Electronic Supporting Material on Analytical Methods entitled

"Facile synthesis of magnetic molybdenum disulfide@graphene nanocomposite with amphiphilic properties and its application in solid-phase extraction for a wide polarity of insecticides in wolfberry samples"

Xiao-Chun Ma[a, ‡], Zong-Qin Ma[a, ‡], Meng-Xin Zhao[a] , Ying-Hui Wang[a], Yuan Peng[a], Xin Guo[a], Fang-HuanWang[b], ZheMeng[a,*], Hao-Bo Zheng[a]

[a]State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, National Demonstration Center for Experimental Chemistry Education, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China

[b]Yinchuan Customs Technology Center, Yinchuan 750000, China

‡ These authors contributed equally.

*Corresponding author:

Prof. ZheMeng, State Key Laboratory of High-Efficiency Utilization of Coal and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China. Tel: +86 951 2061224; Fax: +86 951 2061231.Email: meng_z@nxu.edu.cn
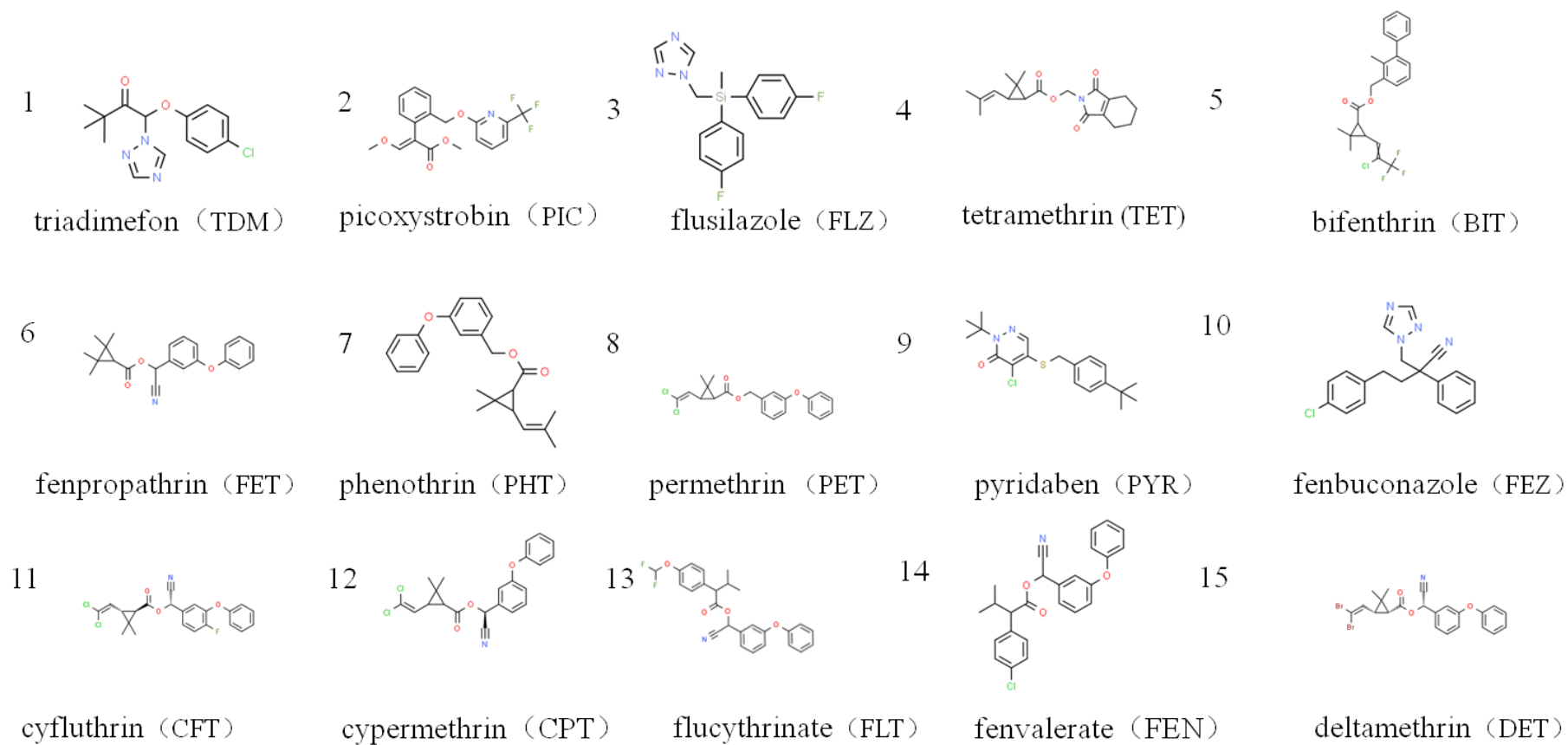
Fig. S1 The chemical structures of the selected compounds

Preparation of adsorbent

The Fe_3O_4 nanoparticles were synthesized via chemical co-precipitation hydrothermal method. [36]   A hydrous sodium acetate (2.94 g), macrogol2000 (0.82 g) and $FeCl_3 \cdot 6H_2O$ (1.0g) were stirred and added with 33 mL of ethylene glycol in a Teflon-lined autoclave at 180 ℃ for 16 h. The Fe_3O_4 was washed with distilled water and ethanol till a neutral, and then dried at 50°C for 24 h under vacuum.

The green method was used to prepare graphene dispersions for liquid phase exfoliation of graphite in a mixture of water and alcohol. [37] The optimum mass fraction of ethanol in water-ethanol mixtures is 55%. 20 mL solution in the glass vessel with initial graphite concentration of 0.2 mg mL^{-1} was sonicated for 2 h in a fixed position in one sonic bath with 20 W. After sonication, the obtained dark dispersion was left to stand for 8 h for the sufficient sedimentation of large particles. Then, the upper less dark dispersion was centrifuged at 3000 rpm for 30 min in a centrifuge to remove any largish flakes, which finally resulted in homogeneous colloidal suspension of graphene sheets standing in the water-alcohol mixtures for 2 weeks. X-ray diffraction (XRD) analysis (**Fig. S2**) was vacuum filtration of the dispersion obtained from the above-mentioned optimizing experiments through a mixed cellulose ester with pore size of 0.22μm. X-ray diffraction (XRD) analysis of exfoliated graphite sheet further proved that the graphene lattice parameters remain, and basal planes were free of structural disorder. Compared with the graphite powder, the exfoliated graphite flakes have a very weak peak at 2θ-26.6° corresponding to the (002) planes. This may be attributed to an unchanged layer-to-layer distance from graphite. The above-mentioned very thin flakes or graphene layers demonstrated high degree of exfoliation.
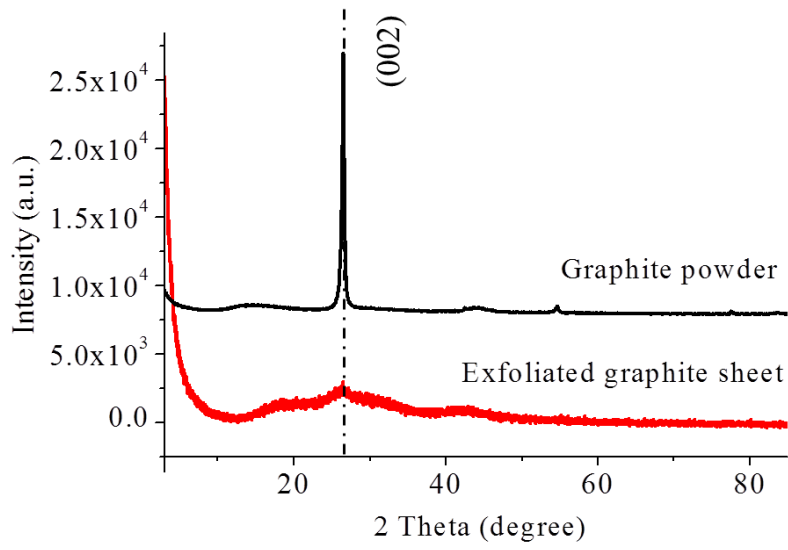
Fig. S2 XRD spectra of the graphite powder and an as-exfoliated graphene layers
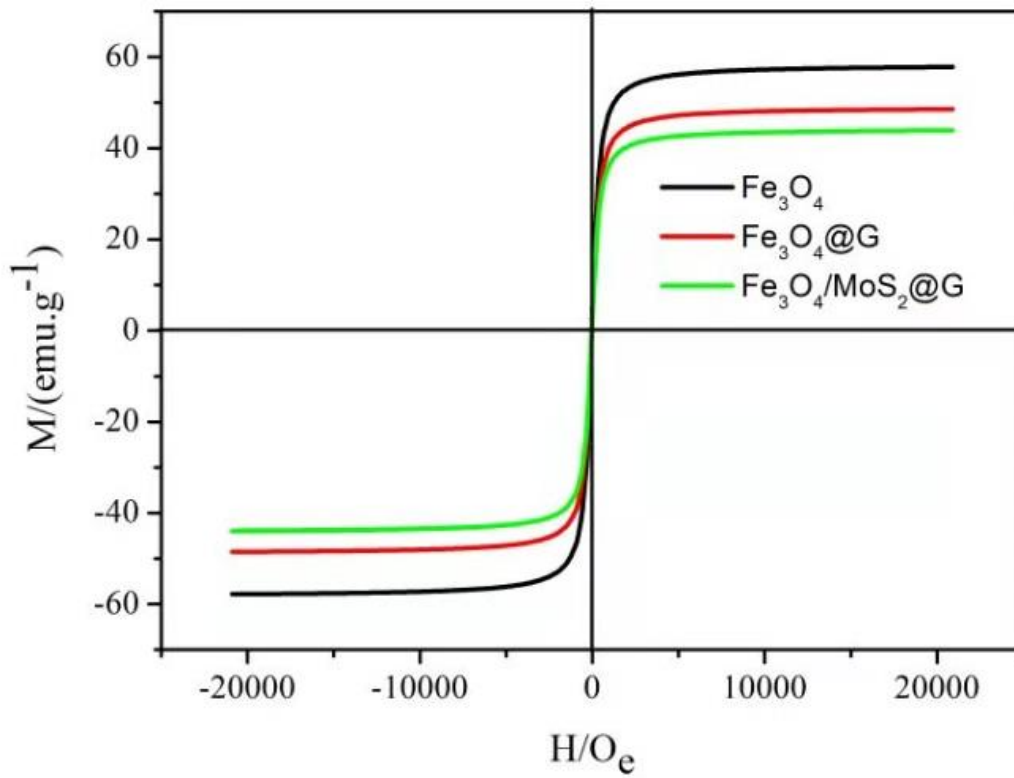

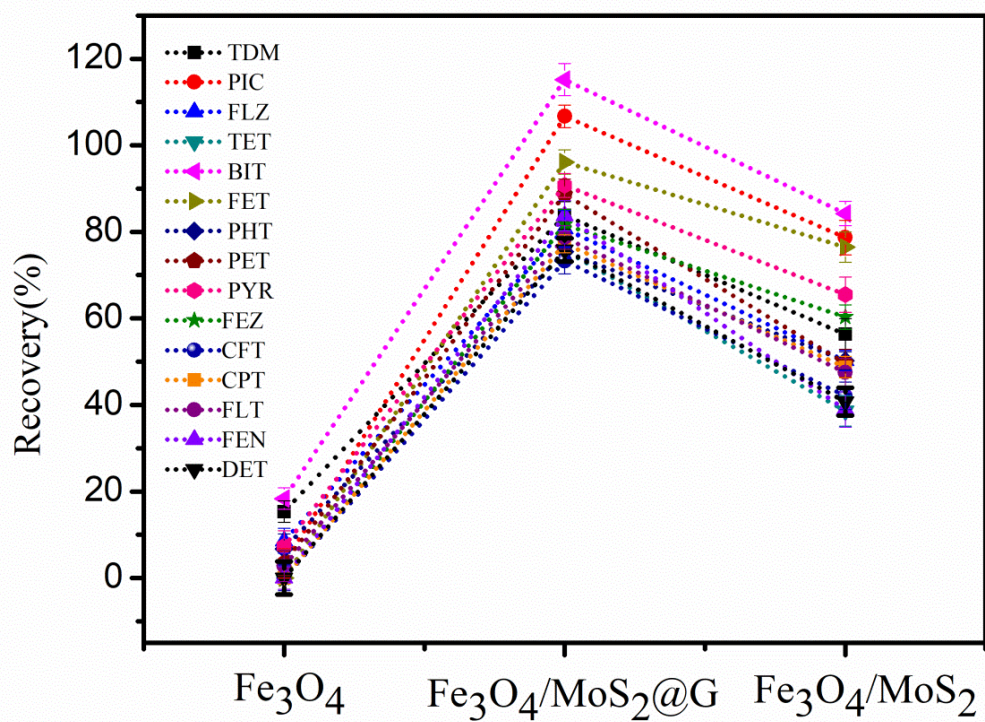**Fig. S3** Magnetic curves of $MoS_2/Fe_3O_4@G$

Fig. S4 The selectivity of different sorbent materials toward 15 selected target analytes.

3.3 Optimization of extraction conditions in MSPE procedure

Before using RSM to optimize the extraction step, the single-factor experiments were carried out to determine the range of variables demands to obtain a more realistic mode (see **Fig. S5** a-d). The pH of the sample solution is an important factor in MSPE procedure, and can influent both the existing form of target compounds and the surface charge of sorbents. The pH of the sample solution was made to range from 2 to 12 by using 1.0 mol L $^{-1}$ HCl or NaOH. Then, the effect of sample solution pH on the extraction of each selected insecticides was studied (**Fig. S5** a). The highest extraction efficiencies for each analytes were obtained at pH of 6. When pH<6 or pH>6, low recoveries were obtained. Based on the results, further studies were performed using pH of 6 as the optimal pH.

The effect of $Fe_3O_4/MoS_2@G$ used on the extraction of each selected insecticides was also studied. The amount of $Fe_3O_4/MoS_2@G$ was range from 3 to 8 mg. The results showed that the highest extraction efficiencies for each analytes were obtained when 5 mg of $Fe_3O_4/MoS_2@G$ was used (**Fig. S5** b). As the amount of $Fe_3O_4 / MoS_2 @ G$ increases to 5 mg, the extraction efficiency increases. Then, it decreases due to the increase in the accumulation of $Fe_3O_4/MoS_2@G$ in emulsified aqueous phase and decrease in dispersibility. According to the results, further studies were performed using 5 mg of $Fe_3O_4/MoS_2@G$ as the optimal the amount of sorbent.

The effect of extraction time on the extraction of each selected insecticides was studied. The extraction time was in the range of 20-80 min. The results showed that the sorption of each target analytes reached equilibrium after 40 min and further extension of extraction time had no significant influence on the extraction efficiency (**Fig. S5** c). According to the results, further studies were performed with 40 min as the optimal extraction time.

In addition, the choice of desorption solvent, as well as optimal elution volume and time were important for the satisfactory extraction efficiency. In this study, different organic

solvents, including acetonitrile (ACN), 0.1% Acetic acid (AA)-ACN, dichloromethane (DCM) and 0.1% AA-DCM were used separately as elution solution in MSPE procedure. Almost all target analytes have the highest dichloromethane recovery, as shown in **Fig. S5** d. We found that 500 μL of dichloromethane could completely elute the extracted target analytes from $Fe_3O_4/MoS_2@G$. In addition, the elution time was optimized by increasing the vortex time from 1.0 to 5.0 min. The result indicated that 2.0 min was enough to elute the extracted 15 selected target analytes from the magnetic sorbent. According to the results, further studies were performed using 500 μL of dichloromethane as the optimal desorption solvent.
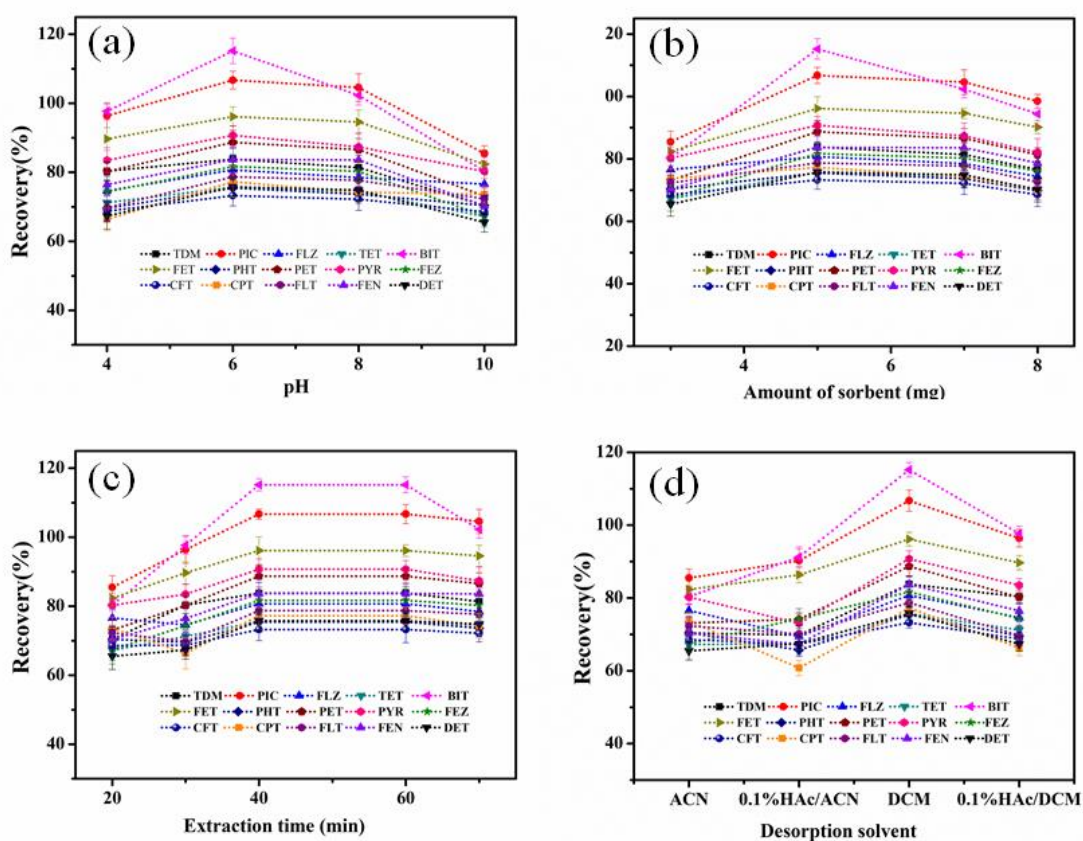

Fig. S5 Effect of (a) the pH of the solution, (b) the amount of sorbent, (c) the extraction time, (d) the desorption solvent on the efficiency of extraction of 15 selected target analytes from blank spiked sample, each insecticide solution at 0.1 μg mL $^{-1}$ except picoxystrobin and

bifenthrin at 0. 01 μg mL $^{-1}$ (n=3).

Table S1 Box-Behnken experiment designs and analysis with the independent variables of the data from each of 15 target analytes

Run	Sorption time (min) （A）	pH (B)	Amount of sorbent (mg) (C)	Recovery (%)														
				TDM	PIC	FLZ	TET	BIT	FET	PHT	PET	PYR	PEZ	CFT	CPT	FLT	FEN	DET
1	0	0	0	82.61	105.00	81.23	76.32	112.78	94.03	76.28	89.64	88.24	82.68	74.26	76.32	79.06	85.64	78.66
2	1	1	0	70.52	93.16	72.56	62.35	98.47	84.36	66.34	72.34	72.28	78.37	66.04	61.32	68.45	70.20	63.22
3	0	0	0	83.78	106.70	80.71	75.69	115.19	96.13	75.44	88.67	90.72	81.66	73.26	77.25	78.69	83.69	75.78
4	1	1	0	51.22	75.26	48.96	43.22	86.75	73.28	47.36	57.36	62.56	52.01	50.32	43.25	42.23	40.35	38.75
5	-1	-1	0	69.85	90.22	69.45	67.45	91.23	86.32	65.73	74.16	73.05	74.35	67.35	60.78	70.14	67.32	67.45
6	0	0	0	84.08	101.22	78.33	72.39	116.33	95.64	73.46	86.30	92.58	84.56	74.68	81.29	85.23	76.77	78.49
7	0	1	1	79.56	89.67	69.45	67.45	102.33	84.17	64.38	70.25	78.02	64.35	70.21	76.88	71.38	68.75	60.17
8	0	1	-1	56.36	78.66	50.27	38.65	84.23	76.45	50.23	49.65	65.47	60.33	42.12	48.75	47.55	38.96	40.78
9	-1	0	-1	54.30	82.11	51.23	40.28	81.66	80.21	47.00	50.36	60.54	64.21	39.65	45.33	47.22	42.57	44.00
10	0	-1	1	75.08	83.45	70.11	68.54	86.35	83.23	60.38	65.48	77.66	74.35	69.47	67.54	70.22	73.22	63.22
11	0	0	0	88.56	97.43	83.07	76.86	102.38	92.44	74.28	78.04	93.01	84.53	77.00	74.29	77.68	84.21	75.48
12	-1	0	1	75.39	80.24	71.25	63.75	86.34	78.98	62.11	70.12	79.88	65.47	60.58	70.24	74.22	71.30	64.35
13	-1	1	0	52.30	75.32	67.88	60.32	80.35	74.02	49.85	47.23	67.80	58.66	60.20	50.20	52.45	50.44	54.21
14	1	0	-1	74.32	78.60	66.44	68.54	83.54	74.35	58.68	66.35	76.54	67.35	63.25	74.35	76.35	74.25	63.27
15	0	-1	-1	68.28	75.36	63.24	61.20	79.64	76.58	50.24	64.23	70.22	62.34	58.32	64.87	61.23	67.35	51.01
16	1	0	1	70.39	85.46	76.58	67.25	80.32	82.33	70.39	73.12	80.24	67.45	68.55	73.64	72.31	70.34	65.48
17	0	0	0	87.05	98.06	84.67	73.45	96.45	91.58	77.08	76.58	92.48	79.20	78.66	75.33	86.02	78.52	73.10

Table S2. Analysis of variance (ANOVA) for response surface quadratic model for extraction process (taking the data obtained for pyridaben as an example)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1596.45	9	177.38	35.75	<0.0001	
A-A	13.55	1	13.55	2.73	0.1425	Not significant
B-B	54.29	1	54.29	10.94	0.0130	Significant
C-C	231.45	1	231.45	46.64	0.0002	Significant
AB	5.02	1	5.02	1.01	0.3481	Not significant
AC	6.53	1	6.53	1.32	0.2891	Not significant
BC	61.15	1	61.15	12.32	0.0099	Significant
A^2	478.40	1	478.40	96.41	<0.0001	Significant
B^2	356.51	1	356.51	71.85	<0.0001	Significant
C^2	263.06	1	263.06	53.01	0.0002	Significant
Residual	34.74	7	4.96			
Lack of Fit	19.14	3	6.38	1.64	0.3156	
Pure Error	15.60	4	3.90			
Cor Total	1631.18	16				
		$R^2=0.9787$		$R^2_{Adj}=0.9513$		$R^2_{Pred}=0.7973$

Table S3. Analysis of variance (ANOVA) for response surface quadratic model for extraction process (taking data for triadimefon as an example)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1878.00	9	208.67	25.31	0.0002	
A-A	73.93	1	73.93	8.97	0.0201	significant
B-B	138.11	1	138.11	16.75	0.0046	significant
C-C	278.01	1	278.01	33.72	0.0007	significant
AB	82.99	1	82.99	10.07	0.0157	significant
AC	67.24	1	67.24	8.15	0.0245	significant
BC	156.50	1	156.50	18.98	0.0033	significant
A^2	355.06	1	355.06	43.06	0.0003	significant
B^2	455.67	1	455.67	55.26	0.0001	significant
C^2	162.53	1	162.53	19.71	0.0030	significant
Residual	57.72	7	8.25			
Lack of Fit	33.03	3	11.01	1.78	0.2894	
Pure Error	24.69	4	6.17			
Cor Total	1935.72	16				
		R^2=0.9702		R^2_{Adj}=0.9318		R^2_{Pred}=0.7071

Table S4. Analysis of variance (ANOVA) for response surface quadratic model for extraction process (taking data for cypermethrin as an example)

| Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1831.75	9	203.53	15.40	0.0008	
A-A	35.36	1	35.36	2.68	0.1459	Not significant
B-B	236.97	1	236.97	17.93	0.0039	Significant
C-C	378.13	1	378.13	28.62	0.0011	Significant
AB	30.91	1	30.91	2.34	0.1700	Not significant
AC	162.05	1	162.05	12.26	0.0100	Significant
BC	164.10	1	164.10	12.42	0.0097	Significant
A^2	421.31	1	421.31	31.89	0.0008	Significant
B^2	313.08	1	313.08	23.69	0.0018	Significant
C^2	23.91	1	23.91	1.81	0.2205	Not significant
Residual	92.49	7	13.21			
Lack of Fit	63.48	3	21.16	2.92	0.1638	
Pure Error	29.01	4	7.25			
Cor Total	1924.24	16				
		$R^2=0.9519$	$R^2_{Adj}=0.8901$		$R^2_{Pred}=0.6786$	
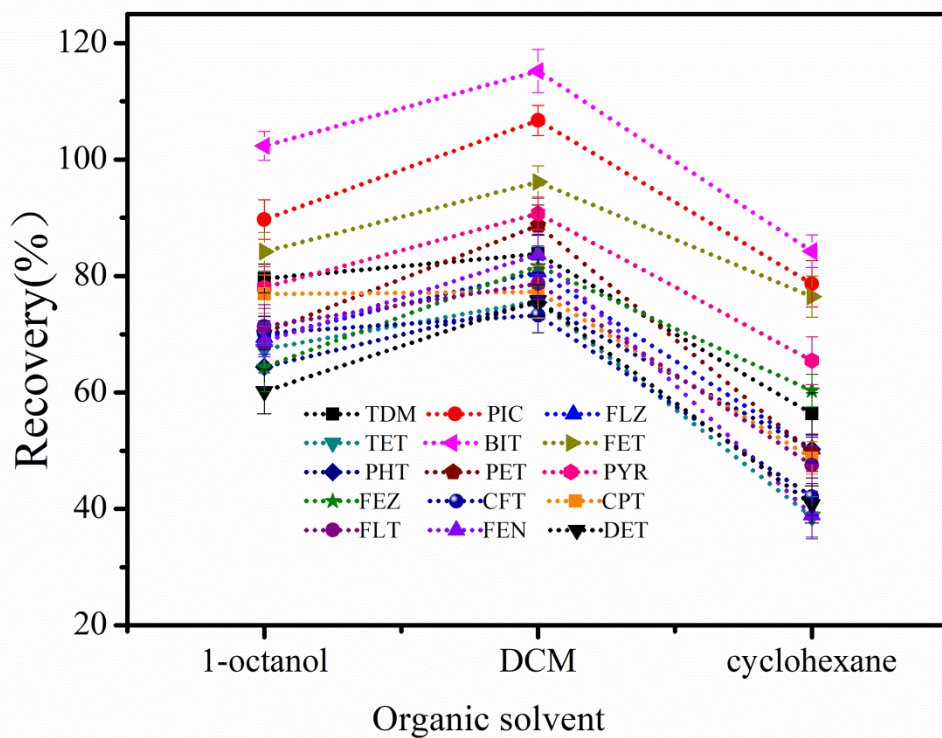
Fig. S6 The effect of organic solvent selected on the formation of emulsified solution

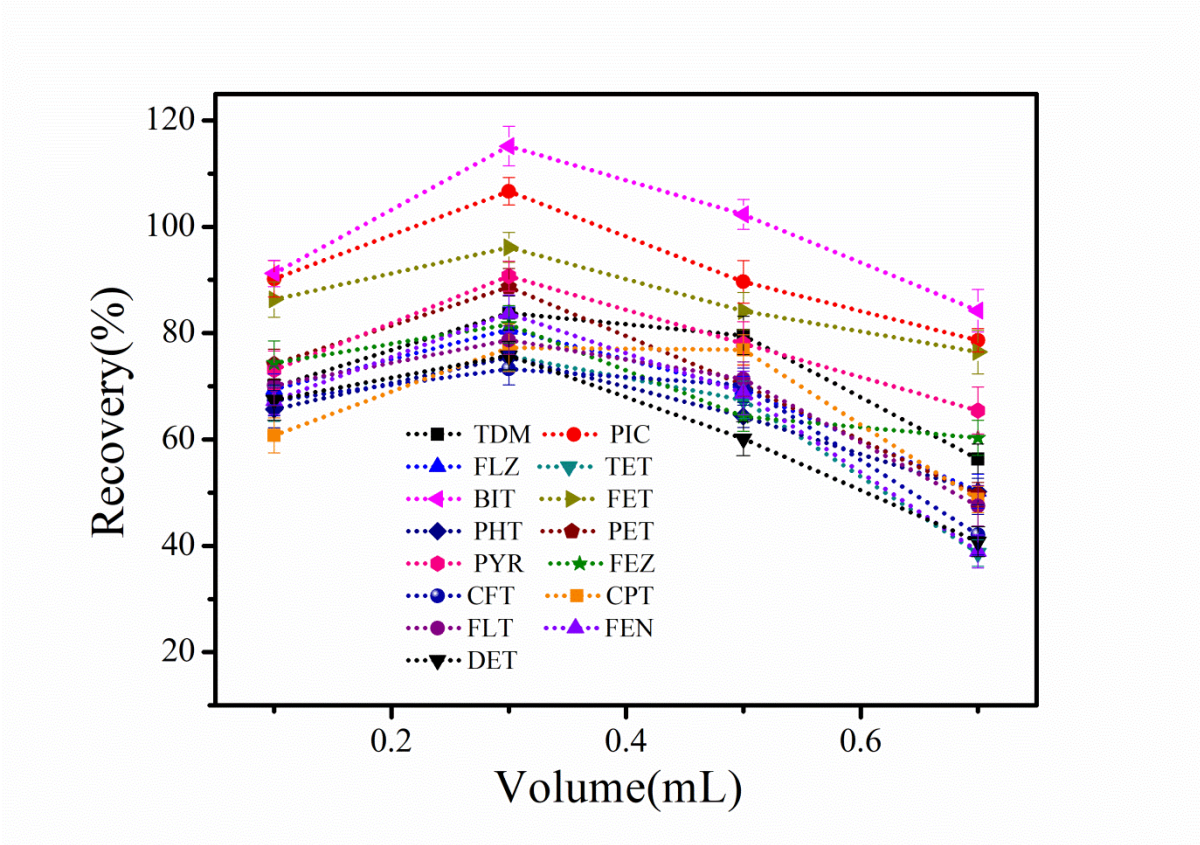**Fig. S7** The effect of the volume of organic solvent selected on the formation of emulsified solution
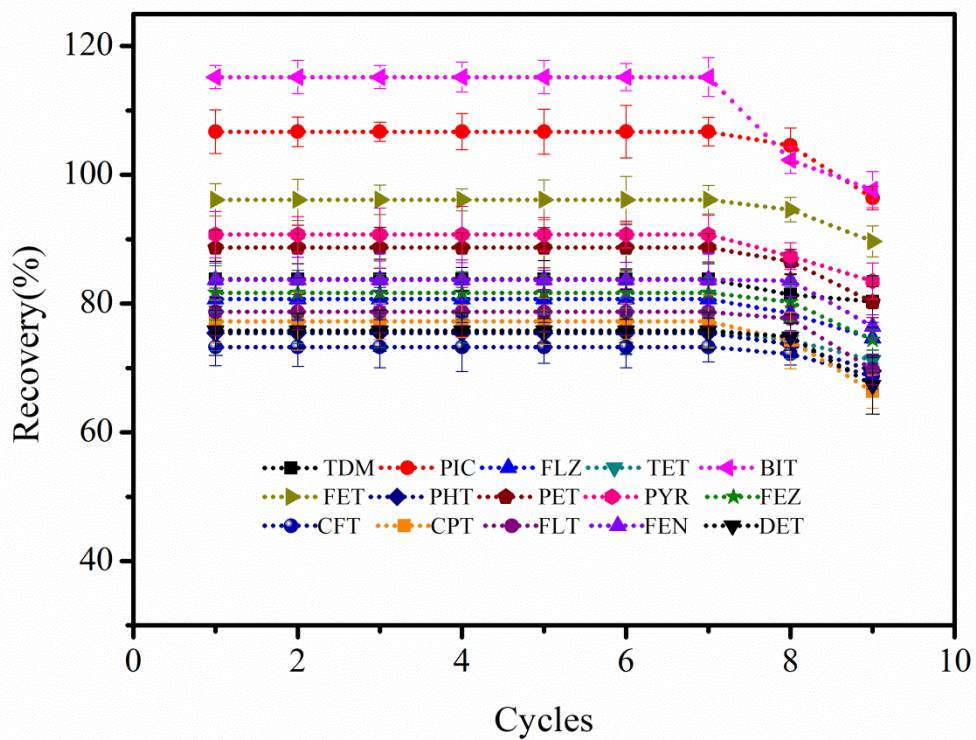
Fig. S8 The reusability of Fe$_3$O$_4$/MoS$_2$@G for the enrichment of all target analytes in MSPE procedure
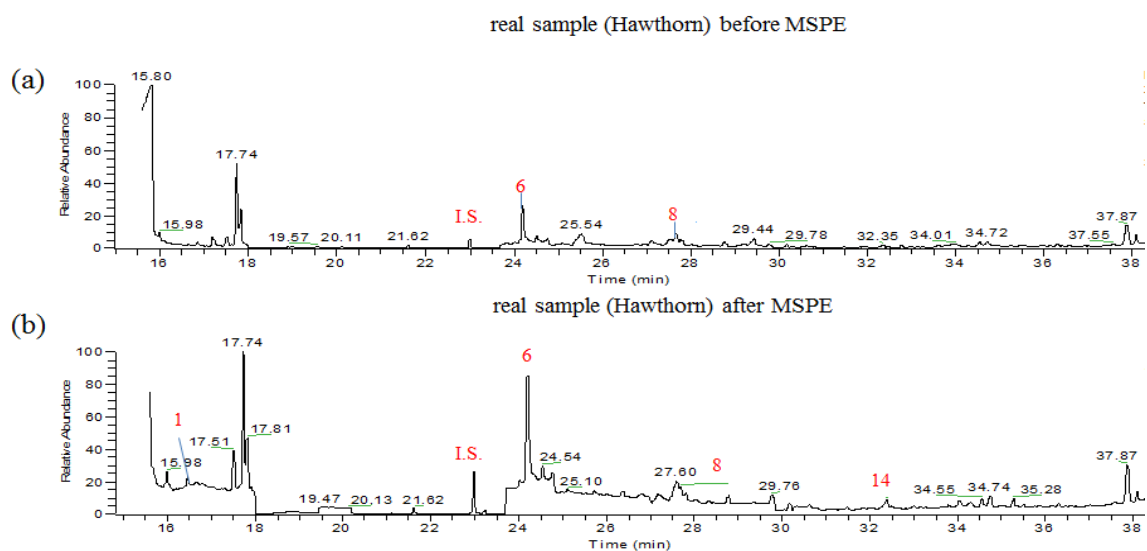
Fig. S9 GC-MS chromatograms obtained for (a) blank hawthorn sample, (b) real hawthorn sample after applying MSPE extraction. The concentration of each target insecticide and optimization condition in MSPE procedure, as with Fig. 6. Peak identification numbers correspond to compounds reported in Table 1.
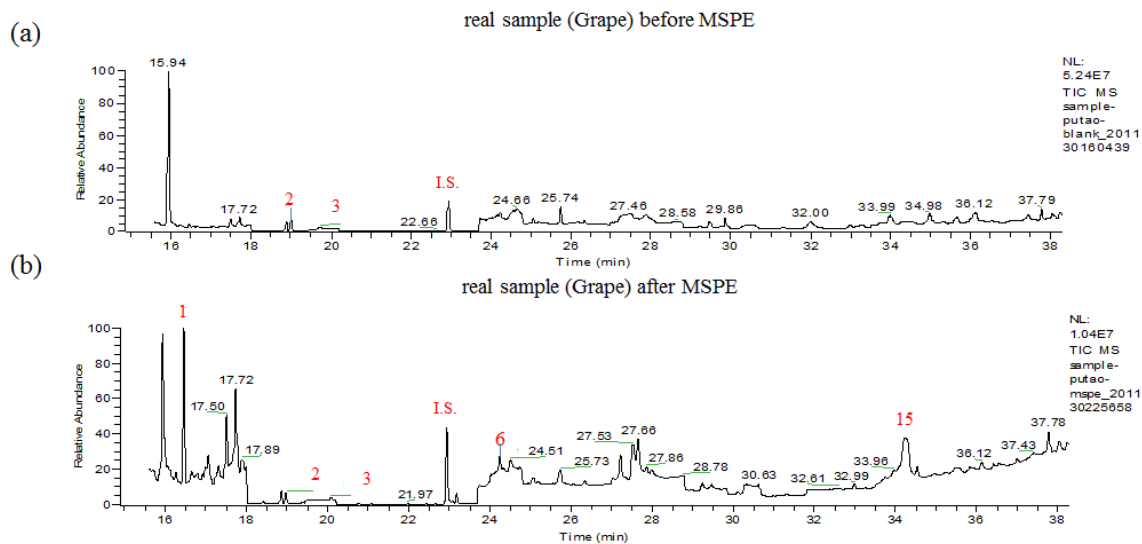
Fig. S10 GC-MS chromatograms obtained for (a) blank grape sample, (b) real grape sample after applying MSPE extraction. The concentration of each target insecticide and optimization condition in MSPE procedure, as with Fig. 6. Peak identification numbers correspond to compounds reported in Table 1.