Preparation of ZIF-67-modified magnetic solid phase extraction material and application in the detection of pyridine ring insecticides

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Preparation of MGO composites

MGO composite was prepared by one-step co-precipitation method. Briefly, GO (0.3g) was dispersed into deionized water (50mL) with ultrasonic treatment for 4h to form a uniform dispersion. Next, $FeCl_3 \cdot 6H_2O$ (4.0g) and $FeCl_2 \cdot 4H_2O$ (2.5g) were dissolved in deionized water and added to the above dispersion. Meanwhile, 25mL ammonia solution was quickly added to the reaction mixture, and 0.75mL oleic acid was injected into the mixture after stirring for 10minutes. Then, the reaction mixture was heated with a thermostatic magnetic stirring at 90 ℃ for 3h. After that, the product was washed several times with deionized water and ethanol. MGO was collected by magnetic separation and dried under vacuum at 70 ℃ overnight.

Preparation of poly-dopamine modified MGO

MGO@PDA was synthesized by DA polymerization in Tris-HCl buffer（pH=8.5）at 25 ℃. Briefly, MGO (0.15g) was poured into deionized water (100mL) with sonicate treatment for 1h to form a homogeneous solution. Subsequently, DA (0.2g) and Tris (0.05g) were added to the dispersion, and continuous ultrasonically shaken for 5min. Then, this mixture was reacted for 24h under mechanically stirring with the speed of 150rpm at room temperature. Next, the obtained product (MGO@PDA) was separated with external magnetic field, which was successively

washed with ultrapure water and ethanol several times. Finally，the product was dried under vacuum oven 60 ℃ overnight.

Representation of different isothermal adsorption equations

Langmuir isotherm model：

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \left(\frac{1}{q_{max}}\right) C_e \quad (1)$$

Freundlich isotherm：

$$Inq_e = InK_F + \frac{InC_e}{n} \quad (2)$$

where q_e (mg·g^{-1}) is the adsorption capacity, C_e (μg·mL^{-1}) is the equilibrium concentration in water, q_{max} (mg·g^{-1}) is the theoretical saturate adsorption capacity in the Langmuir model, and K_L (mL·μg^{-1}) is the Langmuir isotherm constant demonstrating the tendency of adsorption，K_F is the Freundlich isotherm constant and n is the heterogeneity factor.

Representation of different Kinetic adsorption equations

pseudo-first order model:

$$In(q_e - q_t) = Inq_e - k_1 t \quad (3)$$

pseudo-second order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where q_e and q_t (mg g^{-1}) are the amounts of the analyte onto the adsorbents at equilibrium and time t (min). k_1 (min^{-1}) is the rate constant in the pseudo-first order adsorption model. k_2 (g/(mg·min)) is the rate constant in the pseudo-second order adsorption model.

Table S1：The peak areas of praziquantel and pymetrozine at the concentration of 0.1-100 μg·mL^{-1}

Concentration	Peak area (praziquantel)	Peak area (pymetrozine)
0.1μg/mL	10019.7	92485.7
1μg/mL	100387.7	100321.6
5μg/mL	478702.9	496154.8
10μg/mL	971128.5	967214.9
15μg/mL	1467116.6	1425064.2
20μg/mL	1970804.1	1947788.8
30μg/mL	2911799.7	2912494.2
40μg/mL	3900563.8	3881115.4
50μg/mL	4734553.8	4846367.3
60μg/mL	5664812.0	5813337.9
100μg/mL	9350021.9	9567641

As shown in Fig.S1, matrix-matched calibration curves for the relationship between concentrations of analytes and their peak areas were calculated by using weighted least-squares regression.

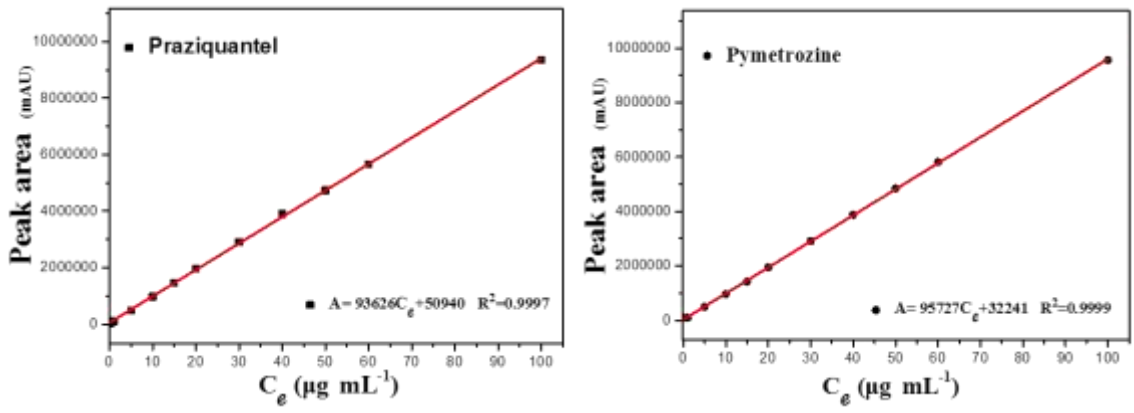


Fig.S1：The standrd curves of praziquantel and pymetrozine at the concentration of 0.1-100 μg·mL^{-1}

Table S2：Analytical performance of the present method

Analytes	Linear range	Regression equation	R^2	LOD	LOQ
praziquantel	0.1-100 μg mL^{-1}	A=93626C$_e$+50940	0.9997	0.21ng mL^{-1}	0.69ng mL^{-1}
pymetrozine	0.1-100 μg mL^{-1}	A=95727C$_e$+32241	0.9999	0.08ng mL^{-1}	0.26ng mL^{-1}

88 **Table S3：Specification of praziquantel and pymetrozine**

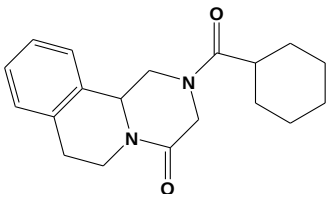
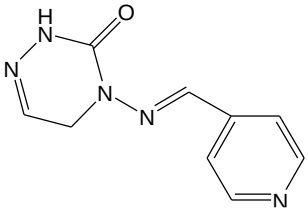
Contaminants	praziquantel	pymetrozine
Structure		
Molecular weight (g/mol)	312.41	217.23
Molecular formula	$C_{19}H_{24}N_2O_2$	$C_{10}H_{11}N_5O$
pKa	-0.98±0.20	12.90±0.40
CAS	55268-74-1	123312-89-0
Melting point (℃)	136-138	217
Physical properties	White crystal powder	White crystal powder

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Table S4：The surface atomic ration of main elements in different materials

Iterms	elements	GO	MGO	MGO@PDA	MGO@PDA@ZIF-67
	C1s	62.93	36.34	65.73	46.32
Surface	N1s	0.30	0.02	8.96	15.13
atomic	O1s	36.77	40.27	21.08	31.27
ratio(%)	Fe2p	0.00	23.36	4.23	3.14
	Co2p	0.00	0.01	0.00	4.14

Table S5 Two isotherm adsorption models parameters onto MGO@PDA@ZIF-67 m-SPE material.

Contaminant	Langmuir model			Freundlich model		
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F (mg^{1-n} L^n g^{-1})	$1/n$	R^2
Praziquantel	**22.68**	**7.113**	**0.9999**	**19.52**	**0.0614**	**0.8595**
Pymetrozine	**24.27**	**8.240**	**0.9998**	**18.86**	**0.0509**	**0.8632**

Table S6 Two Kinetic parameters for the adsorption onto MGO@PDA@ZIF-67 m-SPE material.

Contaminant	Pseudo-first order			Pseudo-second order		
	q_{e1} (mg g^{-1})	K_1 (min^{-1})	R^2	q_{e2} (mg g^{-1})	K_2 (g/(mg·min))	R^2
Praziquantel	**18.84**	**0.0296**	**0.9654**	**24.39**	**0.00248**	**0.9998**
Pymetrozine	**22.95**	**0.0324**	**0.8187**	**26.81**	**0.00237**	**0.9997**

Table S7：Comparison between the developed method and other previously m-SPE-HPLC methods for the extraction and determination of insecticides

Adsorbent	Analysis Method	Dosage of sorbent	Linear range	Recovery (%)	Ref.
Fe_3O_4@SiO_2@KIT-6	m-SPE-HPLC-UV	40mg	0.02-1200 ng·mL^{-1}	86.6-98.8	[41]
Fe_3O_4@COF-$(NO_2)_2$	m-SPE-HPLC-UV	10mg	0.1-30 ng·mL^{-1}	77.5-110.2	[42]
MGO/MIL	m-SPE-HPLC-DAD	20mg	0.064-3500 ng·mL^{-1}	82.13-102.27	[43]
Fe_3O_4@SiO_2-GO-MOF	m-SPE-HPLC-UV	10mg	0.02-1 μg·mL^{-1}	81.2-113.1	[44]
MGO@PDA@ZIF-67	m-SPE-HPLC-UV	5mg	0.10-100 μg·mL^{-1}	92.30-102.8	This work

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