

Supplementary Information

Metal-organic framework-based molecularly imprinted polymers for dispersive solid-phase extraction of fluoroquinolones in coastal zone water and biological samples

Jingying Huang,^{a,b} Jingyi Yan,^a Mingsan Man,^{*a} Saqib Farooq,^c Zihan Qiu,^a Shuai Wu,^d Liangwei Zhang,^a Lingxin Chen^a and Jinhua Li^{*a,b}

^aShandong Key Laboratory of Coastal Zone Environmental Processes and Ecological Security, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China

^bUniversity of Chinese Academy of Sciences, Beijing 100049, China

^cCollege of Tropical Agriculture and Forestry, Hainan University, Danzhou 571737, China

^dYantai Testing Center for Food and Drug, Yantai 264000, China

** Corresponding authors.*

E-mail addresses: msman@yic.ac.cn (M. Man), jhli@yic.ac.cn (J. Li)

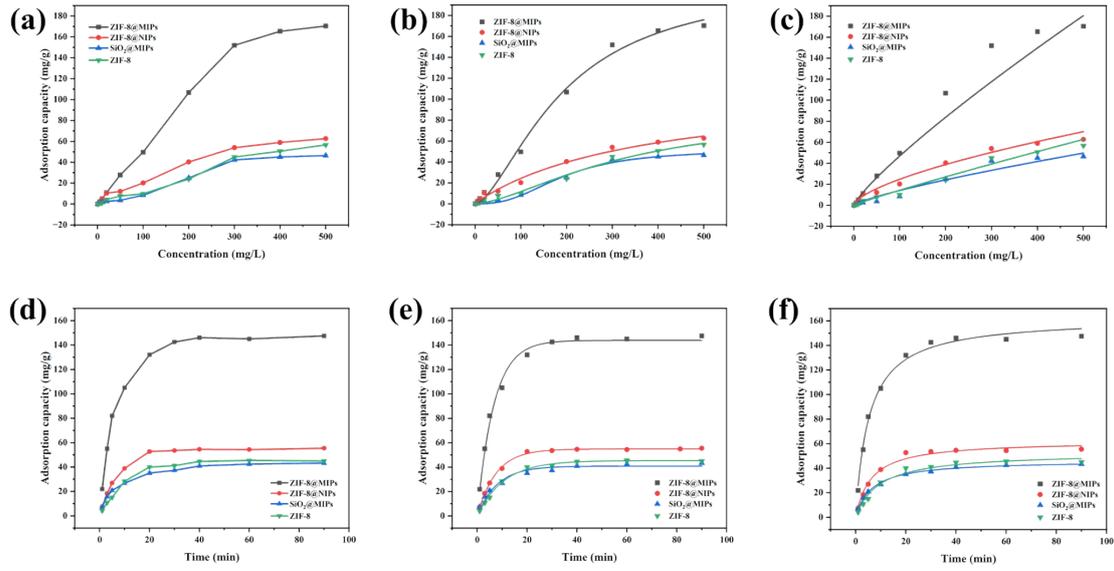


Fig. S1 Static adsorption isotherms and kinetic adsorption behavior of CIP on ZIF-8@MIPs, ZIF-8@NIPs, SiO₂@MIPs and ZIF-8. (a) Static adsorption isotherms, (b) Langmuir model fitting, and (c) Freundlich model fitting. (d) Adsorption kinetics, (e) Pseudo-first-order model fitting, and (f) Pseudo-second-order model fitting.

Table S1. Adsorption isotherm parameters of ZIF-8@MIPs, ZIF-8@NIPs, MIPs, and ZIF-8 for CIP (fitting results of the Langmuir and Freundlich models).

Isotherm model	Parameter	ZIF-8@MIPs	ZIF-8@NIPs	SiO ₂ @MIPs	ZIF-8
Langmuir	R^2	0.9937	0.9860	0.9894	0.9831
	Q_{\max} (mg/g)	214.2630	115.9562	51.6970	87.7595
	K_L (L/mg)	2.2919	0.0031	1.1254	1.0969
Freundlich	R^2	0.9682	0.8866	0.9004	0.9618
	K_F	0.9829	1.2585	0.3756	0.2073
	$1/n$	0.8389	0.6467	0.7857	0.9191

Table S2 Adsorption kinetics parameters of ZIF-8@MIPs, ZIF-8@NIPs, SiO₂@MIPs,

and ZIF-8 for CIP (fitting results of the Pseudo-first-order and Pseudo-second-order models).

Adsorption kinetics model	Parameter	ZIF-8@MIPs	ZIF-8@NIPs	SiO ₂ @MIPs	ZIF-8
Pseudo-first-order	R^2	0.9906	0.9977	0.9607	0.9954
	Q_{\max} (mg/g)	143.8314	54.8662	40.8023	45.3494
	K_1	0.1501	0.1331	0.1252	0.0937
Pseudo-second-order	R^2	0.9909	0.9793	0.9938	0.9766
	Q_{\max} (mg/g)	162.7095	62.2770	46.3800	52.8362
	K_2	0.0327	0.0984	0.1371	0.1764

Table S3 Spiked recoveries and RSDs of the six FQs in beach seawater, river water, and prawn samples (n=3).

FQs	Spiked (µg/L)	Beach seawater			River water			Prawn		
		Found (µg/L)	Recovery (%)	RSD (%)	Found (µg/L)	Recovery (%)	RSD (%)	Found (µg/L)	Recovery (%)	RSD (%)
CIP	0	N.D.	–	–	N.D.	–	–	N.D.	–	–
	5	5.8	116.8	1.5	10.5	110.2	1.9	5.6	112.5	4.3
	10	11.0	109.8	0.7	20.3	105.0	0.4	9.8	97.7	0.7
	20	21.5	107.7	4.7	5.9	101.5	1.5	20.2	101.1	5.2
PEF	0	N.D.	–	–	N.D.	–	–	N.D.	–	–
	5	5.9	118.4	1.9	5.6	112.3	1.3	5.7	113.7	1.2
	10	11.2	112.0	1.2	9.8	98.0	3.3	10.6	105.6	1.8
	20	21.3	106.6	6.1	19.9	99.6	2.4	21.5	107.4	5.1
ENR	0	N.D.	–	–	N.D.	–	–	N.D.	–	–
	5	5.8	116.7	0.8	5.9	118.0	0.3	5.8	116.9	0.7
	10	11.3	113.1	1.8	11.1	111.4	1.3	10.4	104.3	1.4
	20	21.1	105.7	1.0	20.8	104.1	0.4	20.2	100.8	0.8
DIF	0	N.D.	–	–	N.D.	–	–	N.D.	–	–
	5	5.9	118.9	1.0	5.2	103.7	2.2	4.8	96.2	2.2
	10	10.7	107.2	2.8	9.9	99.2	1.1	9.3	92.6	1.1
	20	20.7	103.5	0.5	20.1	100.3	3.1	18.8	93.9	3.1
MOX	0	N.D.	–	–	N.D.	–	–	N.D.	–	–
	5	4.6	92.9	4.5	5.8	115.9	1.8	5.7	113.2	3.3
	10	10.6	106	1.5	9.5	95.4	1.5	10.8	107.6	2.8
	20	20.8	104.1	5.8	19.5	97.6	0.7	19.4	97.2	3.4
CIN	0	N.D.	–	–	N.D.	–	–	N.D.	–	–
	5	5.8	116.7	0.6	5.6	112.3	1.0	5.7	113.8	5.0
	10	10.6	105.8	1.0	10.9	109.2	2.0	9.8	97.6	4.5
	20	20.6	103	0.4	20.6	103.0	0.8	19.3	96.7	1.3

Table S4 Analytical parameters of the ZIF-8@MIPs-DSPE-HPLC-UV method in real coastal zone samples (n=3).

Real Sample	FQs	Regression Equation	R^2	Linearity Range ($\mu\text{g/L}$)	LOD ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)
Beach seawater	CIP	$y=1.276x-3.420$	0.9999	5–500	0.926	3.086
	PEF	$y=1.900x-4.884$	0.9999	5–500	1.333	4.445
	ENR	$y=3.147x-11.062$	0.9998	5–500	0.366	1.221
	DIF	$y=2.699x-5.174$	0.9999	5–500	0.858	2.859
	MOX	$y=0.727x+4.454$	0.9998	5–500	1.260	4.200
	CIN	$y=1.589x-3.106$	0.9999	5–500	0.970	3.234
Seaculture wastewater	CIP	$y=1.283x-1.600$	0.9999	5–500	0.316	1.052
	PEF	$y=1.871x-3.960$	0.9999	5–500	0.200	0.667
	ENR	$y=3.141x-4.499$	0.9999	5–500	0.060	0.201
	DIF	$y=2.673x-2.550$	0.9999	5–500	0.248	0.828
	MOX	$y=0.725x+0.095$	0.9999	5–500	0.567	1.891
	CIN	$y=1.576x-2.333$	0.9999	5–500	0.234	0.780
River water	CIP	$y=1.476x-1.670$	0.9999	5–500	0.550	1.834
	PEF	$y=2.023x-2.029$	0.9998	5–500	0.912	3.039
	ENR	$y=2.827x-5.212$	0.9999	5–500	0.199	0.663
	DIF	$y=2.858x-1.282$	0.9999	5–500	1.405	4.683
	MOX	$y=0.905x-0.011$	0.9999	5–500	1.336	4.452
	CIN	$y=1.759x-2.681$	0.9999	5–500	1.240	4.135
Laizhou Bay seawater	CIP	$y=1.271x-1.436$	0.9998	5–500	0.754	2.513
	PEF	$y=1.907x-5.581$	0.9999	5–500	0.564	1.880
	ENR	$y=3.156x-16.439$	0.9998	5–500	0.110	0.366
	DIF	$y=2.673x+13.702$	0.9950	5–500	0.191	0.638
	MOX	$y=0.709x+9.523$	0.9997	5–500	1.440	4.799
	CIN	$y=1.592x-3.862$	0.9999	5–500	0.363	1.211
Pomfret	CIP	$y=1.409x-1.578$	0.9999	5–500	0.117	0.389
	PEF	$y=2.110x-2.738$	0.9999	5–500	0.260	0.865
	ENR	$y=3.511x-1.777$	0.9999	5–500	0.421	1.405
	DIF	$y=2.975x+0.26$	0.9999	5–500	0.499	1.664
	MOX	$y=0.820x-0.194$	0.9999	5–500	0.366	1.220
	CIN	$y=1.781x+1.012$	0.9999	5–500	0.324	1.080
Prawn	CIP	$y=1.439x-1.562$	0.9999	5–500	0.455	1.518
	PEF	$y=2.166x-3.744$	0.9999	5–500	0.285	0.949
	ENR	$y=3.594x-2.673$	0.9998	5–500	0.102	0.341
	DIF	$y=3.044x-1.105$	0.9999	5–500	0.512	1.707
	MOX	$y=0.825x-0.201$	0.9999	5–500	0.683	2.278
	CIN	$y=1.824x+1.323$	0.9999	5–500	0.657	2.189

Table S5 Comparison with other reported methods for the determination of FQs.

Adsorbent	Method	Sample	LOD ($\mu\text{g/L}$)	Recovery (%)	RSD (%)	Ref.
UiO-66- NH ₂ @MIPs	DSPE- LC- MS/MS	Milk, pork	0.02–0.12	70.2–113.6	0.3–8.3	1
UiO-66- NH ₂ @MIPs	PSPE- HPLC	Lake water	0.19–0.39	92.6–100.5	2.9–6.4	2
MIPs	PSPE-U- HPLC– ESI– MS/MS	Influent and sludge samples of sewage plants	0.006–0.15	≥ 75	≤ 15	3
MIPs	SPE- HPLC- UV	Tap water, wastewater, river water	0.03–0.06	78.0–112.0	3.25–7.40	4
NH ₂ -MIL- 125@MIPs	DSPE- HPLC- UV	Milk, river water	0.93–3.15	80.7–105.9	1.7–5.3	5
MIPs	SPE- HPLC- DAD	Milk	10–20	76.8–97.7	4.2–8.3	6
MIPs	PSPE- HPLC- UV	Lake water, river water, soil, pork	0.11	87.33– 102.50	2.76–9.65	7
MIPs	PT- μSPE - Spectrop hotomete r	Seawater, Pill, Urine, Human blood plasma	0.1	97.4–99.5	1.2–4.7	8
MIPs	MSPE- DLLME- HPLC	Lake water, well water, and Pearl River water	0.011–0.015	89.67– 100.5	3.59–7.12	9
MIPs	Online SPE- HPLC- FLD	River Water	1×10^{-4} – 7×10^{-4}	54–118	≤ 17	10
MIPs	PSPE- LC - MS/MS	Human urine	0.10–0.14	92–113	1–13	11
ZIF-8@MIPs	DSPE-	Beach seawater,	0.060–1.440	92.6–118.9	0.2–6.1	This

References

1. M. Chen, S. Gao, R. Liu, X. Wang, C. Nie, F. Xie, H. Gao, L. Wan. *Lwt*, 2025, **223**, 117743.
2. S. Zhao, Z. Sun, H. Liu, Y. Zhou, J. Li, X. Wang, B. Gong. *J Sep Sci*, 2019, **42**, 3302-3310.
3. R. Yu, L. Chen, R. Shen, P. Li, N. Shi. *Environ Technol Innovation*, 2020, **19**, 100919.
4. Z. Lian, J. Wang. *Mar. Pollut. Bull.*, 2016, **111**, 411-417.
5. J. Li, Y. Zhou, Z. Sun, T. Cai, X. Wang, S. Zhao, H. Liu, B. Gong. *J. Chromatogr. A*, 2020, **1626**, 461364.
6. Y. K. Wang Gengnan, Liu Huizhi, Feng Mengxiao, Wang Jianping. *Anal Methods*, 2016, **8**, 5511-5518.
7. G. Zhu, G. Cheng, P. Wang, W. Li, Y. Wang, J. Fan. *Talanta*, 2019, **200**, 307-315.
8. S. H. Hashemi, M. Kaykhaii, A. J. Keikha, J. Jangizahi. *Curr Anal Chem*, 2023, **19**, 721-731.
9. Y. Fan, G. Zeng, X. Ma. *Environ Sci Pollut Res*, 2019, **27**, 7177-7187.
10. A. N. Baeza, I. Urriza-Arsuaga, F. Navarro-Villoslada, J. L. Urraca. *Molecules*, 2022, **27**, 8120.
11. Y. Wu, J. Xiong, S. Wei, L. Tian, X. Shen, C. Huang. *J Chromatogr A*, 2024, **1714**, 464550.