GRAPHENE OXIDE DISPERSED WITH FERRITE NANO- PARTICLES AS MAGNETIC SOLID PHASE EXTRACTION ADSORBENT FOR CHLORPYRIFOS AND DIAZINON

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Abstract

Magnetic graphene oxide, Fe_3O_4-GO has been synthesized through oxidation of graphite via modified Hummer's method followed by a one step co-precipitation method. Fe_3O_4-GO was used in the extraction of two organophosphorus pesticides (OPPs), namely chlorpyrifos and diazinon using magnetic solid phase extraction (MSPE) technique. The GO and Fe_3O_4-GO synthesised was characterized using Fourier transform infrared spectroscopy (FT-IR), and field emission scanning electron microscopy (FESEM). Optimum conditions obtained from the optimization process were as follows: 80 mL sample volume, 50 mg of adsorbent, 10 min extraction time followed by desorption process using 500 μL of acetonitrile. Under the optimum conditions, Fe_3O_4-GO MSPE method showed excellent linearity in the range of 0.1-10 μg L^{-1} with coefficient of determination (R^2) of 0.9997 for both OPPs. Precision studies found that the repeatability of this Fe_3O_4-GO MSPE method (RSD, n = 3) were 9.95% and 9.05% for chlorpyrifos and diazinon respectively. Meanwhile the reproducibility (RSD, n = 9) observed was 11.45% for chlorpyrifos and 13.35% for diazinon. The limit of detection (LOD = 3 S/N) for chlorpyrifos was 0.034 μg L^{-1} and 0.40 μg L^{-1} for diazinon. Lake water sample was spiked with 0.5 μg L^{-1} of each of the OPPs after confirming the non-detection in the sample using gas chromatography-electron capture detector (GC-ECD). Percentage recoveries of the two OPPs from lake water samples were found to be 57.71% for chlorpyrifos and 73.86% for diazinon. The Fe_3O_4-GO MSPE method was found to be susceptible to matrix effect from the lake water sample analysed. The Fe_3O_4-GO MSPE method was also applied to the determination of the two OPPs from tomato sample using matrix-matched calibration curve in the range of 1-50 μg L^{-1}. Good coefficient of determination (R^2) value of 0.9963 and 0.9897 for chlorpyrifos and diazinon respectively was observed. Both OPPs were found to be present in the tomato sample analysed (0.19 μg L^{-1} of chlorpyrifos and 7.88 μg L^{-1} of diazinon).

Keywords: graphene oxide, ferrite nanoparticles, magnetic solid phase extraction, organophosphorus pesticides

INTRODUCTION

Organophosphorus pesticide (OPPs) is one of the major classes of pesticide and are widely used in many countries for agriculture [1]. Generally, organophosphorus compound is used as herbicide, insecticide and nerve agents. Example of OPPs are parathion, malathion, chlorpyrifos, diazinon, and tetrachlorvinphos [2].

OPPs can be considered hazardous to human since they are readily absorbed through respiratory tract, gut and to a lesser extent; it can absorbed through the skin [3]. Therefore, the content of OPPs in environmental water should be monitored due to its toxicity, persistence and accumulation. In order to measure the content of OPPs in water sample, an effective and easy method should be developed. Considering the low concentration of OPPs in water sample, a sample preparation method is needed since it will be difficult to directly determine the concentration of the analyte by gas chromatography (GC). Sample preparation technique is required to isolate the analyte from sample matrices before further analysis to determine the analyte concentration [2].

Classical method such as liquid-liquid extraction (LLE), Soxhlet extraction and solid phase extraction (SPE) are a well established method used in sample preparation step. LLE and SPE have some drawback as it requires large amount of high purity solvent and requires lengthy of procedure and thus time consuming [2]. Extraction using SPE often experience cartridge plugging problem [4]. In order to overcome the drawbacks in LLE and SPE, an improved version of both of the classical method is established. Method such as solid phase micro extraction (SPME) and liquid phase micro extraction (LPME) were introduced. SPME and LPME improved SPE and LLE respectively by using smaller amount of toxic solvent along the extraction [2].

Magnetic solid phase extraction (MSPE) is one of the developed versions of SPE. Ŝafaříková and Ŝafarik [5] developed an extraction method based on the use of magnetic adsorbent. In MSPE, the magnetic adsorbent prepared were added into the beaker containing sample and the targeted analyte will adsorb onto the magnetic adsorbent. The magnetic adsorbent with analyte is simply separated from the sample by means of an external magnetic field (Ŝafaříková and Ŝafarik, 1999). Then, the analyte were simply desorbed by suitable eluent for further determination by GC.

Graphene oxide (GO) recently used as an adsorbent in MSPE due to its large surface area. Graphene has a very large surface area (2630 m^2/g) compared to graphite (10 m^2/g) and carbon nano tube (1315 m^2/g). The large surface area is due to its unique nano sheet morphology where both surface of the graphene sheet can be used for adsorption. In addition, the nano sheet feature lead to fast adsorption equilibrium and analyte elution [4]. However, GO is an ultra light material and it is hard to be retrieve from a suspension even by high speed

centrifugation. Introduction of magnetic properties into GO will result in a product that combines the high adsorption capacity of GO and the separation convenience of magnetic materials [6].

In this work, Fe_3O_4-GO was synthesized via modified Hummer's method followed by one step co-precipitation of Fe_3O_4 MNPs. The prepared Fe_3O_4-GO was applied for the enrichment and analysis of two OPPs namely chlorpyrifos and diazinon using GC-ECD. Compared to conventional extraction technique, the proposed method is a simpler, more rapid and more cost effective. Finally, the proposed method was applied in the analysis of chlorpyrifos and diazinon from two real samples namely lake water and tomato samples.

EXPERIMENTAL

Reagents and materials

The chemicals used in this study were graphite powder, concentrated sulphuric acid (H_2SO_4, 97%), nitric acid (HNO_3, 65%), ammonia (NH_3, 32%), hydrogen peroxide (H_2O_2, 30%), potassium permanganate ($KMnO_4$), ferrous chloride ($FeCl_2.H_2O$) and ferric chloride ($FeCl_3.H_2O$). Analytical Reagent grade acetonitrile, acetone, methanol, hexane and ethyl acetate solvent was also used. All of the chemical were obtained from QREC (ASIA) Sdn. Bhd. (Selangor, Malaysia). Double distilled deionized water was from a Millipore Simplicity 185 (UV) water system (MA, USA). Chlorpyrifos and diazinon were obtained from Fluka Sigma-Aldrich (Missouri, USA).

Synthesis of GO, Fe_3O_4 and Fe_3O_4-GO

In this study, GO was synthesized via oxidation of graphite using modified Hummer's method [7]. About 3.0 g of graphite powder was added into a mixture of 40 mL HNO_3 (65%) and 80 mL H_2SO_4 (97%). The mixture was left for 24 h at room temperature. Then, 3.0 g of $KMnO_4$ was added slowly to the mixture with stirring at 50°C for 20 h. Then the mixture was poured onto 300 g of ice followed with the addition of 3 mL H_2O_2 (30%). A bright yellow product was formed after the addition of H_2O_2. The product was then diluted with 800 mL deionized water and left overnight at room temperature until the product, GO precipitated out. The supernatant was decanted and the GO was washed using deionized water several times until a neutral pH was obtained.

The Fe_3O_4 synthesised was dispersed onto the GO sheet via a one step co-precipitation method [8]. Approximately 50 mL of the synthesized yellow GO solution was transferred into a beaker. Then, Fe^{2+} and Fe^{3+} were added into the solution in the ratio of 1:2 w/w, respectively. Briefly, 1 g of $FeCl_2.H_2O$ and 2 g $FeCl_3.H_2O$ were mixed in 20 mL deionized water and added into the GO solution. Then the mixture was sonicated and degassed for about 30 min followed by heating at 50°C on a hot plate with vigorous stirring using a magnetic stirrer. Then, 5 mL of ammonia solution (32%) was added drop by drop into the solution until a black precipitate was formed. The heat was turned off but the magnetic stirring was continued vigorously for the next 3 h. The product obtained was then washed with deionized water several times. Then, the supernatant was decanted with the assistant from an external magnet. The black precipitate was then dried at 80°C for 24 h to produce dark black powder of Fe_3O_4-GO) as the new product.

Characterization and analysis

The *as-synthesized* GO and Fe_3O_4-GO was characterized using a Perkin Elmer Frontier Fourier Transform–Near Infrared/Mid Infrared Spectrometers (Waltham, United State). The solid samples were mixed with potassium bromide (KBr) powder in a weight ratio of 1:100, respectively. The mixture was ground finely using a mortar and pestle until a homogeneous mixture was obtained. The mixture was then converted into disc film. The disk was inserted into the sample holder and the spectrum was recorded in the range of 400-4000 cm^{-1}.

Morphologies of the *as-synthesised* GO and Fe_3O_4-GO were determined using a Zeiss Supra 55VP Field Electron Scanning Electron Microscope equipped with secondary electron (SE2) detector (Jena, Germany). Micrographs of both the GO and Fe_3O_4-GO were obtained at an acceleration voltage of 5.0 kV. The working distance selected for the operation was in the range of 7.7 to 10.1 mm. Meanwhile the magnification was set to be in the range of 25,000 and 50,000 to ensure clear micrograph can be obtained.

GC analysis of chlorpyrifos and diazinon was performed on an Agilent A7600 model gas chromatography equipped with an electron capture detector (San Jose, United State). An Ultra 2 column (30 m × 0.2 mm i.d; 0.25 μm film thickness) was used in the analysis. Helium was used as the carrier gas at flow rate of 1 ml min^{-1} and nitrogen was used as make up gas at a flow rate of 32.4 mL min^{-1}. The oven temperature was set at 140°C at 4°C min^{-1} and then ramped at 10°C min^{-1} to 250°C. The detector temperature was set at 280°C.

Samples preparation

Lake water sample was collected from Universiti Teknologi Malaysia (UTM) Lake. Water samples collected were filtered through a Whatman filter paper to remove any suspended solids. The presence of chlorpyrifos and diazinon in the water sample was determined based on external standard calibration method.

Tomato samples were purchased from a supermarket in Skudai. The samples were chopped and homogenized using a domestic blender. The homogenized samples were filtered to obtain the juice for MSPE process to determine the presence and concentration of the two selected OPPs. Matrix-matched calibration was used to determine the amount of chlorpyrifos and diazinon in the tomato sample analysed.

MSPE procedure and Optimisation of MSPE

MSPE process was performed as follows: Firstly, 50 mg of the *as-prepared* Fe_3O_4-GO adsorbent was dispersed in 80 mL deionized water in a vial. The adsorbent was then allowed to adsorb the analytes of interest from the water sample for 10 min. After 10 min, the Fe_3O_4-GO magnetic adsorbent was collected using an external magnet. The water sample (less the extracted analytes) was then decanted leaving the magnetic adsorbent in the sample vial. The trapped analytes were then desorbed from the adsorbent by using 500 μL of the selected desorption solvent with the aid of sonication for several minutes. Analytes solution was then injected into the gas chromatography system equipped with an electron capture detector (GC-ECD).

Optimization of MSPE process was performed using one variable at a time (OVAT) parameter. Parameters optimised were extraction time, mass of adsorbent, sample volume, desorption solvent and desorption volume.

Optimisation of MSPE conditions

The optimisation of MSPE process was performed based on extraction and desorption conditions using distilled water as the matrix. The parameters optimized for extraction process were amount of adsorbent, sample volume and extraction time. The desorption process optimised were type and volume of solvent.

Validation of method

The linearity of the Fe_3O_4-GO MSPE method was investigated by performing extractions using optimum conditions on eight standard solutions mixture in the range of 0.1 to 10 μg L^{-1}. The limit of detection (LOD = 3 S/N) and limit of quantification (LOQ = 10 S/N) were calculated from the calibration graph. Repeatability and reproducibility of the method was studied by performing intraday ($n = 3$) and interday ($n = 9$) analysis of standard OPPs mixture under the optimum conditions. Relative standard deviation (RSD) was calculated based on the obtained peak areas.

Application of Fe_3O_4-GO MSPE method

The proposed analytical method using Fe_3O_4-GO MSPE was used for the determination of chlorpyrifos and diazinon in UTM lake water and tomato sample. To assess the accuracy (% recovery) of the developed method, triplicate lake water samples were spiked with 0.5 μg L^{-1} of the OPPs mixed standard solution after confirming the non-detection of the analytes. As for the tomato sample, matrix-matched calibration was performed after confirming that matrix affects the performance of the developed Fe_3O_4-GO MSPE method.

RESULTS AND DISCUSSION

Characterization of Fe_3O_4-GO

Characterization of Fe_3O_4-GO adsorbent prepared was performed using Fourier transform infrared spectroscopy (FTIR) to confirm that Fe_3O_4 has been successfully dispersed on the GO sheet. The IR spectra of GO and Fe_3O_4-GO are shown in Fig 1(a) and (b), respectively.

GO was successfully converted from graphite as the spectrum (Figure 1a) shows absorption bands of several functional groups. Both IR spectra of GO and Fe_3O_4-GO show absorption peaks at 3422.78 and 3414.00 cm^{-1} respectively which is attributed to O-H functional group of the graphene oxide. The next adsorption band at 1630.59 and 1602.70 cm^{-1} corresponds to the stretching of C=O band. The absorption band of C=C of graphene that normally arise around 1500 to 1600 cm^{-1} might be overlapped by the C=O band. Both spectra of GO and

Fe_3O_4.GO also show the rise of absorption peak at 1386.73 and 1383.30 cm^{-1} due to O-H deformation of the C-OH groups. The absorption band at 1096.73 and 1095.00 cm^{-1} in GO and Fe_3O_4-GO are corresponds to C-O stretching band. The IR spectrum of Fe_3O_4-GO display strong absorption band at 587.71 cm^{-1} which is assigned to the vibration of Fe-O functional group. This shows that Fe_3O_4 magnetic nanoparticles have been dispersed onto the GO sheet.
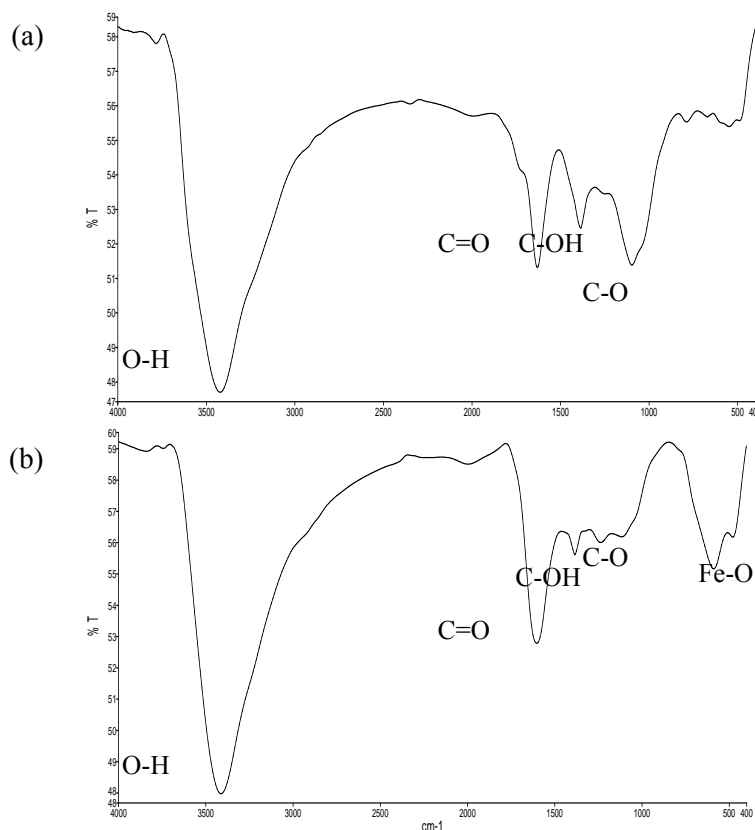
Figure 1: IR spectrum of (a) GO and (b) *as-synthesised* GO-Fe_3O_4

Morphologies of GO and *as-synthesised* Fe_3O_4-GO are shown in Fig 2(a) and 2(b), respectively. As shown in Fig 2(a), the synthesized GO is sheet-like in shape with a smooth surface and single layer structure with wrinkled edges. It also shows that GO has nano porous structure which results from exfoliation process [9]. While a large number of granular particles were closely attached on the surface of GO sheets after the addition of Fe^{2+} and Fe^{3+}, indicating the formation of loosely packed Fe_3O_4 on the surface of the GO sheets (Fig 2 (a)) [10]. Twenty points of Fe_3O_4 magnetic nanoparticles in the micrographs were randomly selected to calculate the average size of the MNPs (~ 56 nm).
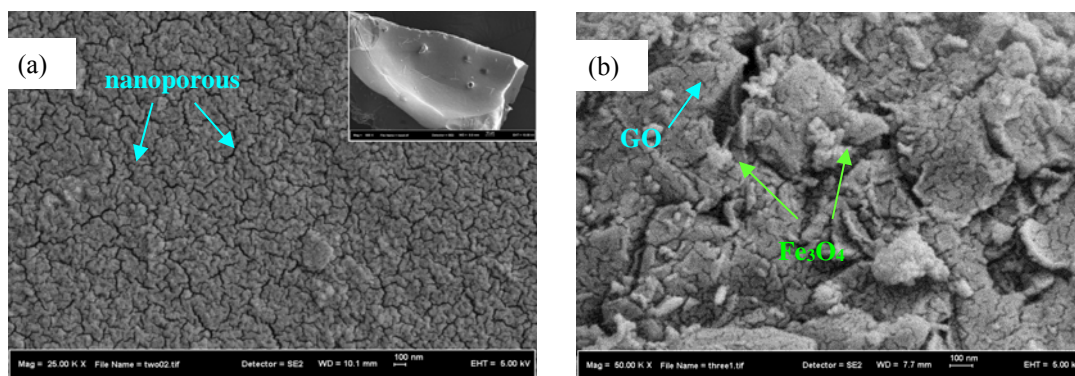
Figure 2: FESEM micrograph of (a) GO and (b) *as-synthesised* GO-Fe$_3$O$_4$

Optimization of MSPE conditions

Effect of Type and Volume of Solvent

Desorption efficiency of five different types of organic solvent namely acetone, acetonitrile, ethyl acetate, *n*-hexane and methanol was investigated (Fig. 3). Results showed that the use of acetonitrile produced the highest extraction efficiency (based on peak area). Acetonitrile has the highest polarity index (5.8) amongst the solvents used and was able to best desorbed chlorpyrifos and diazinon from the adsorbent.
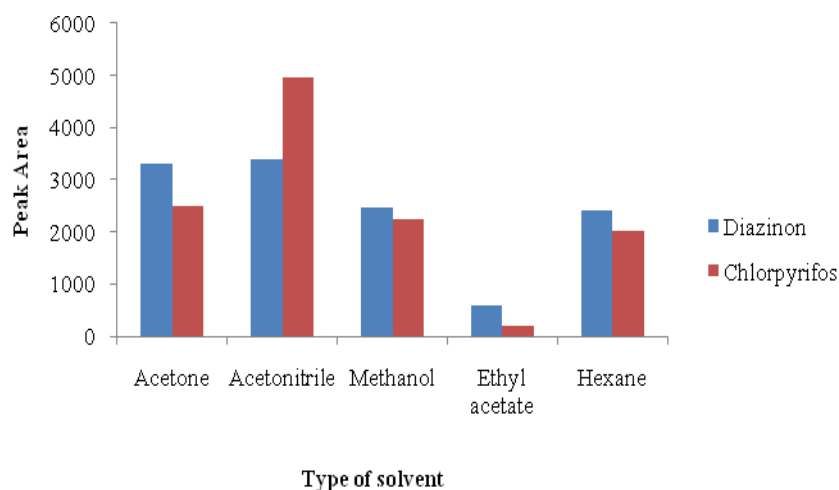
Figure 3: Effect of five different desorption organic solvents on the extraction efficiency (based on peak area) for diazinon and chlorpyrifos using the *as-synthesised* Fe$_3$O$_4$-GO MSPE. MSPE Conditions: 1 mL desorption solvent volume, 5 min extraction time, 10 mL sample volume, 20 mg adsorbent, 1 µg L^{-1} concentration of each chlorpyrifos and diazinon standard

Fig 4 shows the effect of acetonitrile volume (0.5 to 5 mL) used on the extraction efficiency. It was found that 0.5 mL of acetonitrile was sufficient to completely desorb the analytes and gave the highest peak area response for both chlorpyrifos and diazinon. Thus, 0.5 mL of acetonitrile was selected for the next optimization process.
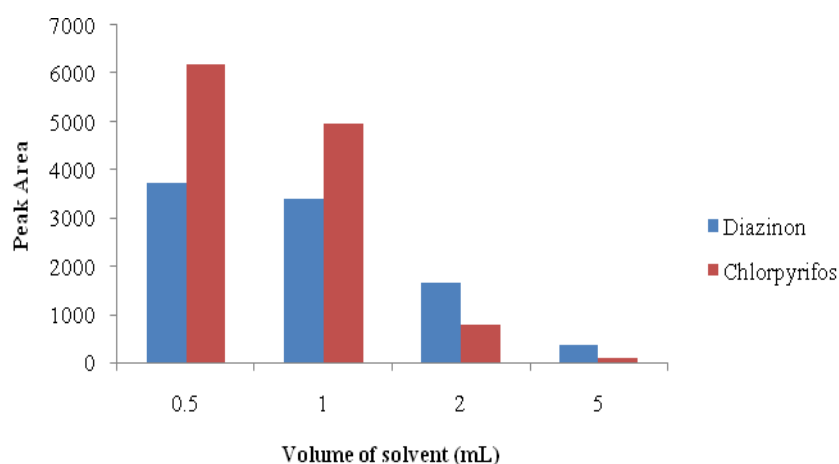
Figure 4: Effect of acetonitrile volume used on the extraction efficiency (based on peak area) for diazinon and chlorpyrifos using the *as-synthesised* Fe$_3$O$_4$-GO MSPE. Conditions: Acetonitrile as desorption solvent volume, 5 min extraction time, 10 mL sample volume, 20 mg adsorbent, 1 µg L^{-1} concentration of mixed chlorpyrifos and diazinon standard
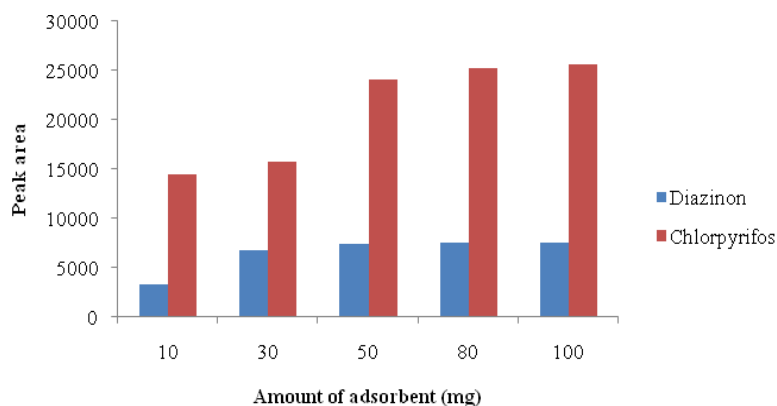
Extraction time

Extraction time is one of the important parameters to be optimized to ensure optimal extraction efficiency. Various extraction times from 1 to 30 min was evaluated (Fig 5). As shown in Fig. 5, the extraction efficiency increased with increasing extraction time from 1 to 10 min, and then remained almost constant at 30 min. Therefore, the extraction time of 10 min was selected as the optimal extraction time.
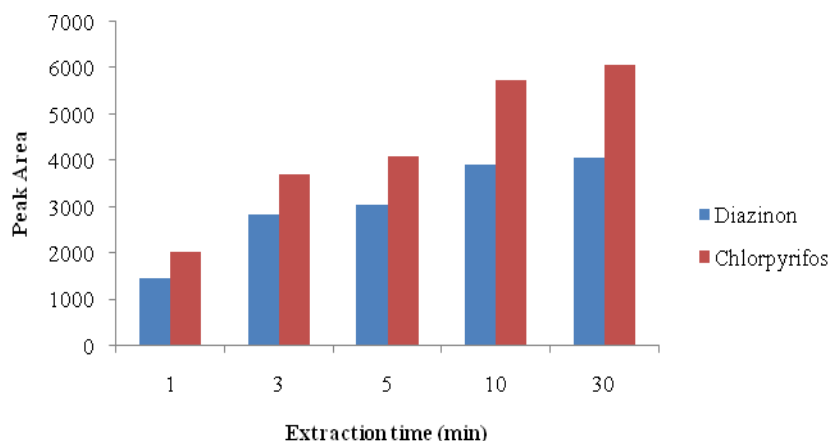
Figure 5: Effect of different extraction time on the extraction efficiency (based on peak area) for diazinon and chlorpyrifos using the *as-synthesised* Fe_3O_4-GO MSPE. MSPE conditions: 0.5 mL desorption solvent volume, 10 mL sample volume, 20 mg adsorbent, 10 μg L^{-1} concentration of mixed chlorpyrifos and diazinon standard

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Mass of adsorbent

The amount of Fe_3O_4-GO adsorbent (50 to 100 mg) used in the extraction process was also optimized. Figure 6 illustrates the effect of amount of adsorbent used on the GC-ECD response. Based on the bar chart illustrated, it was observed that peak area of the analytes detected increased rapidly as the mass of adsorbent increased. A plateau was achieved for both chlorpyrifos and diazinon when the mass of adsorbent was increased to 50 mg. The amount of analyte extracted was almost constant, indicating that 50 mg adsorbent is sufficient to extract both analytes from the solution. The response of the extracted chlorpyrifos and diazinon remain almost constant until further increase in adsorbent mass to 100 mg. Therefore, 50 mg of Fe_3O_4-GO was used in the next optimization step taken into consideration that bigger adsorbent mass means greater cost of analysis. It can also be observed that the *as-synthesised* Fe_3O_4-GO adsorbent has much higher selectivity for chlorpyrifos.

Figure 6: Effect of amount of adsorbent used on the extraction efficiency (based on peak area) for diazinon and chlorpyrifos using the *as-synthesised* Fe_3O_4-GO MSPE. MSPE conditions: 0.5 mL acetonitrile as desorption solvent, 10 min extraction time, 10 mL sample volume, 10 μg L^{-1} concentration of mixed chlorpyrifos and diazinon standard

Sample Volume

In this optimization step, the volumes of sample were varied from 5 to 100 mL (Figure 7) to study the effect on the extraction efficiency. Figure 7 shows that the analyte response showed an increased from 5 mL to 50 mL sample volume and a sharp increased in response from 50 to 80 mL sample volume. No additional increment in the extraction efficiency (peak area) was observed with further increase of sample volume up to 100 mL. Thus, 80 mL was selected as the optimum sample to be used in the next step analysis.
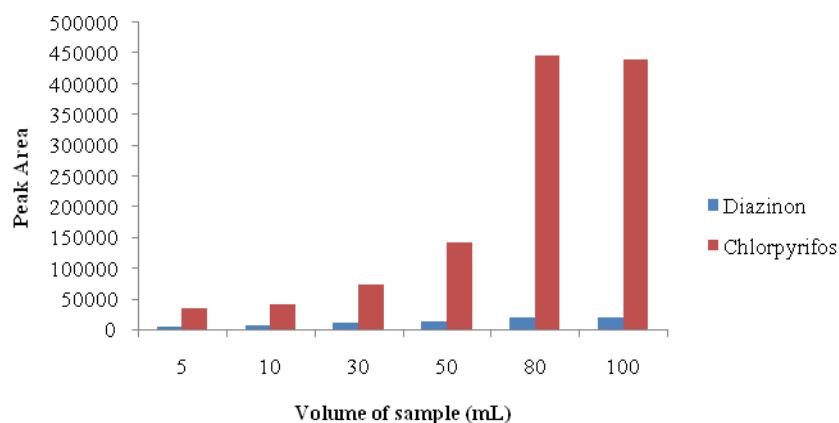
Figure 7: Effect of volume of sample on the extraction efficiency (based on peak area) for diazinon and chlorpyrifos using the *as-synthesised* Fe_3O_4-GO MSPE. MSPE conditions: 0.5 mL acetonitrile as desorption solvent, 10 mL sample volume, 20 mg adsorbent, 10 µg L^{-1} of mixed chlorpyrifos and diazinon standard

Method Validation

Under the optimal experimental conditions (10 min extraction time, 50 mg adsorbent mass, 80 mL sample volume and 500 µL acetonitrile as desorption volume), the linearity, precision, LOD (3 S/N), LOQ (10 S/N) and precision of the proposed method were studied. To obtain the method linearity, standard OPPs solutions from 0.1 to 10 µg L^{-1} were analyzed by using Fe_3O_4.GO MSPE followed by GC-ECD analysis. Method repeatability was assessed by using three parallel intraday extractions of mixed standard OPPs. Inter-day analysis (n = 9) was also performed to investigate the reproducibility of the proposed MPSE method. Table 1 shows the summary of LOD, LOQ, coefficient of determination (R^2) and precision of chlorpyrifos and diazinon using the proposed Fe_3O_4-GO MSPE method. High R^2 and low LOD indicate the sensitivity of the developed MSPE method towards the two selected OPPs. The LOD obtained for chlorpyrifos is 33× lower than the pesticides MRL allowed in water samples (0.1 ng mL^{-1} of each pesticide) [11].

Table 1: Figure of merits of the developed MSPE-GC-ECD method

Analyte	Linear range (µg/L)	R^2	LOD (µg/L)	LOQ (µg/L)	RSD (%)	
					Intraday (n = 3)	Interday (n = 9)
Chlorpyrifos	0.1 – 10	0.9997	0.034	0.133	9.95	11.45
Diazinon	0.1 – 10	0.9997	0.40	1.33	9.05	13.35

Sample analysis of OPPs in lake water sample

The applicability of the Fe_3O_4-GO MSPE method developed was performed on three replicates of UTM lake water sample. No residues of chlorpyrifos and diazinon were detected in the UTM lake water sample. To assess the effect of matrix, the UTM lake water sample was spiked at concentration level of 0.5 µg L^{-1}. The results obtained are summarized in Table 2. The result shows satisfactory recoveries of chlorpyrifos (57.71%) and diazinon (73.86%) with RSD in the range of 17.5% and 18.00%. The low recovery of the OPPs implies that

matrices had some interference with the performance of the Fe_3O_4-GO MSPE method. Thus, a matrix matched calibration is more appropriate.

Table 2: Analytical results for OPPs in lake water sample using Fe_3O_4-GO MSPE method

Spiking level ($\mu g\ L^{-1}$)	Chlorpyrifos			Diazinon		
	Found ($\mu g\ L^{-1}$)	Recovery (%)	RSD (%)	Found ($\mu g\ L^{-1}$)	Recovery (%)	RSD (%)
0.00	nd	-	-	Nd	-	-
0.5	0.29	57.71	17.50	0.35	73.86	18.00

nd: Not detected

Sample analysis of OPPs in tomato sample

The Fe_3O_4-GO MSPE method was further applied to the analysis of these two OPPs from tomato samples. Since the method is susceptible to matrix effect, matrix-matched calibration curve for chlorpyrifos and diazinon were constructed in the range of 1 to 50 $\mu g\ L^{-1}$ for its analysis from tomato samples. R^2 value of 0.9963 and 0.9897 for chlorpyrifos and diazinon respectively indicates good linearity of the method. The percentage recovery of chlorpyrifos was found to be in the range of 84.8 to 107.3% and 41.90 to 66.0% for diazinon. From the matrix-matched calibration, 0.19 $\mu g\ L^{-1}$ chlorpyrifos and 7.88 $\mu g\ L^{-1}$ diazinon were found in the tomato samples analysed. The maximum residue limit of pesticide in vegetable is 10 $\mu g\ kg^{-1}$. Therefore, the tomato sample analysed is safe to be eaten since the content is below the MRL value. The analytical results for determination of chlorpyrifos and diazinon in tomato sample are summarized in Table 4.4.

Table 3: Analytical results for the analysis of OPPs in tomato samples using the Fe_3O_4-GO MSPE method

Analyte	Linear range ($\mu g\ L^{-1}$)	R^2	Found ($\mu g\ L^{-1}$)	Recovery (%)
Chlorpyrifos	1 -50	0.9963	0.19	84.8-107.3
Diazinon	1 – 50	0.9897	7.88	41.9-66.0

CONCLUSION

In this work, Fe_3O_4-GO was successfully synthesized by using the modified Hummer's method followed by a one step co-precipitation method. The *as-synthesised* Fe_3O_4-GO was assessed for its suitability as adsorbent for chlorpyrifos and diazinon from lake water and tomato samples. Matrix from lake water sample was found to affect the performance of the *as-synthesised* Fe_3O_4-GO MSPE adsorbent. Thus, for tomato sample, matrix-matched calibration was used. Quantitative recovery (> 80%) was observed for chlorpyrifos in tomato sample analysed but the recovery of diazinon was still low (42-66%). Further modification of the adsorbent is needed to enhance its efficiency, precision (RSD) and accuracy (recovery) of the method

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