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Modified Peanut Shell as an Eco-Friendly Biosorbent for Effective Extraction of Triazole Fungicide Residues in Surface Water and Honey Samples before Their Determination by High-Performance Liquid Chromatography

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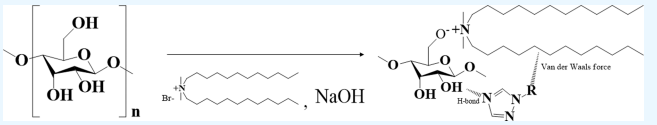
ABSTRACT: An eco-friendly sample preparation method that is based on the use of a modified peanut shell as an efficient biosorbent for the extraction of triazole residues before their analysis by high-performance liquid chromatography was reported. The four triazole fungicides were separated on a Purospher STAR RP-18 endcapped (4.6 × 150 mm, 5 μm) column with a mobile phase of 50% (v/v) acetonitrile at a flow rate of 1.0 mL min^{-1} and detection wavelength set at 220 nm. Peanut shells modified by didodecyldimethylammonium bromide were selected as an effective biosorbent material in the microextraction method. Scanning electron microscopy, transmission electron microscopy, and Fourier transform infrared spectroscopy were used to characterize the biosorbent. The effect of dominant parameters on the proposed microextraction method including the amount of sorbent, kind and concentration of surfactant, sodium hydroxide concentration, kind and amount of salt, sample volume, adsorption time, kind and volume desorption solvent, and desorption time was studied. Under the optimum condition, a good analytical performance for the proposed microextraction method was obtained with a wide linear range within the range of 9−1000 μg L^{-1}, and low limits of detection (0.03 μg L^{-1} for all analytes) were obtained. Enrichment factors were achieved within the range of 30−51. The intra and interday precision values were evaluated in terms of percentage relative standard deviations (%RSD) and were less than 0.09 and 5.34% for the retention time and peak area, respectively. The proposed microextraction methods were used for extraction and analysis of triazole fungicides in water and honey samples. The recoveries in a satisfactory range of 70.0−118.8% were obtained.



1. INTRODUCTION

Biological carbon is a carbon-rich byproduct derived by pyrolyzing biomass (e.g., agricultural waste, wood chips, algae, manure, sewage sludge, etc.) under oxygen-limited conditions. Because of its property, it has been widely used as the low-cost adsorbent to adsorb heavy metals, nutrients (ammonium, nitrate, and phosphate), dyes, and organic contaminants from aqueous solutions.[1,2] Therefore, the development of proper utilization of these materials is necessary. They mainly include wheat straw, straw, corn cob, bagasse, peanut shell, wood chips, leaves, and so on.[3] A peanut shell is a kind of agricultural waste with low density and high volume, which was always used in animal feed formulations or energy for burning. It is mainly composed of lignin, hemicellulose, and cellulose and includes many hydroxyl groups, carboxyl groups, and other groups,[4] which are beneficial to the adsorption of some pollutants and can be applied in the field of decontamination. However, if a peanut shell is directly used as an adsorbent, there would be some disadvantages, such as lower adsorption capacity toward negative pollutants and secondary pollution from leaching some pollutants (COD, BOD) existing in peanut shells.[5] To make it more valuable and improve its service efficiency, attention has been focused on the utilization of peanut shells as an adsorbent in recent years.[6] However, because of the negatively charged surface and little anion exchange capacity, biological carbon generally has no capability to adsorb anions.[7] In general, the use of biosorbents from raw peanut shells has been reported mostly for the removal of cationic compounds, such as metals,[8,9] cationic dyes,[10,11] and pesticides.[12] However, the extraction of triazole fungicides which are nonionic compounds by using a peanut shell biosorbent material has not been reported in the literature.

Triazole fungicides are a group of highly effective systemic fungicides containing a hydroxyl group (ketone group), a substituted phenyl group, and a 1,2,4-triazole group in the main

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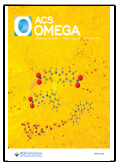

chain.[13] Triazole fungicides have a broad fungicidal spectrum and good control effects on a variety of crop diseases. Because of their antifungal properties, they are widely used for controlling diseases widely used in agriculture for prevention of various fungal diseases such as powdery mildew, gray mold, spotted deciduous disease, black star disease, brown spot disease, and rust disease in agricultural products.[14,15] However, triazole fungicides have high stability and lipophilicity and a long residual duration and are not easily degraded, leading to easy accumulation in human and environmental media. Codex Alimentarius Commission (CAC) have set up the maximum residue limits (MRLs) of triazole fungicides in different matrices to protect human health.[13] For example, the MRL of hexaconazole, triadimefon, and bitertanol is 0.01−0.02 mg kg^{-1}; the MRL of tebuconazole is 0.02−5.0 mg kg^{-1}; and the MRL of myclobutanil is 0.05−3.0 mg kg^{-1}.[13] Thus, the determination of triazole fungicides at a low concentration level in food and the environment is important.[16]

High-performance liquid chromatography (HPLC)[17,18] and gas chromatography (GC)[19,20] with different detection systems have become more favorite methods for triazole fungicide determinations. However, it is difficult for these methods to detect them directly because triazole fungicides are usually found at a low concentration level in real sample matrices.[21] Therefore, sensitive sample preparation is of interest for the determination of triazole residues in various matrices.

Solid-phase extraction (SPE)[22−24] is widely used for the extraction and enrichment of trace target analytes, especially in complex sample matrices. However, the traditional materials used for SPE, such as silica-based generic sorbents (e.g., C8, C18), have poor selectivity and specificity, leading to unavoidable matrix interference, and cannot satisfy the requirements for detection of triazoles at low concentration levels.[25−27] However, these methods require a large amount of organic solvents and considerable time and usually have poor accuracy and low recovery.[28] To solve these problems, the efficient methods namely microsolid phase extraction (μ-SPE) are investigated. Less organic solvent usage and low consumption of sorbent are the benefits of μ-SPE over traditional extraction methods. Consequently, it has some advantages of simplicity, rapidity, high reusability, and low solvent consumption.[29]

The purpose of this study was to modify peanut shells as an effective biosorbent for applications in the μ-SPE for triazole fungicides. Another way of peanut shell utilization in decontamination of solution containing triazole fungicides is explored. Various μ-SPE parameters were optimized to obtain the best extraction efficiency. Single chain cationic surfactant (DTAB) and double chain cationic surfactant (DDAB) were studied because of their lower price and more availability than other kinds of cationic surfactants. The developed μ-SPE method coupled with the HPLC analysis has been favorably applied to determine the triazole fungicide residues in water and honey samples.

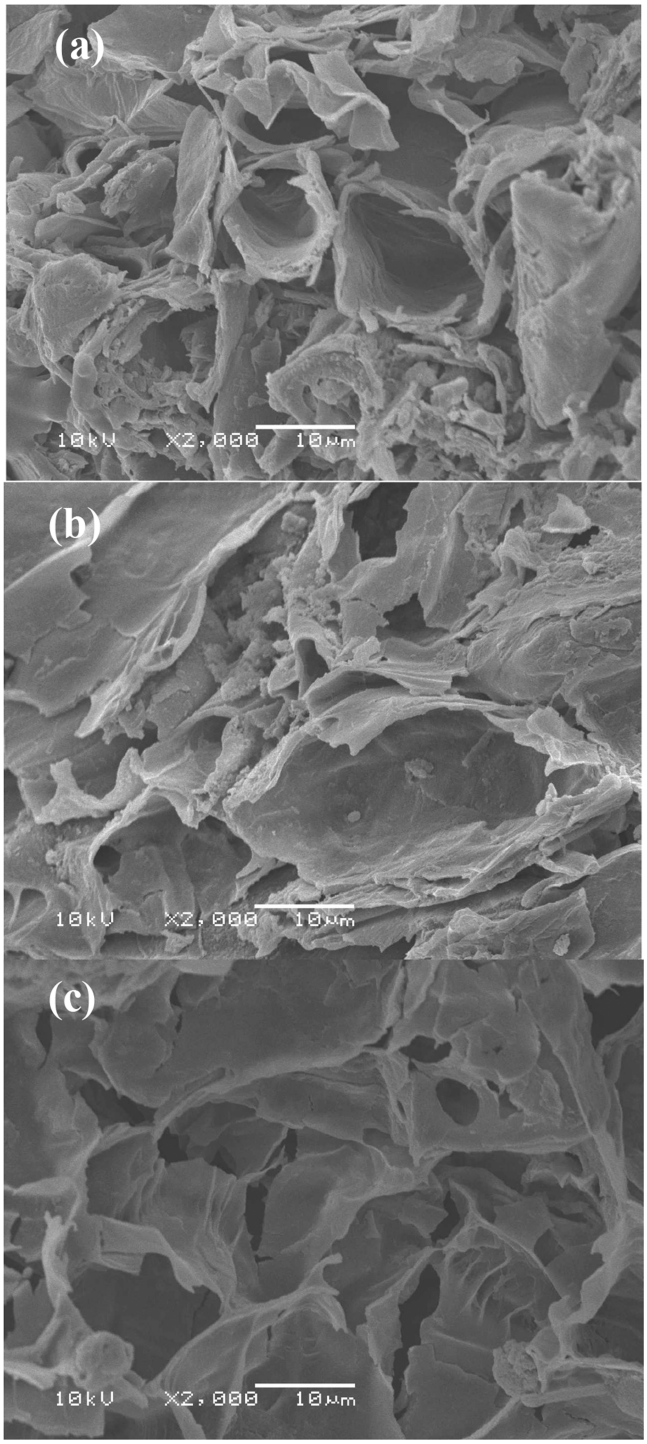

Figure 1. SEM images of (a) peanut shells, (b) peanut shells after adsorption of triazoles (100 $\mu g\ L^{-1}$ each), and (c) peanut shells after the desorption process.

2. RESULTS AND DISCUSSION

2.1. Characterization of Sorbents. To investigate the morphology of the materials, scanning electron microscopy (SEM) was applied. The result is shown in Figure 1. The adsorbent consists of an irregularly porous surface before (Figure 1a), after some modification (Figure 1b) and after the desorption process (Figure 1c). It was found from observing the surface area of the sorbent after modification and the adsorption process that the sorbent exhibited large and shallow pores sizes because of the replenishment from the adsorption. The triazole molecules could fulfill in biosorbent pores by dispersion of their molecules from the aqueous solution to sorbent surface through its boundary layer.[30] These triazole molecules were migrated from the biosorbent surface to inner pores of the adsorbent and then adsorbed at the available sites on its surface. It might be physical adsorption (physisorption), through mechanical adhesion of analytes on the adsorbent.[31]

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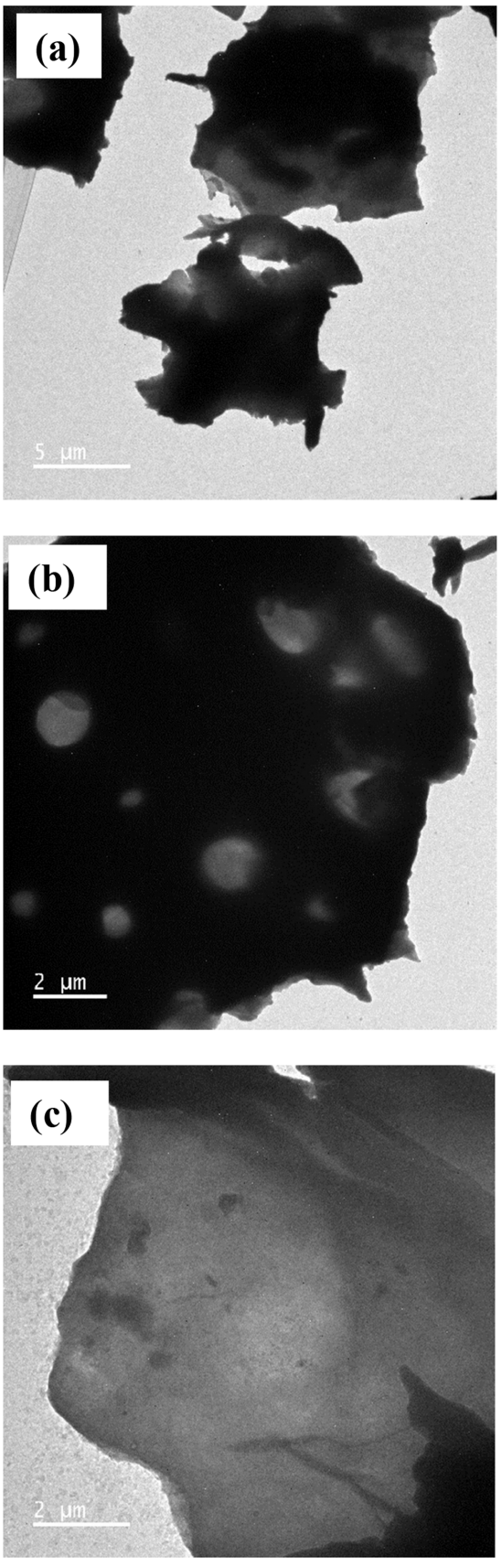

Figure 2. TEM images of (a) peanut shells, (b) peanut shells after adsorption of triazoles (100 μg L^{-1} of each), and (c) peanut shells after desorption.

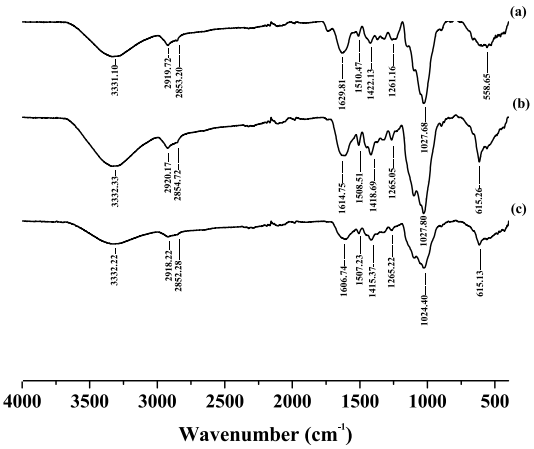

Figure 3. FTIR spectra of (a) peanut shells, (b) peanut shells after adsorption with triazole fungicides (100 μg L^{-1} of each), and (c) peanut shells after the desorption process.

To study the morphological features of the materials, transmission electron microscopy (TEM) was performed. TEM images of peanut shells, peanut shells after adsorption, and peanut shells after desorption are presented in Figure 2a−c, respectively. The results found that the triazoles were successfully adsorbed as a monolayer adsorption type. After the desorption process (as seen in Figure 2c), the surface of the biosorbent material was reduced owing to the desorption procedure as a result of the optimum desorption solvent for the proposed microextraction method.

Peanut shells, which are vegetable biomass, are composed of cellulose, hemicellulose, and lignin. Peanut shells mainly consist of polysaccharides, proteins, and lipids, offering many functional groups such as carboxyl, carbonyl, hydroxyl, and amino with characteristic chemical structures.[32] Fourier transform infrared (FTIR) spectroscopy was selected to study the functional groups of peanut shells (as shown in Figure 3). The FTIR spectrum for peanut shells after adsorption (in Figure 3a) showed various groups and bands in spirit of their respective wave number (cm^{-1}), which is the complex nature of the adsorbent. The broad band around 3331.10 cm^{-1} is considered to be due to the surface hydroxyl groups (−OH), which are most apparently due to the interaction and existence of alcoholic, phenolic, amino, and carboxylic derivatives. The peak at 2919.72 cm^{-1} is assigned to the C−H asymmetrical stretching band of most aromatics, aliphatics, and olefins.[33] The peaks at 2852 cm^{-1} are characteristic of the C−H stretching band, representing aldehyde groups. The peak associated with the stretching in C═C and C═O (noncyclic amides) is verified at 1629.81 and 1510.47 cm^{-1} and is ascribed to aldehydes alkenes, amides, esters, and aromatic groups, respectively. The absorption peaks at 1422.13 and 1261.16 cm^{-1} could be due to C−O, C−H, or C−C stretching vibrations. The peak observed at 1027.68 cm^{-1} is due to the C−O group in carboxylic and alcoholic groups. The peak at 558.65 cm^{-1} is due to the vibrational bending in the aromatic compounds of lignin.

The treatment with alkali (as shown in Figure 3b,c) changed the congenital cellulose by a procedure known as alkalization. From the spectrum, it can be seen that in the unmodified peanut shell a broad peak at 3331.10 cm^{-1}, which is characteristic of the cellulosic −OH groups. However, this intensity is reduced in alkali-treated peanut shell because of the removal of the −OH group by −Ona.[34] The decrease in the strength of all other peaks

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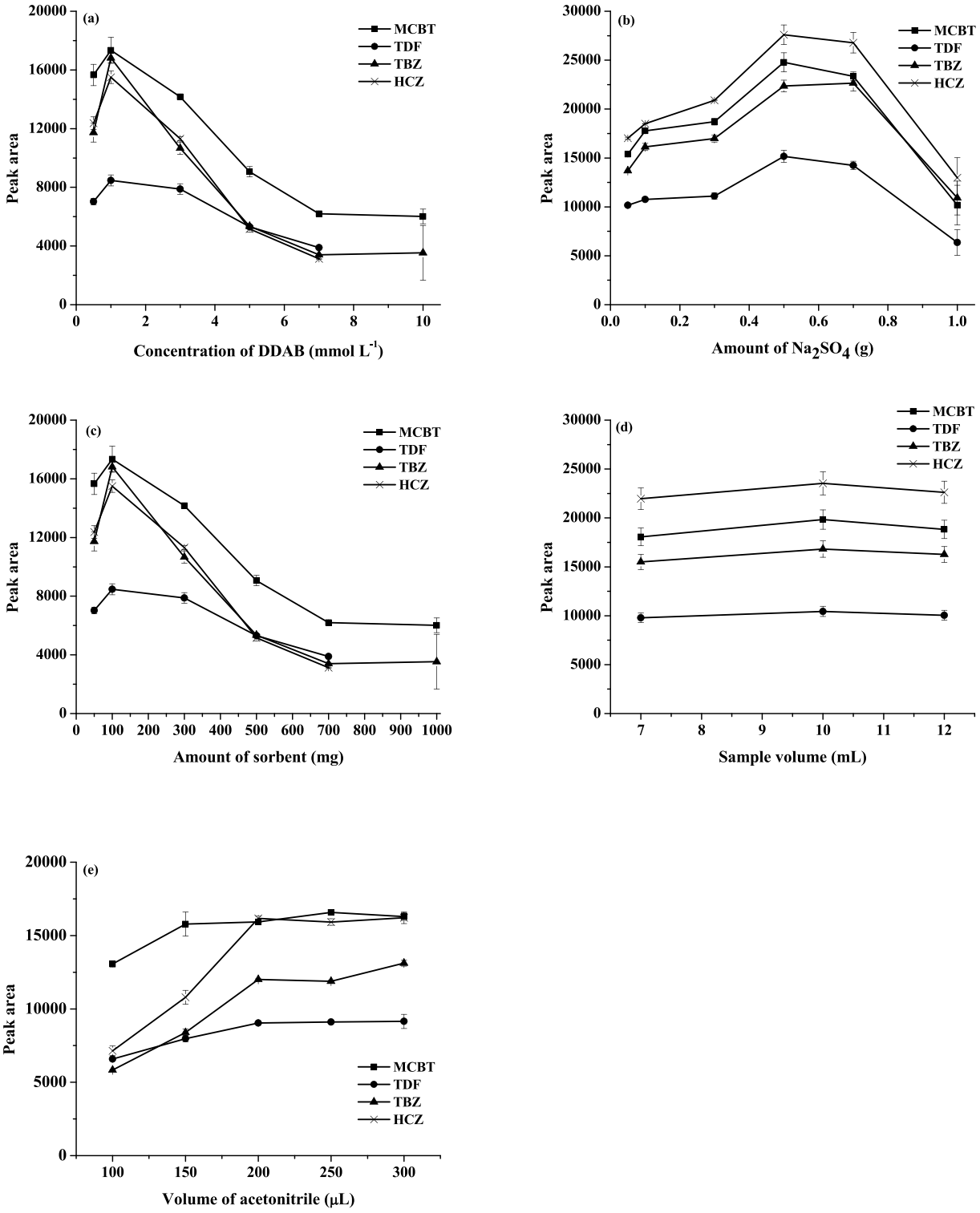

Figure 4. Effect of extraction condition on the extraction efficiency: (a) concentration of DDAB (mmol L^{-1}), (b) amount of Na_2SO_4 (g), (c) amount of sorbent (mg), (d) sample volume (mL), and (e) volume of acetonitrile (μL).

has also been observed in the alkali-treated peanut shell spectrum, which is due to the removal of lignin and impurities after alkali treatment.

2.2. Optimization of Microsolid Phase Extraction (μ-SPE) Conditions. Several parameters affecting the extraction efficiencies of the proposed method were tested, including the amount of sorbent, kind and concentration of surfactant, sodium hydroxide concentration, kind and amount of salt, sample volume, adsorption time, kind and volume desorption solvent, and desorption time. A mixed triazole standard containing 100 μg L^{-1} of each was used to examine the extraction efficiency of the method. In this experiment, various parameters were studied by a one parameter at a time while the other factors were kept constant. All optimization experiments were carried out in triplicate ($n = 3$). Peak areas were used to evaluate the extraction efficiency of the investigated method.

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Table 1. Analytical Features of the Proposed Microextraction Method for Determination of Triazole Fungicides

								intraday precision (n=3), RSD (%)		interday precision (n=5×3 days), RSD (%)	
analyte	linear range (μg L^{-1})	linear equation	R^2	LOD (μg L^{-1})	LOQ (μg L^{-1})	%ER	EF (C_{ex}/C_0)	t_R	peak area	t_R	peak area
myclobutanil	9−1000 (300−7000)[a]	y = 186,732x + 631.01 (y = 54,685x + 438.4)	0.9944 (0.9996)	0.03	0.09	68.30	34.15	0.04	2.92	0.08	4.63
triadimefon	9−1000 (300−7000)	y = 97,908x − 1158 (y = 47,839x − 1387)	0.9989 (0.9998)	0.03	0.09	60.94	30.47	0.05	2.12	0.09	3.99
tebuconazole	9−1000 (300−7000)	y = 204,844x + 668.38 (y = 15,998x − 1478)	0.9956 (0.9992)	0.03	0.09	85.60	42.80	0.03	3.12	0.07	4.67
hexaconazole	9−1000 (300−7000)	y = 234,935x + 707.64 (y = 38,920x + 3789.2)	0.9939 (0.9996)	0.03	0.09	100.72	50.36	0.02	2.28	0.06	5.04

[a]The values in parentheses are direct HPLC analysis.

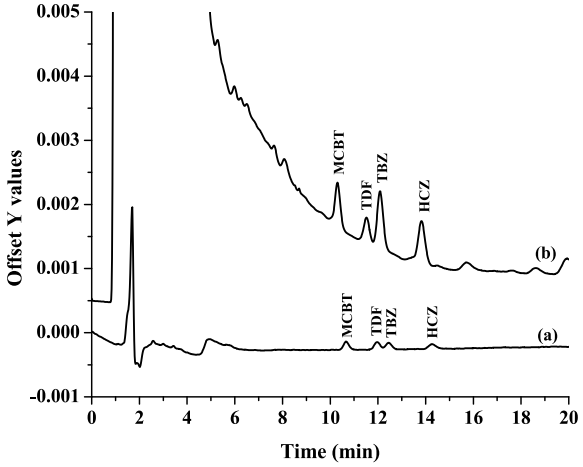

Figure 5. Chromatograms of standard triazoles obtained by (a) without preconcentration and (b) with microsolid phase extraction using a modified peanut shell: concentration of each standard was 100 μg L^{-1}.

Table 2. Matrix Effect (ME, %)

sample	MCBT	TDF	TBZ	HCZ
surface water I	64.96	88.77	88.31	118.53
surface water II	64.72	102.02	112.83	111.76
honey I	119.47	103.18	91.30	111.33
honey II	92.65	12.63	78.45	114.49
honey III	99.89	89.92	100.04	101.45

However, because of the negatively charged surface and little anion exchange capacity, the peanut shell biosorbent was modified using a cationic surfactant in order to absorb triazole fungicides. Single chain cationic surfactant (DTAB) and double chain cationic surfactant (DDAB) were studied (data not shown). It was found that the double chain cationic surfactant (DDAB) modified on the peanut shell biosorbent provided high extraction efficiency on the extraction of triazole fungicides. Therefore, DDAB was selected. The concentration of DDAB was studied in the range 0.5−10 mmol L^{-1}. The result is shown in Figure 4a. It was found that DDAB 1 mmol L^{-1} provided high extraction efficiency. Thus, DDAB 1 mmol L^{-1} was used for further studies.

The ionic strength adjustment by the salt addition in the samples was an important parameter that affects the extraction efficiency of the target analytes.[28] In this study, different electrolyte salts were investigated (i.e., NaCl and Na_2SO_4) at 0.3 g and compared with no salt addition (data not shown). Because the ionic strength of Na_2SO_4 (≈0.633) was higher than that of NaCl (≈0.513), therefore Na_2SO_4 provides high extraction efficiency. Therefore, Na_2SO_4 was chosen. The amount of Na_2SO_4 was investigated in the range of 0.1−1 g (Figure 4b). The extraction efficiency increased with increasing the amount Na_2SO_4 in the range of 0.1−0.5 g; it could effectively reduce solubility of fungicides and improve the extraction recovery by decreasing water molecules surrounding the fungicide molecules. After that, the peak area decreased because a high salt concentration can decrease the mass transfer of analytes. The results demonstrate that the highest response was obtained when the amount of Na_2SO_4 was 0.5 g. The higher amount of Na_2SO_4 indicated higher viscosity of aqueous solution, leading to an inefficient molecular mass transfer rate. This further illustrated $\pi-\pi$ stacking/ interaction between triazole fungicides

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Table 3. Recovery Obtained from the Determination of Studied Triazoles in Studied Samples (n = 3)

		MCBT		TDF		TBZ		HCZ	
sample	added (μg L^{-1})	%RR[a]	%RSD[b]	%RR	%RSD	%RR	%RSD	%RR	%RSD
surface water I	0								
	90	117.6	1.8	119.7	0.7	117.5	1.1	100.0	0.4
	150	107.9	0.5	109.3	3.0	115.2	1.0	118.8	1.2
	250	118.6	2.8	100.1	5.6	109.5	5.6	112.9	4.0
surface water II	0								
	90	70.0	1.8	118.6	0.4	105.0	4.4	102.4	1.6
	150	97.9	5.0	98.0	5.7	112.7	5.2	89.7	3.6
	250	100.3	6.0	106.7	5.7	117.3	5.6	89.7	4.7
honey I	0								
	90	116.8	1.2	111.4	2.8	77.5	2.8	95.5	4.3
	150	110.8	0.2	107.4	2.1	107.2	0.8	114.9	0.2
	250	111.3	0.2	108.9	2.1	111.8	2.0	108.7	0.9
honey II	0								
	90	111.6	0.7	108.6	2.1	87.9	1.5	103.8	2.4
	150	98.1	5.8	89.0	3.5	100.9	3.5	98.0	3.4
	250	88.9	8.7	89.9	4.5	102.5	3.4	89.5	3.0
honey III	0								
	90	100.5	8.4	107.8	4.2	103.5	4.3	98.5	8.4
	150	98.6	6.4	99.8	0.3	97.2	1.5	87.9	0.9
	250	98.1	0.9	85.9	0.7	98.1	0.6	90.9	0.9

[a]RR: relative recovery. [b]RSD: relative standard deviation.

and biosorbent. Therefore, Na_2SO_4 0.5 g was selected for further experiments.

The pH of the sample solution shows a crucial part in the μ-SPE method, because it affects the existing forms of analytes and the interaction between adsorbents and analytes. The effect of pH in this experiment was investigated by adding NaOH at different concentrations in the range of 50−150 mmol L^{-1} (data not shown). At higher alkalinity, an increase in the signal was observed for all triazoles. Therefore, 130 mmol L^{-1} of NaOH was selected.

To achieve the highest extraction efficiency, different amounts of peanut shell biosorbent ranging from 50 to 1000 mg were examined to extract the studied fungicides. The results in Figure 4c indicated that the peak areas of all analytes reached the maximum at 100 mg. After that, the peak areas of the studied triazoles dramatically decreased, possibly because of insufficient amount of surfactant and volume of the desorption solvent. As a result, 100 mg of peanut shell biosorbent was selected for further studies.

The sample volume is an important parameter in the μ-SPE process because it affects the loading capacity of the sorbent. The effect of sample volume on the extraction efficiency was studied in the range from 7 to 12 mL. The results is shown in Figure 4d. It was found that the peak areas of all analytes increased as the sample volume increased from 7 to 10 mL and then slightly decreased. This might be that strong adsorption leads to the difficulty which incurred during the desorption process.[35] Thus, 10 mL of sample solution was used.

Kind of desorption solvent is an important factor to obtain the efficient elution of the analyte from the biosorbent. In agreement with the principle of like dissolves like, polar solvents are useful for dissolution of polar analytes.[35] Based on this point, polar desorption solvents, including ethanol (log K_{ow} value = −0.31), acetonitrile (log K_{ow} value = −0.34), and methanol (log K_{ow} value = −0.77) were studied for desorption of triazole fungicides. When acetonitrile was used as a desorption solvent (data not shown), good extraction efficiency was obtained. Acetonitrile has high solvent eluotropic strength, which makes it suitable for interrupting between analyte and sorbent interactions.[36] Moreover, the volume of desorption solvent (acetonitrile) was examined in the range of 100−300 μL. The extraction efficiency gradually increased with an increasing desorption solvent volume from 100 to 200 μL and then remained almost constant afterward (as shown in Figure 4e). Therefore, the volume of acetonitrile as a desorption solvent of 200 μL was selected as optimum.

2.3. Method Validation. Under the selected and optimized conditions, the analytical performance of the proposed method was evaluated in terms of linear range, limit of detection (LOD), limit of quantification (LOQ), precision, and accuracy. The performance data of the developed procedure are summarized in Table 1. The method exhibited wide linearity of the calibration graphs in the range of 9−1000 μg L^{-1} with a coefficient of determination (R^2) of greater than 0.99. The LODs and LOQs, which were calculated based on the signal-to-noise ratios of 3 and 10, respectively, were 0.03 and 0.09 μg L^{-1} for all analytes, respectively. The enrichment factors (EFs), calculated from the ratio of the extracted analyte concentration in the precipitate phase to its initial concentration in the aqueous sample solution, were found to be in the range of 30−51. The precisions were evaluated from the relative standard deviations (RSDs) of retention time and peak area obtained from intra (n = 3) and interday experiments were greater than 0.09% and 5.04%. Chromatograms of the studied triazoles obtained by direct HPLC and the proposed microextraction method are presented in Figure 5.

2.4. Application to Real Samples. The applicability of the proposed microextraction method was investigated for the analysis of triazole fungicide residues in environmental water and honey samples. To study the matrix effect of real samples, a matrix-match calibration method was used. The matrix-match calibration was studied by spiked real samples in the range of 90−250 μg L^{-1} of each target analyte. The target analytes exhibit wide linearity with R^2 greater than 0.9. The matrix effect (ME)

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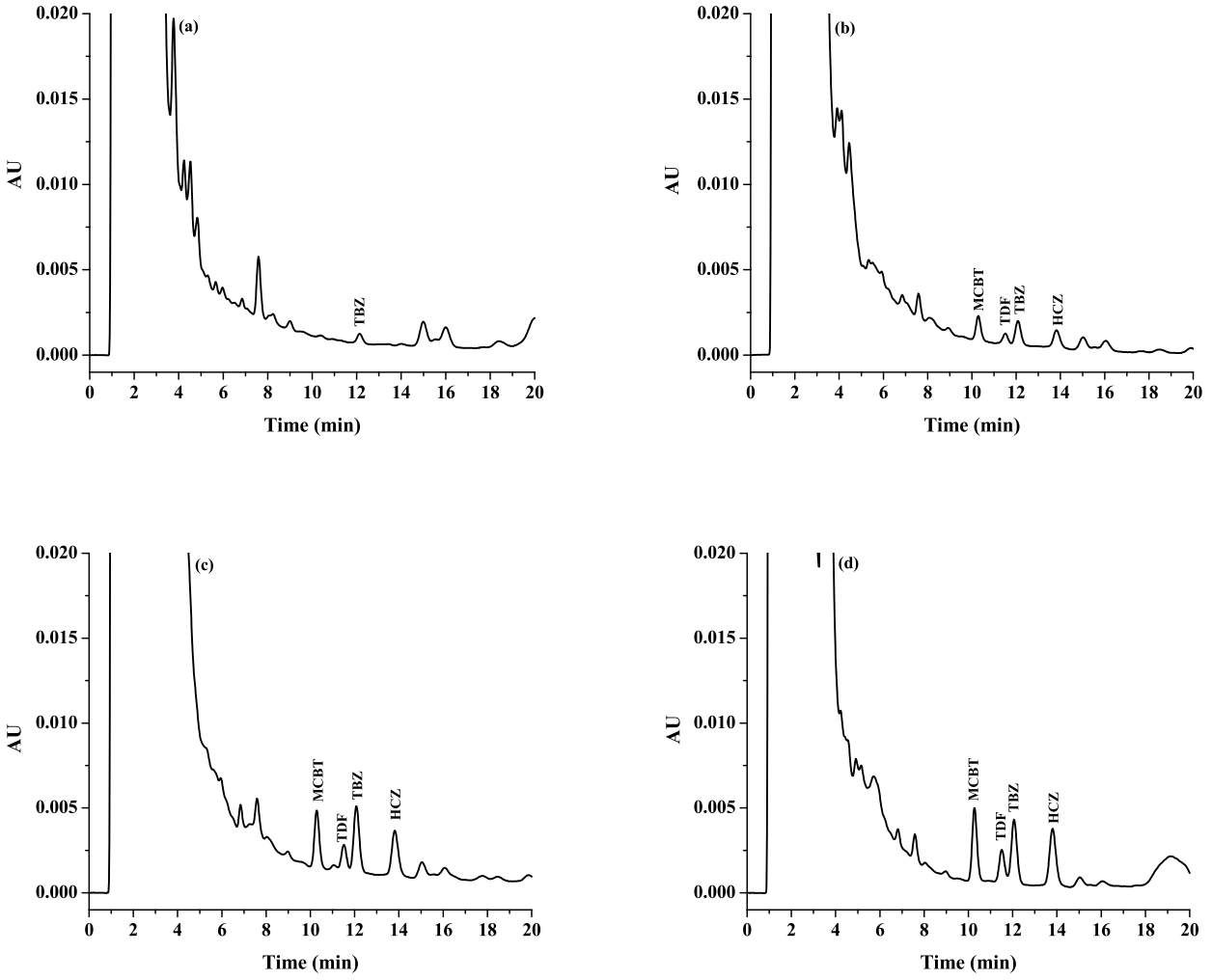

Figure 6. Chromatograms of (a) honey sample, (b) spiked honey sample (90 μg L^{-1}), (c) spiked honey sample (150 μg L^{-1}), and (d) spiked honey sample (250 μg L^{-1}).

was calculated by comparing the ratio of the slopes of the matrix-matched curve to that of the solvent (as eq 1)

$$\text{ME}\ (\%) = (S_m/S_s) \times 100 \quad (1)$$

where S_m and S_s are the slopes of the calibration curve in the matrix and solvent, respectively. Generally, ME between 80 and 120% indicates no matrix effects, ME between 50−80% and 120−150% refers to minor matrix effects, and ME <50% or >150% indicates major matrix effects.[37,38] As seen in Table 2, no ME to a minor ME was observed for all samples. The presented method achieves a low MDL, which is below the MRLs established by CAC for triazole fungicides. It was found that tebuconazole was found in the range of 150−300 μg L^{-1} in all honey samples studied.

The accuracy and repeatability of the proposed method using the modified peanut shell sorbent were evaluated by spiking the real samples with three triazole fungicides at concentration levels of 90, 150, and 250 μg L^{-1}. The recoveries (as shown in Table 3) in the range of 85−120% were obtained with RSDs in the range of 0.2−8.4%. Figure 6 illustrates the chromatograms of the blank honey and spiked samples. Based on these observations, it can be concluded that the proposed μ-SPE method modified peanut shell powder has excellent applicability for the selective extraction of the studied compounds in environmental water and honey samples.

2.5. Comparison of Our Proposed Method with Other Sample Preparation Methods. Table 4 shows a comparison of the developed μ-SPE method using the peanut shell biosorbent in this work with other published methods based on determination of triazole fungicides.[20,39−41] Comparing the microextraction method, the present work provides a fast, simple, environmentally friendly using the greenest sorbent and cost-effective method. Additionally, our work presented a shorter extraction time, lower LOQs, and comparable accuracy for the simultaneous extraction and determination of triazole fungicides. The proposed method can be used as a powerful alternative miniaturized extraction and preconcentration method for the analysis of triazole fungicides in water and honey samples.

3. CONCLUSIONS

Herein, a simple, rapid, cost-effective, and environmentally friendly μ-SPE method using a peanut shell biosorbent was developed for the selective enrichment of triazole fungicides in environmental water and honey samples. The peanut shell was modified by didodecyldimethylammonium bromide (DDAB) before used. The proposed μ-SPE method exhibited good linearity, high sensitivity, and satisfactory accuracy and precision. In addition, this method was successfully applied to determine triazole fungicides in environmental water and honey

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Table 4. Comparisons of the Proposed Method with Other Methods for the Determination of Triazole Fungicides[a]

method	analyte/sample	extraction condition	analytical technique	LODs	LOQs	%RR	ref
SPME	triazole fungicides/water and fruit juices	sorbent: 30 mg GO-P*m*AP sample: 100 mL desorption: 5 mL methanol extraction time: 25 min	HPLC-UV		0.2−0.4 $\mu g\ L^{-1}$	95.2−98.0	39
MSPE	triazole fungicides/river water, wheat flour and rice samples	sorbent: 5 mg Fe_3O_4@PC sample: 10 mL desorption: 200 μL acidic methanol (19:1 $v_{methanol}/v_{acetic\ acid}$) extraction time: 5 min	HPLC-UV	0.2−0.3 $\mu g\ L^{-1}$	0.8−1 $\mu g\ L^{-1}$	82.8−113.2	21
dSPE	triazole fungicides/tobacco (*Nicotiana tabacum*)	sorbent: 50 mg PSA + 50 mg C18 + 25 mg GCB + 100 mg $MgSO_4$ sample: 20 g extraction solvent: 10 mL ethyl acetate extraction time: 6 min	HPLC-Quadrupole-Orbitrap MS		10 − 40 $ng\ g^{-1}$	70−120	40
SLE-QuEChERS	triazole fungicides/fruit and vegetable samples	sorbent: 4 g anhydrous $MgSO_4$ + 1 g NaCl +40 mg PAS sample: 20 g extraction solvent: 10 mL acetonitrile extraction time: 11 min	UHPLC-Q-Orbitrap-MS^2	0.005−0.14 $\mu g\ kg^{-1}$	≤10 $\mu g\ kg^{-1}$	70−120	41
μSPE	triazole fungicides/environment water and honey samples	Sorbent: 100 mg Peanut shell sample volume: 10 mL adsorption: vortex for 20 s, centrifuge at 2000 rpm for 20 min elution solvent: 200 μL acetonitrile desorption: vortex for 20 s, centrifuge at 2500 rpm for 10 min	HPLC-DAD	0.03 $\mu g\ mL^{-1}$	0.09 $\mu g\ mL^{-1}$	70.0−118.8	this work

[a]SPME; solid-phase microextraction, MSPE; magnetic solid-phase extraction, dSPE; dispersive solid-phase extraction, SLE-QuEChERS; solid liquid extraction-Quick, Easy Cheap, Effective, Rugged and Safe, μSPE; micro solid phase extraction, GO-P*m*AP; Graphene oxide-poly-3-aminophenol, Fe_3O_4@PC; magnetic porous carbon, PSA; primary secondary amine, C18; octadecyl sorbent, GCB; graphitized carbon black, $MgSO_4$; magnesium sulfate.

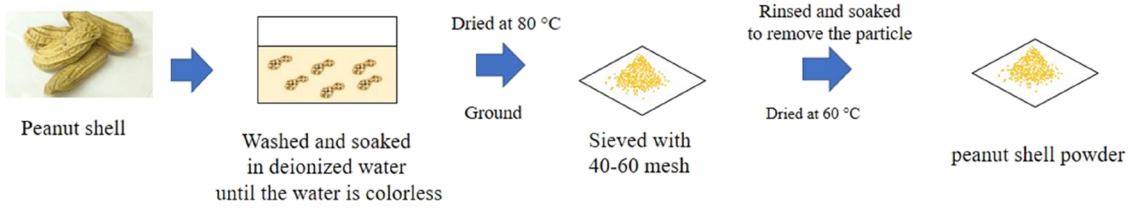

Figure 7. Schematic of the preparation of biosorbent (Photograph courtesy of "Wannipha Khiaophong". Copyright 2022).

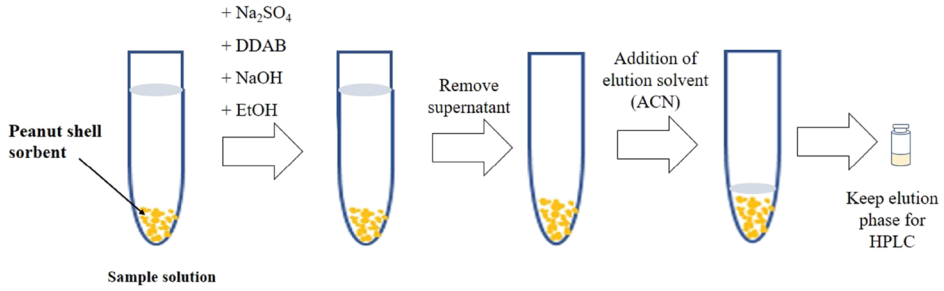

Figure 8. Schematic of the proposed μ-SPE method using the modified peanut shell prior to HPLC analysis (Photograph courtesy of "Wannipha Khiaophong". Copyright 2022).

samples by providing satisfactory recoveries. This is the first time for applicability of modified peanut shells using DDAB in the extraction of triazole fungicides.

4. EXPERIMENTAL SECTION

4.1. Chemicals and Reagents. All standard triazole fungicides with ≥99% purity, including myclobutanil (MCBT), triadimefon (TDF), tebuconazole (TBZ), and hexaconazole (HCZ), were obtained from Dr. Ehrenstorfer

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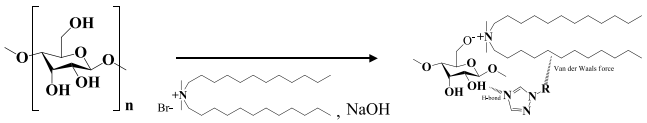

Figure 9. Modification process of the peanut shell-involved proposed reaction mechanism.

GmbH (Germany). Stock solutions of each fungicide at a concentration of 1000 μg mL^{-1} were prepared using methanol as the solvent. Type I deionized water (18.2 MΩ cm) used throughout this work was produced using a RiOs Simplicity 185 water purification system (Millipore, USA). HPLC-grade of methanol, acetonitrile, and ethanol were purchased from Merck (Darmstad, Germany). Sodium chloride (NaCl), ammonium chloride (NH_4Cl), anhydrous sodium sulfate (anh. Na_2SO_4) and sodium hydroxide (NaOH) were obtained from Ajax Finechem (New Zealand). Sodium acetate (CH_3COONa) was purchased from Carlo Erba (France). Didodecyldimethylammonium bromide (DDAB) was obtained from Sigma-Aldrich (India). All solutions were filtered through a 0.45-μm membrane filter prior to the HPLC system.

4.2. Instrumentation. The HPLC system (Waters, USA) consisted of a Waters 1525 Binary HPLC pump (Water, Massachusetts, USA) equipped with an in-line degasser and a Waters 2489 UV/Visible detector. Rheodyne injector with a 20 μL loop was used. Empower 3 software was to acquire and analyze the chromatographic data. The triazole fungicides were separated using a Purospher STAR RP-18 endcapped (4.6 × 150 mm, 5 μm) column (Merck, Germany). The mobile phase was 50% *v*/*v* acetonitrile. The flow rate was 1.0 mL min^{-1}. The detection wavelength was set at 220 nm. Four triazole fungicides were separated within 15 min with the elution order of myclobutanil (MCBT) (t_R = 10.30 min), triadimefon (TDF) (t_R = 11.50 min), tebuconazole (TBZ) (t_R = 12.00 min), and hexaconazole (HCZ) (t_R = 13.80 min).

FTIR spectroscopy (Bruker Invenio-S FTIR, Bruker Corp, Massachusetts, USA) was performed using a diamond lens attenuated total resistance (ATR), which is used for characterization of the functional groups of biosorbents. Scanning electron microscopy (SEM; Model JEOL JSM-6460LV, Canada) and transmission electron microscopy (TEM; FEI Tecnai G220) were used to examine the morphologies of the biosorbent.

Other instruments, including a centrifuge (Centurion, England), a vortex (Fisher Scientific, USA), and an oven UF55 (Memmert, Germany), were also used.

4.3. Preparation of the Peanut Shell Biosorbent. Peanut shells were procured from Maha Sarakham province, Northeast Thailand. The schematic diagram of the preparation of biosorbent is shown in Figure 7. The peanut shells were washed and soaked in deionized water until the water is colorless. The clean peanut shells were then dried at 80 °C until constant mass. The dried peanut shells were ground and sieved with 40−60 mesh to obtain the desired particle size. Then the particle was rinsed and soaked in deionized water until the water is colorless and dried at 60 °C until constant mass. The peanut shell powder was stored in a desiccator until use.

4.4. Microsolid Phase Extraction Method. The schematic of the proposed μ-SPE method using modified peanut shell prior to HPLC analysis is schematically depicted in Figure 8. Peanut shell powder (0.10 g), Na_2SO_4 (0.5 g), DDAB (0.10 mmol L^{-1}) and NaOH (130 mmol L^{-1}) to 10 mL of mixed standard/sample solution in a centrifuge tube. After that, vortexing at 1500 rpm for 20 s and centrifugation at 2000 rpm for 5 min were performed to enhance the adsorption of the target analytes, and the supernatant was decanted. After adding acetonitrile (200 μL), the mixture was then vortexed at 1500 rpm for 2 min and centrifuged at 2500 rpm for 5 min to desorb the analytes from the sorbent. After that, a clear supernatant was collected and then filtered through a 0.45 μm membrane filter before being subjected to HPLC. The modification process of peanut shell-involved proposed reaction mechanism is shown in Figure 9.

4.5. Sample Preparation. *4.5.1. Environmental Water Samples.* Environmental water samples were collected from the different natural located near agricultural in Maha Sarakham province. The sample was then filtered through a Whatman (no.1) filter paper to remove particulate matter and then passed through a 0.45 μm membrane filter before extract using the proposed method.

4.5.2. Honey Samples. Honey samples were purchased from a supermarket in Maha Sarakham province. Five grams of honey sample was weighed into a 50 mL volumetric flask and diluted to the marker. The sample was filtered through a Whatman (no.1) filter paper to remove particulate matter and then passed through a 0.45 μm membrane filter before extract using the proposed method.

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Notes

The authors declare no competing financial interest.

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