# **Supplementary Information**

# Ternary deep eutectic solvent-modified magnetic mixed iron hydroxide@MIL-101(Cr)-

# NH<sub>2</sub> composite as a sorbent in magnetic solid phase extraction of organochlorine pesticides

### prior to GC–MS

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 Table S1 Abbreviations of TDESs and their molar ratios.

	Abbreviation	log [P]	TDES1	TDES2	TDES3	TDES4	TDES5	TDES6
lar ratio	Menthol	2.66	1	1	3	5	5	3
	Thymol	3.30	1	3	5	3	5	5
Mo	Dodecanoic acid	4.48	1	1	1	1	3	5



Fig. S1Extraction efficiency of the magnetic-metal organic framework modified with different ternary deep eutectic solvents. The magnetic solid phase extraction conditions were as follows: sorbent, 30 mg; extraction/desorption time, 30 s; desorption solvent, 0.5 mL of ethyl acetate; sample volume, 10 mL containing 50 µg L<sup>-1</sup> of each organochlorine pesticide.



**Fig. S2** Mole fraction of menthol, thymol and dodecanoic acid in the ternary deep eutectic solvents.

Table S2 Experimental factors, levels, and matrix of the Box–Behnken design for studying the synthesis conditions of MIH@MIL-101(Cr)-NH<sub>2</sub>-TDES and the central composite design for optimizing the conditions of magnetic solid phase extraction.

Factor			Levels		
Box–Behnken design		-1	0	+1	
$x_l$ : MOF amount (mg)		100	550	1000	
<i>x</i> <sub>2</sub> : TDES volume (mL)		0.10	0.55	1.00	
$x_3$ : Time (min)		30	60	90	
Central composite design	-2	-1	0	+1	+2
<i>X<sub>l</sub></i> : Sorbent amount (mg)	10	25	40	55	70
$X_2$ : NaCl concentration (% w/v)	0	2.5	5.0	7.5	10.0
<i>X</i> <sub>3</sub> : Extraction time (s)	10	30	50	70	90
<i>X</i> <sub>4</sub> : Sample volume (mL)	10	20	30	40	50

	Box–Behnken d	lesign			Central composite design						
Run	<i>x</i> <sub><i>l</i></sub> :	<i>x</i> <sub>2</sub> :	<i>x</i> <sub>3</sub> :	Response:	$X_l$ :	<i>X</i> <sub>2</sub> :	<i>X</i> <sub>3</sub> :	<i>X</i> <sub>4</sub> :	Response:		
	MOF amount	TDES volume	Time	Avg. of EFs	Sorbent amount	NaCl concentration	Extraction time	Sample volume	Avg. of EFs		
	(mg)	(mL)	(min)		(mg)	(% w/v)	(s)	(mL)			
1	100	1.00	60	20.53	55	2.5	30	20	23.01		
2	550	0.55	60	25.70	25	2.5	70	20	21.80		
3	550	0.10	30	5.18	55	2.5	70	20	27.49		
4	100	0.55	30	17.68	55	7.5	30	40	37.06		
5	100	0.55	90	19.25	40	5.0	50	30	46.82		
6	550	1.00	90	28.50	25	7.5	30	20	29.55		
7	1000	1.00	60	22.92	25	7.5	30	40	32.00		
8	1000	0.55	30	20.61	40	5.0	10	30	46.80		
9	100	0.10	60	2.42	70	5.0	50	30	37.04		
10	550	0.55	60	25.02	25	7.5	70	20	32.81		
11	550	1.00	30	24.16	55	7.5	70	20	37.41		
12	550	0.55	60	25.78	40	10.0	50	30	31.55		
13	1000	0.10	60	4.00	40	5.0	50	30	47.47		
14	1000	0.55	90	20.98	25	7.5	70	40	40.93		
15	550	0.10	90	10.19	25	2.5	30	40	42.81		
16	-	-	-	-	55	7.5	70	40	54.30		
17	-	-	-	-	40	5.0	50	50	47.55		
18	-	-	-	-	40	5.0	50	10	19.84		
19	-	-	-	-	10	5.0	50	30	32.24		
20	-	-	-	-	55	2.5	70	40	49.22		
21	-	-	-	-	40	5.0	90	30	49.59		
22	-	-	-	-	40	5.0	50	30	47.08		
23	-	-	-	-	25	2.5	70	40	38.83		
24	-	-	-	-	40	5.0	50	30	46.15		
25	-	-	-	-	40	5.0	50	30	46.66		
26	-	-	-	-	55	7.5	30	20	28.00		
27	-	-	-	-	40	0.0	50	30	26.42		
28	-	-	-	-	25	2.5	30	20	30.07		
29	-	-	-	-	40	5.0	50	30	49.07		
30	-	-	-	-	55	2.5	30	40	46.13		

 Table S3 Experimental design of the Box–Behnken design, the central composite design, and their responses.

Source	Sum of Squares	df	Mean Square	F value	p value	
Box–Behnken design						
Model	1021.50	9	113.50	77.95	< 0.0001	significant
$x_l$ : MOF amount	9.31	1	9.31	6.39	0.0526	
$x_2$ : TDES volume	690.43	1	690.43	474.18	< 0.0001	
<i>x</i> <sub>3</sub> : Time	15.93	1	15.93	10.94	0.0213	
$x_1 x_2$	0.1640	1	0.1640	0.1127	0.7508	
$x_1 x_3$	0.3600	1	0.3600	0.2472	0.6401	
$x_2 x_3$	0.1122	1	0.1122	0.0771	0.7924	
$x_l^2$	100.03	1	100.03	68.70	0.0004	
$x_2^2$	226.23	1	226.23	155.37	< 0.0001	
$x_{3}^{2}$	1.63	1	1.63	1.12	0.3381	
Residual	7.28	5	1.46			
Lack of Fit	6.93	3	2.31	13.25	0.0710	not significant
Pure Error	0.3488	2	0.1744			
Cor Total	1028.78	14				
Central composite desig	n					
Model	2703.82	14	193.13	76.90	< 0.0001	significant
$X_l$ : Sorbent amount	78.55	1	78.55	31.28	< 0.0001	
$X_2$ : NaCl concentration	21.97	1	21.97	8.75	0.0098	
<i>X</i> <sub>3</sub> : Extraction time	65.80	1	65.80	26.20	0.0001	
<i>X</i> <sub>4</sub> : Sample volume	1155.93	1	1155.93	460.28	< 0.0001	
$X_1 X_2$	5.22	1	5.22	2.08	0.1699	
$X_1X_3$	73.44	1	73.44	29.25	< 0.0001	
$X_l X_4$	57.99	1	57.99	23.09	0.0002	
$X_{2}X_{3}$	118.37	1	118.37	47.14	< 0.0001	
$X_2X_4$	90.73	1	90.73	36.13	< 0.0001	
$X_3X_4$	16.81	1	16.81	6.69	0.0206	
$X_l^2$	290.23	1	290.23	115.57	< 0.0001	
$X_2^2$	597.33	1	597.33	237.85	< 0.0001	
$X_3^2$	0.5061	1	0.5061	0.2015	0.6599	
$X_{4}^{2}$	333.92	1	333.92	132.97	< 0.0001	
Residual	37.67	15	2.51			
Lack of Fit	32.55	10	3.25	3.18	0.1070	not significant
Pure Error	5.12	5	1.02			

Table S4 ANOVA for the quadratic model of Box–Behnken design and central composite

design.



Fig. S3Effect of (A) sorbent amount, (B) pH of sample solution, (C) salt addition, (D) extraction time, and (E) sample volume. The magnetic solid phase extraction conditions were as follows: amount of sorbent, 30 mg; extraction/desorption time, 30 s; desorption solvent, 500 μL; and sample volume, 20 mL, containing 5 μg L<sup>-1</sup> of each OCP.



Fig. S4 Effect of (A) desorption solvent, (B) desorption solvent volume, and (C) desorption time. The magnetic solid phase extraction conditions were as follows: sorbent, 45 mg; extraction time, 70 s; and sample volume, 40 mL containing 5% (w/v) sodium chloride.



Fig. S5 Extraction efficiencies of various sorbents. The magnetic solid phase extraction conditions were as follows: sorbent, 45 mg; extraction time, 70 s; desorption time, 2.5 min; desorption solvent, 225 μL of acetone/ethyl acetate (1:2, v/v); and sample solution, 40 mL of OCP solution (5 μg L<sup>-1</sup> of each) containing 5% (w/v) sodium chloride.

		Lincor rongo		LODa	LOOs	RS	SDs <sup>a</sup>
Matrix	Analyte	(ng·g <sup>-1</sup> )	$\mathbb{R}^2$	$(nq \cdot q^{-1})$	$(nq \cdot q^{-1})$	Intraday	Interday
		(lig g )		(lig g )	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	(n = 5x3)	
Honey	α-HCH	0.80 - 1000	0.9993	0.50	0.80	4.5	5.2
	β-НСН	1.0 - 1000	0.9996	0.70	1.00	3.7	3.1
	γ-HCH	1.0 - 1000	0.9998	0.70	1.00	1.9	7.9
	δ-НСН	1.0 - 1000	0.9963	0.80	1.00	4.2	5.2
	Heptachlor	0.40 - 1000	0.9979	0.25	0.40	6.3	5.1
	Aldrin	0.50 - 1000	0.9967	0.30	0.50	6.9	6.6
	Isobenzan	0.50 - 1000	0.9976	0.30	0.50	5.5	6.0
	o,p´-DDE	0.10 - 1000	0.9946	0.07	0.10	7.6	7.0
	p,p´-DDE	0.10 - 1000	0.9945	0.07	0.10	7.4	7.4
	o,p´-DDD	0.30-1000	0.9951	0.15	0.30	5.4	4.1
	p,p′-DDD	0.50-1000	0.9970	0.25	0.50	4.1	6.3
Tea	α-HCH	4.0-2500	0.9956	3.0	4.0	3.1	6.5
leaves	β-НСН	1.5-2500	0.9980	1.0	1.5	3.5	4.9
	γ-HCH	5.0-2500	0.9977	3.0	5.0	3.6	5.3
	δ-НСН	10.0-2500	0.9977	8.5	10.0	4.3	5.1
	Heptachlor	4.0-2500	0.9997	2.5	4.0	2.8	4.9
	Aldrin	4.0-2500	0.9982	2.5	4.0	1.5	6.9
	Isobenzan	4.0-2500	0.9980	2.5	4.0	1.8	7.4
	o,p´-DDE	1.0-2500	0.9982	0.7	1.0	3.8	5.9
	p,p′-DDE	1.0-2500	0.9974	0.7	1.0	3.7	4.9
	o,p´-DDD	2.0-2500	0.9995	1.5	2.0	6.2	8.2
	p,p′-DDD	10.0-2500	0.9983	8.5	10.0	7.7	7.4

**Table S5** Analytical performance for the determination of OCPs in honey and tea samples.

<sup>a</sup>Spiked at 20 ng·g<sup>-1</sup> and 100 ng·g<sup>-1</sup> of each OCP in honey and tea samples, respectively.

Analyta	ME (%) <sup>a</sup>								
Analyte	Honey1	Honey2	Honey3	Wulong tea	Biluochun tea	Longjing tea			
α-HCH	-7.8	-11.2	-24.6	-30.1	-31.5	-20.9			
β-НСН	-19.6	-20.9	-15.6	-9.3	-3.7	-10.7			
γ-HCH	-29.8	-21.9	-6.5	-0.4	-12.1	-5.6			
δ-НСН	-67.8	-82.5	-45.3	-40.3	-39.9	-30.6			
Heptachlor	-50.7	-60.1	-71.0	-50.8	-32.5	-38.3			
Aldrin	-49.4	-48.1	-15.1	-10.9	-5.9	-7.7			
Isobenzan	-50.2	-37.3	-19.0	-19.4	-21.5	-18.3			
o,p´-DDE	-53.5	-47.9	-29.2	-22.5	-9.4	-20.1			
p,p′-DDE	-52.0	-47.9	-27.8	-17.6	-6.8	-15.9			
o,p´-DDD	-36.6	-40.7	-19.1	-1.6	-9.4	-10.0			
p,p′-DDD	-16.4	-21.7	-41.3	-27.2	-11.7	-22.3			

Table	<b>S6</b>	Matrix	effects	of	each	real	samp	le.

<sup>a</sup> Matrix effect

	Addad	Honey1		Honey2		Honey3	
Analyte	$(ng \cdot g^{-1})$	Found	$R^{a}\pm RSD^{b}$	Found	$R \pm RSD$	Found	$\textbf{R} \pm \textbf{R}\textbf{S}\textbf{D}$
		$(ng \cdot g^{-1})$	(%)	$(ng \cdot g^{-1})$	(%)	$(ng \cdot g^{-1})$	(%)
α-HCH	-	N.D.°	-	N.D.	-	N.D.	-
	1.00	0.91	$90.9\pm5.3$	0.95	$94.7\pm6.7$	1.05	$104.8\pm1.0$
	2.00	2.01	$100.3\pm1.6$	2.09	$104.4\pm1.2$	1.86	$92.9\pm 6.8$
	4.00	3.96	$98.9\pm5.9$	3.97	$99.1 \pm 2.9$	3.97	$99.2 \pm 3.4$
β-НСН	-	N.D.	-	N.D.	-	N.D.	-
	1.00	0.87	$86.7 \pm 5.8$	0.94	$94.3\pm7.8$	1.01	$100.7\pm0.7$
	2.00	2.07	$103.3 \pm 1.0$	1.96	$98.0 \pm 0.6$	2.12	$106.1 \pm 1.8$
	4.00	4.14	$103.5 \pm 2.0$	3.93	$98.1 \pm 1.0$	3.62	$90.5 \pm 1.5$
ү-НСН	-	N.D.	-	N.D.	-	N.D.	-
	1.00	0.86	$85.8 \pm 5.4$	0.93	$92.9 \pm 4.8$	1.09	$109.2 \pm 2.3$
	2.00	2.02	$101.2 \pm 7.0$	1.83	$91.7 \pm 0.9$	1.83	$91.5 \pm 4.4$
	4.00	3.96	<b>99.</b> 1 ± 7.7	3.91	$97.7 \pm 2.8$	3.88	$96.9 \pm 3.1$
б-НСН	-	N.D.	-	N.D.	-	N.D.	-
	1.00	1.07	$107.3 \pm 2.2$	0.92	$91.8 \pm 1.8$	0.91	$90.7 \pm 2.1$
	2.00	1.82	$91.2 \pm 8.8$	1.80	$89.8 \pm 3.3$	1.72	$86.0 \pm 2.2$
	4.00	3.97	99.2 ± 7.1	3.93	$98.4 \pm 3.0$	3.89	97.4 ± 5.5
Heptachlor	-	N.D.	-	N.D.	-	N.D.	-
	1.00	0.91	$91.2 \pm 4.1$	0.91	$90.7 \pm 4.6$	1.02	$102.4 \pm 0.1$
	2.00	2.03	$101.5 \pm 9.6$	2.06	$102.8 \pm 0.9$	1.88	$94.2 \pm 2.8$
	4.00	3.80	95.0 ± 7.7	4.07	$101.7 \pm 2.7$	3.52	88.1 ± 4.3
Aldrin	-	N.D.	-	N.D.	-	N.D.	-
	1.00	0.89	$88.8 \pm 2.0$	0.89	$89.2 \pm 1.4$	0.99	$98.8 \pm 0.2$
	2.00	2.15	$10/.3 \pm 2.7$	1.98	$98.9 \pm 0.4$	1.96	$98.0 \pm 5.4$
T. 1	4.00	3./5 ND	93.6 ± 6.4	4.15 ND	$103.9 \pm 0.8$	3.58	89.6 ± 2.7
Isobenzan	-	N.D.	-	N.D.	-	N.D.	-
	1.00	0.85	$85.2 \pm 2.9$	0.85	$85.4 \pm 7.0$	0.96	$96.0 \pm 0.7$
	2.00	2.10	$103.0 \pm 0.8$ 04.5 ± 5.7	1.95	$9/.4 \pm 1.0$ 86.2 ± 1.2	2.01	$100.7 \pm 1.0$
	4.00	3.70 ND	94.3 ± 3.7		$60.2 \pm 1.2$	<u> </u>	00.J ± 2.2
0,р -DDE	-	N.D. 0.95	$-$ 05 3 $\pm$ 3 2	IN.D. 1.00	$\frac{-}{1003 \pm 6.6}$	N.D.	$-020 \pm 10$
	2.00	0.95	$95.5 \pm 5.2$ 105.6 ± 3.3	1.00	$100.3 \pm 0.0$	0.93	$92.9 \pm 1.9$ 101 1 $\pm$ 0 2
	2.00	2.11	$103.0 \pm 3.3$ $94.4 \pm 5.1$	1.83	$91.0 \pm 0.8$ $100.6 \pm 0.7$	2.02	$101.1 \pm 0.2$ 90 5 + 1 8
n n'-DDF	00	<u> </u>	-	N D	-	N D	-
p,p DDL	1.00	0.97	97 1 + 3 5	0.85	848+11	0.87	$87.5 \pm 1.1$
	2.00	2.11	$105.7 \pm 7.8$	1.80	$90.0 \pm 0.7$	1 99	$99.5 \pm 0.7$
	4.00	3.78	$94.4 \pm 5.9$	4.20	$105.0 \pm 0.9$	3.72	$93.0 \pm 2.5$
o.p'-DDD	-	N.D.	-	N.D.	-	N.D.	-
JI	1.00	0.82	$81.7 \pm 0.7$	0.93	$93.4\pm3.9$	1.04	$103.7\pm2.5$
	2.00	1.97	$98.6 \pm 3.2$	1.85	$92.5 \pm 0.7$	2.15	$107.5 \pm 6.4$
	4.00	3.67	$91.7 \pm 6.2$	5.30	$88.4 \pm 0.8$	3.36	$84.0 \pm 3.1$
p,p'-DDD	-	N.D.	-	N.D.	-	N.D.	-
1 /1	1.00	0.86	$85.7\pm0.3$	0.98	$97.8 \pm 1.1$	1.00	$100.4\pm0.4$
	2.00	1.75	$87.4 \pm 1.6$	1.98	$98.8\pm0.5$	1.93	$96.3\pm3.5$
	4.00	4.04	$101.0\pm4.3$	3.59	$89.8 \pm 1.0$	3.41	$85.3\pm5.1$

 Table S7 Recoveries of the spiked honey samples.

<sup>a</sup> Recovery, <sup>b</sup> Relative standard deviation, <sup>c</sup> Not detected

	Added	Wulong tea		Biluochun	tea	Longjing te	a
Analyte	$(ng \cdot g^{-1})$	Found	$R^{a}\pm RSD^{b}$	Found	$\textbf{R} \pm \textbf{R}\textbf{S}\textbf{D}$	Found	$R \pm RSD$
		$(ng \cdot g^{-1})$	(%)	$(ng \cdot g^{-1})$	(%)	$(ng \cdot g^{-1})$	(%)
α-HCH	-	N.D.°	-	N.D.	-	N.D.	-
	10.0	9.5	$95.5\pm2.3$	10.4	$104.0\pm0.4$	10.2	$102.4\pm0.5$
	15.0	15.5	$103.6\pm6.7$	14.6	$97.6\pm0.3$	15.1	$100.5\pm3.1$
	20.0	21.9	$109.3 \pm 1.4$	20.3	$101.6 \pm 2.4$	20.5	$102.4\pm2.0$
β-НСН	-	N.D.	-	N.D.	-	N.D.	-
	10.0	9.2	$92.2\pm6.0$	10.1	$100.7\pm5.0$	9.7	$96.8\pm5.5$
	15.0	14.8	$98.7\pm4.8$	14.9	$99.6 \pm 2.2$	14.7	$97.8 \pm 2.5$
	20.0	21.3	$106.6 \pm 4.4$	19.5	$97.7 \pm 1.1$	19.7	$98.3 \pm 1.0$
ү-НСН	-	N.D.	-	N.D.	-	N.D.	-
	10.0	9.7	$97.3 \pm 5.5$	8.5	85.4 ± 2.9	8.7	$87.5 \pm 1.7$
	15.0	16.3	$108.7 \pm 4.3$	14.4	$96.1 \pm 1.8$	14.8	$98.6 \pm 1.0$
	20.0	20.8	$103.8 \pm 3.8$	20.4	$102.2 \pm 0.7$	21.2	$106.2 \pm 3.3$
б-НСН	-	N.D.	-	N.D.	-	N.D.	-
	10.0	9.9	$99.1 \pm 3.9$	10.3	$102.7 \pm 5.6$	9.7	$96.6 \pm 4.9$
	15.0	13.1	$87.5 \pm 3.4$	14.6	$9^{\prime}/.1 \pm 0.4$	15.5	$103.5 \pm 5.1$
TT - 11	20.0	21.3	$106.5 \pm 0.8$	20.0	99.9 ± 2.1	19.8	99.1 ± 2.1
Heptachlor	-	N.D.	-	N.D.	-	N.D.	-
	10.0	9.5	$94.6 \pm 5.0$	9.5	$95.4 \pm 0.7$	9.7	$97.0 \pm 2.8$
	15.0	13.2	$88.1 \pm 1.6$	14.7	$98.1 \pm 1.1$	14.7	$98.1 \pm 2.0$
	20.0	20.3	$101.5 \pm 0.5$	20.0	$100.1 \pm 2.7$	20.3	$101.4 \pm 3.6$
Aldrin	-	N.D.	-	N.D.	- 09.2 + 1.2	N.D.	-
	10.0	9.5	$94.7 \pm 2.9$	9.8	$98.2 \pm 1.3$	10.0	$99.6 \pm 1.8$
	15.0	15.3	$101.7 \pm 3.8$	14./	$98.0 \pm 0.2$	14./	$98.2 \pm 1.9$
	20.0	21.2 N.D	$103.8 \pm 0.9$	20.0 N.D	$100.0 \pm 0.3$	19.8 ND	$98.8 \pm 3.0$
Isobenzan	-	N.D.	-	N.D. 0.7	- 07.1 + 1.6	N.D.	-
	10.0	9.0	$95.5 \pm 5.5$	9.7	$9/.1 \pm 1.0$	9.0	$90.1 \pm 1.5$
	13.0	13.2	$101.1 \pm 0.0$ $106.2 \pm 1.3$	20.0	$99.9 \pm 0.7$	13.1	$100.3 \pm 2.4$ 08 5 ± 4 4
o n' DDE	20.0	N D	$100.2 \pm 1.3$	20.0 N D	$100.0 \pm 1.1$	19.7 N D	<i>70.3</i> ± 4.4
0,р -ррг	-	N.D. 10.5	$\frac{-}{1053+81}$	N.D. 00	- 00 1 + 0 7	N.D. 00	- 00 1 + 3 1
	15.0	15.3	$103.3 \pm 3.1$ $101.8 \pm 7.0$	14.6	$97.1 \pm 0.7$ $97.6 \pm 0.3$	14.5	$99.1 \pm 3.4$
	20.0	21.1	$101.0 \pm 7.0$ $105.7 \pm 1.2$	20.0	$99.9 \pm 0.6$	20.6	$103.1 \pm 2.8$
n n'-DDF	-	ND	-	N D	-	N D	-
p,p DDL	10.0	97	$97.2 \pm 4.1$	10.0	99 5 $\pm$ 0 1	9.8	$97.6 \pm 1.7$
	15.0	14.8	$98.5 \pm 4.0$	14.5	$96.4 \pm 0.1$	15.0	1002 + 33
	20.0	21.5	$107.3 \pm 2.1$	20.0	$99.9 \pm 0.2$	20.6	$100.2 \pm 3.3$ $102.9 \pm 3.7$
o.p'-DDD	-	N.D.	-	N.D.	-	N.D.	-
-,r 200	10.0	9.2	$92.5 \pm 0.7$	10.2	$101.9 \pm 1.3$	10.1	$101.1 \pm 4.1$
	15.0	15.8	$105.1 \pm 2.4$	13.5	$89.7 \pm 1.7$	13.8	$92.3 \pm 3.2$
	20.0	20.1	$100.6 \pm 1.5$	20.0	$99.9 \pm 0.5$	20.3	$101.5 \pm 4.3$
p.p'-DDD	_	N.D.	-	N.D.	-	N.D.	-
ryr 222	10.0	9.0	$90.2 \pm 7.6$	9.8	$98.1 \pm 4.4$	9.9	$99.1 \pm 4.7$
	15.0	13.9	$92.4 \pm 1.7$	14.5	$96.9 \pm 0.2$	14.7	$98.0 \pm 1.7$
	20.0	21.2	$106.2\pm0.9$	20.1	$100.6 \pm 1.9$	19.3	$96.6\pm4.7$

 Table S8 Recoveries of the spiked tea samples.

<sup>a</sup> Recovery, <sup>b</sup> Relative standard deviation, <sup>c</sup> Not detected



Fig. S6 Reusability of the sorbent MIH@MIL-101(Cr)-NH<sub>2</sub>-TDES for the enrichment of organochlorine pesticides. The magnetic solid phase extraction conditions were as follows: sorbent, 45 mg; extraction time, 70 s; desorption time, 2.5 min; desorption solvent, 225 μL of acetone/ethyl acetate (1:2, v/v); and sample solution, 40 mL of OCP solution (1 μg L<sup>-1</sup> of each) containing 5% (w/v) sodium chloride.

Extractants <sup>Ref.</sup>	Method	Number of analytes	Matrix	Extraction time	Linear range	LODs	Recoveries (%)	RSDs (%)
CD-MOF/TiO <sub>2</sub> <sup>3</sup>	D- SPE/GC–MS/MS	14	Honeys	5 min	1-500 ng·g <sup>-1</sup>	0.01–0.04 ng g <sup>-1</sup>	76.4–114.3	< 11.3
MFCNTs <sup>4</sup>	MSPE/GC-ECD	8	Honeys	40 min	$0.02-80 \ \mu g \cdot L^{-1}$	1.3–3.6 ng L <sup>-1</sup>	83.2–128.7	< 6.4
			Tea leaves				72.6–111.0	< 6.8
Porous polypropylene membrane <sup>7</sup>	UAE/GC-MS	13	Tea leaves	60 min	5–500 ng·g <sup>-1</sup>	1.4–7.2 ng g <sup>-1</sup>	86.1–100.3	< 16
Fe <sub>3</sub> O <sub>4</sub> @MIL-100 (Fe) <sup>8</sup>	MCMSPE/GC-MS	5	Tea leaves	40 s	13–2130 ng $\cdot$ g <sup>-1</sup>	0.62–3.92 ng g <sup>-1</sup>	81.5–113.6	< 9.9
Fe <sub>3</sub> O <sub>4</sub> -NH <sub>2</sub> @MIL- 101(Cr) <sup>18</sup>	MAE-MSPE/GC- ECD	8	Soils	5 min	$0.50-80 \text{ ng} \cdot \text{g}^{-1}$	0.15–0.28 ng·g <sup>-1</sup>	71.2–102.4	< 4.9
M-M-ZIF-67 <sup>28</sup>	MSPE/GC-MS/MS	9	Agricultural irrigation water	20 min	1–200 μg·L <sup>-1</sup>	$0.07 - 1.03 \ \mu g \cdot L^{-1}$	74.9–116.3	< 8.5
Fe <sub>3</sub> O <sub>4</sub> @PDA@Zr-	MSPE/GC-ECD	8	Environmental	8 min	$0.05 - 300 \ \mu g \cdot L^{-1}$	$0.005 - 0.016 \ \mu g \cdot L^{-1}$	82–118	< 7.7
$SO_3H^{29}$			water					
MIH@MIL-101(Cr)-	MSPE/GC-MS	11	Honey	70 s	$0.1{-}1000 \text{ ng} \cdot \text{g}^{-1}$	$0.07 – 0.80 \text{ ng} \cdot \text{g}^{-1}$	81.7–107.3	< 7.9
$NH_2\text{-}TDES^{This\ study}$			Tea leaves		$1.0-2500 \text{ ng} \cdot \text{g}^{-1}$	0.7–8.5 ng·g <sup>-1</sup>	85.4–109.3	< 8.2

Table S9 Comparison of the proposed MSPE/GC–MS with other methods for the determination of OCPs.

CD-MOF/TiO<sub>2</sub>: β- Cyclodextrin/metal organic framework grafted onto titanium dioxide

MFCNTs: Magnetic cobalt ferrite-filled carbon nanotubes

M-M-ZIF-67: Zeolitic imidazolate framework based on magnetic multiwalled carbon nanotubes

Fe<sub>3</sub>O<sub>4</sub>@PDA@Zr-SO<sub>3</sub>H: metal organic framework functionalized with sulfonic acid combined with magnetic nanoparticles

D-SPE: dispersive solid phase extraction

MSPE: Magnetic solid phase extraction

UAE: Ultrasound-assisted extraction

MCMSPE: Mechanochemical magnetic solid phase extraction

MAE-MSPE: Microwave-assisted magnetic solid phase extraction