Electronic Supplementary Material (ESI) for Analyst.
This journal is © The Royal Society of Chemistry 2023

Supplementary Materials

A magnetic porous carbon material derived from MIL-101(Fe) complex for the efficient magnetic solid phase extraction of fluoroquinolone antibiotics

Xuening Gao[1], Jingwen Lin, Tianning Li, Xiaoqing Zhang, Baizhao Zeng, Xiaoling Wang*, Faqiong Zhao*

College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, Hubei Province, P. R. China

*Corresponding author.
Tel: 86-27-68752701, Fax: 86-27-68754067.
E-mail address: wangxiaoling@whu.edu.cn (X. L. Wang); fqzhao@whu.edu.cn (F.Q. Zhao)

Table of contents

Reagents and apparatus

Table. S1. Structures and properties of the studied FQs.

Table. S2. Content of component elements in MPCs.

Table. S3. Comparison of fitting parameters of Langmuir equation and Freundlich equation for FQs on MPCs.

Table. S4. Comparison of fitting parameters of Pseudo-first-order model and Pseudo-second-order model.

Fig. S1. The N_2 adsorption-desorption isotherms of MIL101-(Fe)-MWCNTs-GO.

Fig. S2. Optimization of MPC component.

Fig. S3. Optimization of MSPE parameters.

Fig. S4. Optimization of elution parameters.

Fig. S5. Reusable times of MPCs.

Fig. S6. Chromatograms of FQs in actual sample.

Reagents and apparatus

MWCNTs and GO were purchased from XFNANO Materials Tech (Nanjing, China). Iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), 2-aminoterephthalic acid, N, N-dimethylformamide (DMF), sodium hydroxide (NaOH), hydrochloric acid (HCl), acetic acid (CH_3COOH) and ammonium hydroxide ($NH_3 \cdot H_2O$) were obtained from Sinopharm Chemical Reagent (Shanghai, China). polyvinyl pyrrolidone K13-18 (PVP), ciprofloxacin (CIP), enrofloxacin (ENO), lomefloxacin (LOM), ofloxacin (OFX) and formic acid were purchased from Aladdin-reagent (Shanghai, China). Methanol and acetonitrile (ACN, chromatographic grade) were obtained from Fisher Chemical (Shanghai, China). The chemical structures of the Fluoroquinolones are shown in Table. S1.

Scanning electron microscopy (SEM) imagines were obtained by field emission SEM (ZEISS SIGMA, Germany). Fourier transform Infrared (FT-IR) absorption spectrum were measured with model Nexus-670 spectrometer (Nicolet, USA). The X-ray diffraction spectrometry (XRD) analysis were tested by using Fixed Target X-ray powder crystal diffractometer Bruker D8 Advance (Germany). X-ray photoelectron spectroscopy (XPS) data were measured on ESCALAB 250Xi spectrometer (Thermo Fisher Scientific Inc, America). The magnetic hysteresis loop was recorded on vibrating sample magnetometer (PPMS-9VSM, QUANTUM, America). The pore size and N_2 adsorption experiments were measured with a TriStar II plus (Micromeritics (Shanghai) Instruments Co.). Thermogravimetric curves was obtained on the SETSYS- 16 thermal gravimetric analyzer (TGA setaram, France). The zeta potential was measured with a Nano ZS90 Zeta Potential Analyzer (Malvern, England).

Table. S1. Structures and properties of the studied FQs.

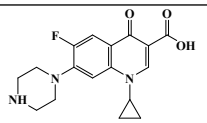
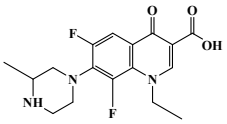
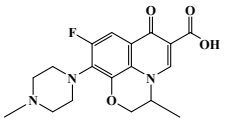
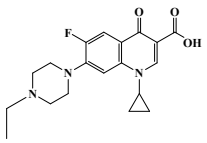
Component	CAS#	Molecular formula	Molecular weight	Molecular Structure	Melting point (℃)
CIP	85721-33-1	$C_{17}H_{18}FN_3O_3$	331		255-257
LOM	98079-51-7	$C_{17}H_{19}F_2N_3O_3$	351		239-240
OFX	82419-36-1	$C_{18}H_{20}FN_3O_4$	361		270-275
ENO	93106-60-6	$C_{19}H_{22}FN_3O_3$	359		225

Table. S2. Content of component elements in MPCs.

Name	C 1s	N 1s	O 1s	Fe 2p
Atomic(%)	89.32	5.28	4.54	0.86

Table. S3. Comparison of fitting parameters of Langmuir equation and Freundlich equation for FQs on MPCs

Analytes	Langmuir equation			Freundlich equation		
	Q_{max} (mg g^{-1})	K_l (L mg^{-1})	R^2	K_F	n	R^2
OFX	43.54	0.02224	0.9711	1.4622	2.6189	0.9698
CIP	104.06	0.00972	0.9803	1.4477	1.2729	0.9812
LOM	110.62	0.00945	0.9799	1.7362	1.3227	0.9734
ENO	117.37	0.00878	0.9836	1.5372	1.3644	0.9857

Table. S4. Comparison of fitting parameters of Pseudo-first-order model and Pseudo-second-order model

Analytes	Pseudo-first-order model			Pseudo-second-order model		
	Q_e (mg g^{-1})	K_1	R^2	Q_e(mg g^{-1})	K_2	R^2
OFX	4.9218	0.0351	0.7859	12.7307	0.0237	0.9745
CIP	6.6852	0.0275	0.4575	15.8002	0.3671	0.9923
LOM	5.4903	0.0481	0.7305	14.2859	0.0340	0.9954
ENO	4.0349	0.0308	0.6472	21.1148	0.0267	0.9930

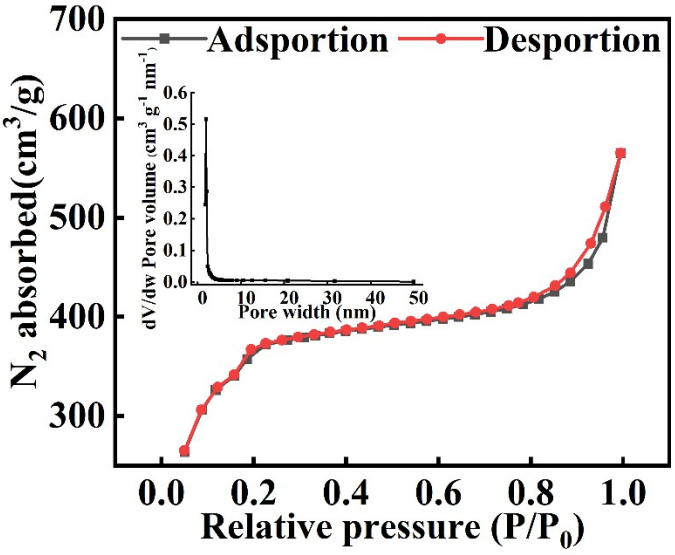


Fig. S1. The N_2 adsorption-desorption isotherms of MIL101-(Fe)-MWCNTs-GO. (inserted figure was the pore-size distribution curve).

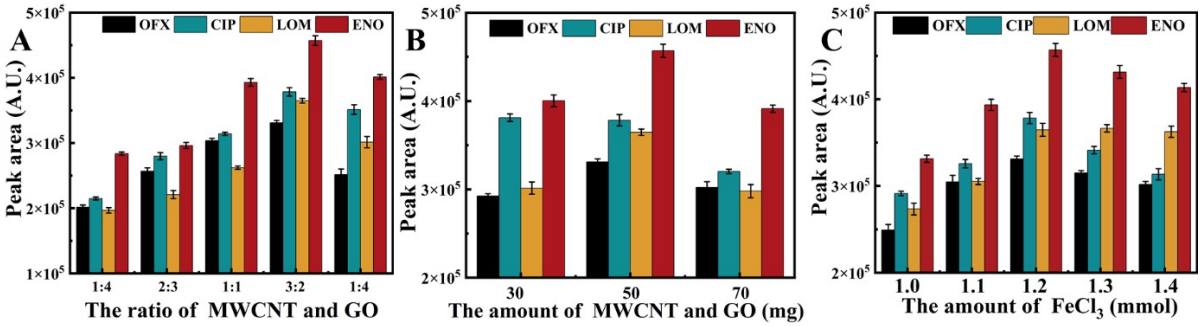


Fig. S2. Optimization of MPC component: (A) the ratio of MWCNT and GO, (B) the amount of MWCNT and GO and (C) the amount of $FeCl_3 \cdot 6H_2O$. Common experimental conditions: DMF solution 40 mL, extraction and elution condition.

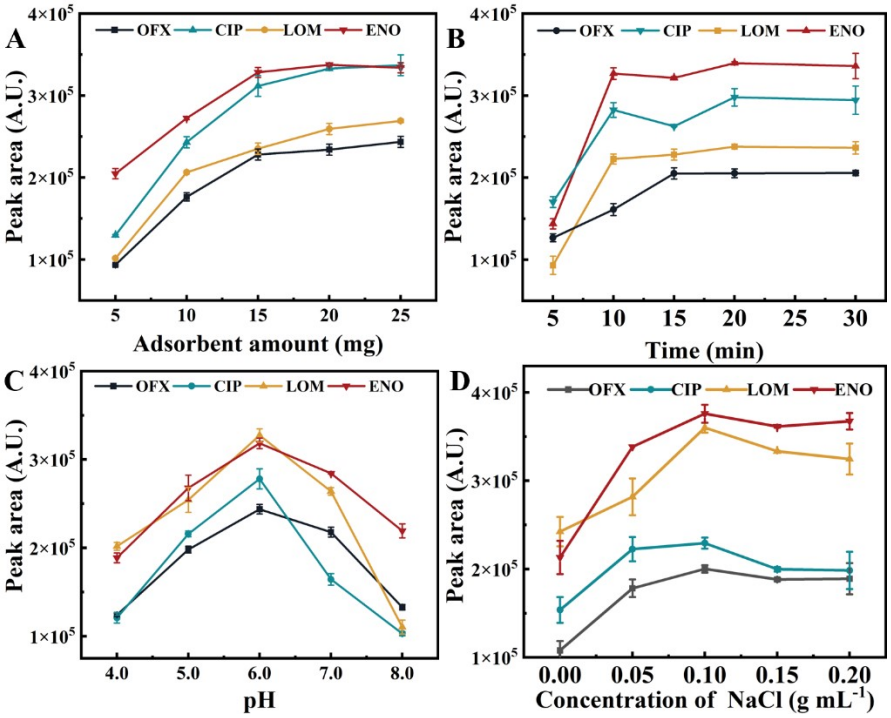


Fig. S3. Optimization of MSPE parameters: (A) solvent amount, (B) extraction time, (C) pH, (D) ionic strength. Common experimental conditions: elution solvent MeOH, elution volume 1.5 mL, desorption time 10 min.

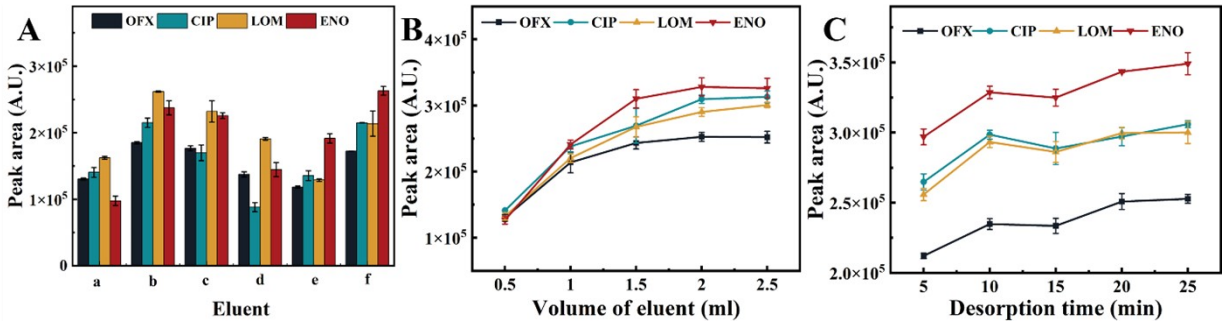


Fig. S4. Optimization of elution parameters: (A) Influence of elution solvent, (B) elution volume and (C) desorption time. A: (a) MeOH, (b) MeOH+5% ammonia, (c) MeOH +10% ammonia, (d) ACN, (e) ACN+5% ammonia, (f) ACN+10% ammonia. Common experimental conditions: solvent amount 15 mg, extraction time 15 min, pH 6.

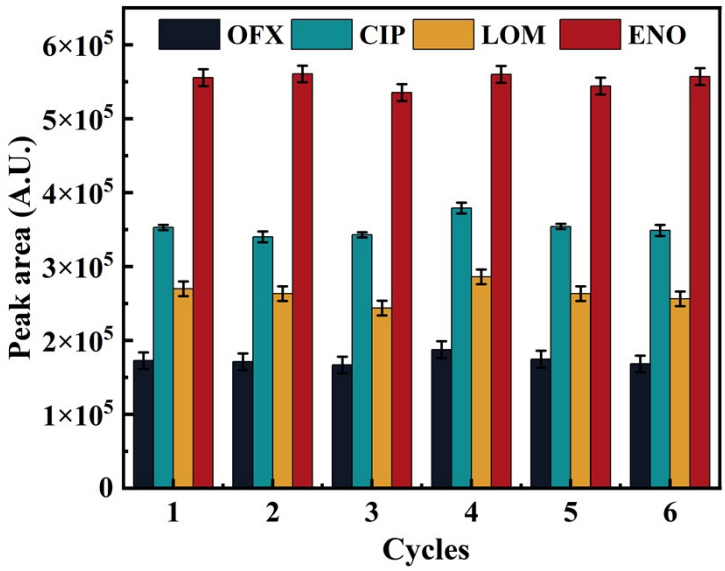


Fig. S5. Reusable times of MPCs

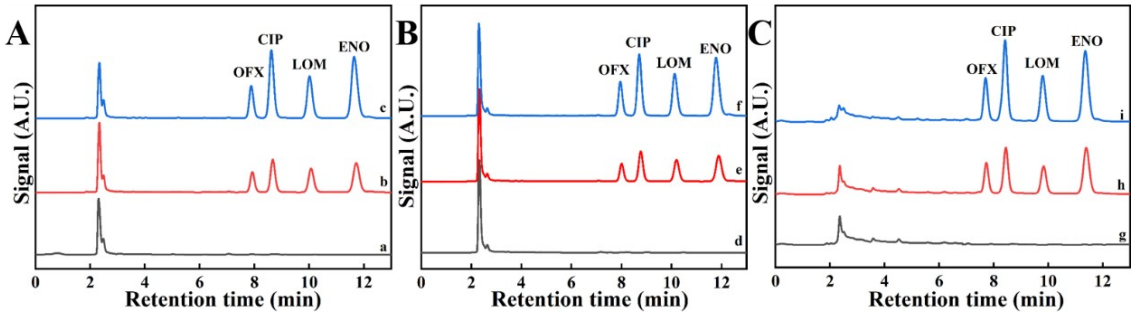


Fig. S6. Chromatograms of FQs in (A) milk, (B) pork and (C) lake water after MSPE. a, d, g: blank samples; b, e, h: spiked samples with 50 μg L^{-1} target FQs; c, f, i: spiked samples with 100 μg L^{-1} FQs.