Electronic Supplementary Material (ESI) for Analytical Methods.

This journal is © The Royal Society of Chemistry 2022

TiO₂@MOF-919(Fe-Cu) as a sorbent for extraction of benzoylurea pesticides from irrigation water and fruit juices

Ling Mei^{a,b}, Tiantian Si^{a,b}, Shuai Wang^a, Jie Zhu^c, Hao Tang^{c,d*}, Xiaojing Liang^{a*}

^a CAS Key Laboratory of Chemistry of Northwestern Plant Resources and Key

Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical

Physics, Chinese Academy of Sciences, Lanzhou 730000, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c College of pharmacy, Gansu University of Chinese Medicine, Lanzhou 730000,

China

^d Department of Pharmacy, Gansu Provincial Hospital, Lanzhou 730000, China **E-mail:** <u>xjliang@licp.cas.cn</u> (Xiaojing Liang); <u>naomitang@hotmail.com</u> (Hao Tang) **Phone:** + 86 931 4968266

Fax: +86 931 4968013



Fig. S1 Characterization of the prepared materials: (a) The N_2 adsorption–desorption isotherms of TiO₂, TiO₂@MOF–919(Fe-Cu); (b)TGA spectra of TiO₂@MOF–919(Fe-Cu).



Fig. S2 Characterization of 3D radial TiO_2 bare spheres: (a) SEM spectra; (b) TEM spectra; (c) FTIR spectra; (d) XRD spectra.



Fig. S3 Effect of the amount of 3D radial TiO_2 bare spheres.



Fig. S4 Characterization of MOF-919(Fe-Cu): (a) SEM spectra; (b) TEM spectra.



Fig. S5 The state of TiO₂@MOF-919(Fe-Cu) before and after loading.



Fig. S6 (a) Langmuir plots and (b) Freundlich plots for the adsorption of BUs on $TiO_2@MOF-919$ (Fe-Cu).



Fig. S7 The adsorption kinetic models of BUs on $TiO_2@MOF-919$ (Fe-Cu). (a) pseudo-first-order model; (b) pseudo-second-order model.



Fig. S8 The reusability of TiO₂@ MOF-919(Fe-Cu) on adsorption of BUs.

	Langmuir model			Freundlich model			
Analyte	q _m (mg g ⁻¹)	K _L (L mg ⁻¹⁾	R ²	K _F (mg g ⁻¹)	1/n	R ²	
triflumuron	14.68	0.643	0.9927	1.80	0.589	0.983	
chlorbenzuron	13.46	0.706	0.9914	2.04	1.601	0.977	
teflubenzuron	14.49	1.647	0.9934	1.65	2.160	0.963	
diflubenzuron	10.14	0.962	0.9922	2.10	1.633	0.987	

Table S1 The fitting results of Langmuir model and Freundlich model.

Table S2 The fitting results of adsorption kinetics for BUs.

Analyte	Pseudo-first-order kinetic			Pseudo-second-order kinetic			
	k ₁ (min ⁻¹)	q _e (mg g ⁻¹)	R ²	$\begin{array}{c} k_2 \\ (g mg^{-1} min^{-1}) \end{array}$	q _e (mg g ⁻¹)	R ²	
triflumuron	4.901	4.035	0.774	2.562	14.306	0.998	
chlorbenzuron	3.366	2.850	0.777	2.475	13.870	0.998	
teflubenzuron	1.338	2.346	0.778	2.390	15.244	0.999	
diflubenzuron	2.125	3.493	0.752	□ 1.493	15.748	0.996	

Analytes	Linear	Calibration	Correlation	Limits of	RSDs (%) $(n = 7)$	
	range (µg L ⁻¹)	curve	coefficient (R ²)	detection (µg L ⁻¹)	Intraday	Interday
triflumuron	1-400	y = 0.5338x - 2.0326	0.9994	0.53	1.78	4.27
chlorbenzuron	1-400	y = 0.5599x + 2.1653	0.9995	0.56	3.24	5.08
teflubenzuron	1-400	y = 0.4826x - 0.7781	0.9997	0.48	2.36	4.50
diflubenzuron	1-400	y = 0.399x + 0.2646	0.9998	0.40	2.21	4.07

Table S3 Analytical data for the determination of BUs by the method.

Table S4 Comparison of the methods for the determination of BUs.

Method	Extraction sorbent	Sample	Reused times	Analytical ranges (µg L ⁻¹)	LODs (µg L ⁻¹)	Recovery (%)	Ref
MSPE ^a	ATP@Fe ₃ O ₄ @ZIF- 8 ^b	Tea	5	2.5–500	0.36–0.66	78.9–114.0	[1]
DSPE ^c	[C ₁₆ MIM]Br-AL ^d	Water, tea beverages	1	1–500	0.14-0.23	72.8-89.3	[27]
DLLME ^e	[N ₈₈₈₁][PF ₆]	Water, tea beverages	/	2–500	0.29–0.59	85.93–90.52	[28]
SPE	TiO ₂ @MOF- 919(Fe)	Tap water, juices	10	1-400	0.40-0.56	72.3–108.4	This work

^aMSPE: magnetic solid-phase extraction ; ^bATP@Fe₃O₄@ZIF-8: attapulgite-modified magnetic metal-organic frameworks; ^cDSPE: dispersive solid-phase adsorbent; ^d[C₁₆MIM]Br-AL: ionic liquid 1-hexadecyl-3- methylimidazolium-alkalized luffa sponge fibers bromide-alkalized luffa sponge fibers; ^cDLLME: dispersive liquid-liquid microextraction