	83.9 ± 6.3	21.2 ± 0.7 ^A	99.8 ± 0.8	ND ^A	71.7 ± 5.3	ND ^A	76.6 ± 7.6
Fenvalerate	ND ^A	78.0 ± 5.2	ND ^A	95.0 ± 4.1	ND ^A	79.8 ± 9.5	ND ^A	93.7 ± 8.0
Pesticide	Organic Broccoli		Conventional Broccoli		Organic Cucumber		Conventional Cucumber	
	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)
Parathion	ND ^B	104.0 ± 6.2	13.7 ± 0.7 ^A	97.4 ± 10.4	ND ^B	90.1 ± 4.0	14.0 ± 0.9 ^A	113.5 ± 10.2
Isocarbophos	24.9 ± 2.1 ^A	111.3 ± 11.8	12.2 ± 1.9 ^B	123.4 ± 2.7	ND ^B	117.1 ± 3.4	14.7 ± 1.5 ^A	95.6 ± 5.7
Triazophos	ND ^A	101.9 ± 4.3	ND ^A	105.9 ± 9.7	ND ^A	83.4 ± 3.8	ND ^A	115.5 ± 9.1
Bifenthrin	ND ^A	61.9 ± 4.2	ND ^A	67.4 ± 1.1	ND ^A	63.7 ± 6.2	ND ^A	67.4 ± 8.5
Permethrin	8.6 ± 0.7 ^A	85.2 ± 2.6	ND ^B	76.9 ± 5.6	ND ^A	96.5 ± 6.1	ND ^A	95.7 ± 9.7
Fenvalerate	ND ^A	89.1 ± 12.3	ND ^A	69.1 ± 4.6	ND ^A	95.2 ± 11.7	ND ^A	97.6 ± 9.3
Pesticide	Organic Celery		Conventional Celery		Organic Spinach		Conventional Spinach	
	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)
Parathion	ND ^B	89.3 ± 1.4	9.9 ± 1.2 ^A	99.6 ± 11.4	ND ^B	104.1 ± 3.3	13.6 ± 0.5 ^A	124.1 ± 5.8
Isocarbophos	ND ^A	86.4 ± 2.9	ND ^A	114.5 ± 12.3	ND ^A	85.4 ± 3.2	ND ^A	119.4 ± 5.2
Triazophos	ND ^A	104.7 ± 1.5	ND ^A	88.6 ± 8.6	ND ^A	95.0 ± 3.1	ND ^A	113.7 ± 6.6
Bifenthrin	ND ^A	72.3 ± 1.4	ND ^A	78.0 ± 7.7	5.5 ± 0.8 ^A	63.5 ± 2.2	ND ^B	65.6 ± 5.7
Permethrin	ND ^A	81.3 ± 1.5	ND ^A	119.8 ± 3.8	ND ^A	81.7 ± 4.3	ND ^A	95.6 ± 4.6
Fenvalerate	ND ^A	94.7 ± 1.6	ND ^A	121.4 ± 3.7	ND ^A	99.8 ± 9.1	ND ^A	103.5 ± 13.8
Pesticide	Organic Cabbage		Conventional Cabbage		Organic Mushroom		Conventional Mushroom	
	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)	Detected (ng/g)	Recovery (%)
Parathion	ND ^B	80.5 ± 1.4	13.5 ± 0.9 ^A	118.5 ± 6.6	ND ^B	112.6 ± 1.4	8.2 ± 0.5 ^A	102.7 ± 5.2
Isocarbophos	ND ^A	64.7 ± 1.3	ND ^A	108.4 ± 8.6	ND ^B	66.0 ± 1.4	3.6 ± 1.4 ^A	92.7 ± 5.1
Triazophos	ND ^A	108.9 ± 5.1	ND ^A	119.8 ± 4.3	ND ^A	114.8 ± 3.8	ND ^A	95.3 ± 4.0
Bifenthrin	ND ^A	60.8 ± 3.2	ND ^A	79.7 ± 11.3	ND ^A	65.2 ± 1.2	ND ^A	61.8 ± 2.3
Permethrin	7.8 ± 0.5 ^A	74.2 ± 1.3	ND ^B	96.2 ± 10.3	6.6 ± 0.7 ^A	88.9 ± 2.1	ND ^B	83.5 ± 4.5
Fenvalerate	ND ^A	80.1 ± 4.6	ND ^A	96.4 ± 4.9	ND ^A	97.6 ± 1.0	ND ^A	106.4 ± 7.8

Note: ND: not detectable or lower than limits of detection.

Capital letters A and B: Within each pesticide, means with different capital letters are significantly different ($P < 0.05$) between organic and corresponding conventional vegetable samples.

vegetables were tested with this established method. For each vegetable, the sample analysis experiment and the sample spiked experiment (50 ng/g) were also carried out in triplicate and independently. As revealed in Table 4, the recovery in studied vegetables almost are in the range of 70–120%, indicating the method is reliable for detecting the OPP and PYR pesticides in various vegetables.

The organic foods are becoming more and more popular because chemical pesticides and fertilizers are forbidden in the planting process. In recent years, researchers have focused on the microbiological safety (Mao et al., 2020), less attention has been paid to pesticide residues in organic foods (Baker, Benbrook, Groth III, & Benbrook, 2002). In this work, this proposed technique was introduced to detect pesticide in the corresponding organic vegetables in Singapore. The analytical results of real samples are shown in Table 4. As presented in Table 4, the pesticides are detected in the both of organic and conventional vegetables. For lettuce and carrot samples, no significant difference was found in

organic and corresponding conventional vegetable samples. For other eight vegetable samples, the concentrations of some pesticides were significant difference between organic and corresponding conventional vegetable samples in this work. Luckily, the concentrations of pesticides in all of vegetables are not over the MRLs provided in Table 2. It means that the consumption of these vegetables has a low risk, especially for the consumption of organic vegetables.

4. Conclusion

In this study, a microporous UiO-66 has been successfully developed and proved as an efficient sorbent in d-SPE technique to determine pesticide residues in vegetables. In this method, the sorbent UiO-66 effectively adsorbed the target pesticides while excluded the matrix compounds from vegetables. No additional cleanup procedure was needed and the matrix effect could be well eliminated. Meanwhile, the

developed method was validated to be excellent performance with satisfactory sensitivity, accuracy and precision. And the sorbent UiO-66 could be easily recycled and reused at least 20 times. These indicate that the current method is a simple, reliable and robust method for the determination of pesticide residues in vegetables. Moreover, the established method was applied to detect the OPP and PYR in various organic and conventional vegetables. This work provides a novel route to solve the problem for detecting the trace amount hazardous compounds in the complex vegetable matrices.

CRedit authorship contribution statement

Xuejin Mao: Conceptualization, Investigation, Methodology, Validation, Formal analysis, Data curation, Writing - original draft. **Weiming Xiao:** Conceptualization, Investigation, Data curation, Formal analysis, Writing - original draft. **Yiqun Wan:** Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Zhanming Li:** Investigation, Methodology. **Dongmei Luo:** Resources, Formal analysis. **Hongshun Yang:** Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2020.128807>.

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