Electronic Supplementary Material

Dual-template molecularly imprinted polymers for dispersive solid-phase extraction of fluoroquinolones in water samples coupled with high performance liquid chromatography

Wenhui Lu[a,c], Jie Liu[b,c], Jinhua Li[c], Xiaoyan Wang[c], Min Lv[c], Rong Cui[b]*, Lingxin Chen[c,d]*

[a] *School of Light Industry and Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, China*

[b] *School of Environment and Materials Engineering, Yantai University, Yantai 264005, China*

[c] *CAS Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Research Center for Coastal Environmental Engineering and Technology, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China*

[d] *College of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, 273165, China*

* Corresponding author.

E-mail addresses: glorytre@163.com (Cui), lxchen@yic.ac.cn (Chen).

Contents

Experimental S1. *Selective adsorption experiment and stastical analysis*

To estimate the selectivity of dt-MIPs for NOR and ENR, other four analogues of pefloxacin (PEF), danofloxacin (DAN), enoxacin (ENO) and ciprofloxacin (CIP) were chosen and investigated according to the selective adsorption experiment. Briefly, 5 mg dt-MIPs or NIPs were dispersed in 4 mL of aqueous solution of the above six FQs with the concentration of 80 mg L^{-1} individual in 10 mL centrifuge tubes. Then the mixture was shaken for 24 h at room temperature, followed by centrifugation and filtration with 0.22 μm cellulose acetate membrane filters before detected by HPLC.

The results of adsorption capacity were analyzed for statistically significant difference by two sample Student *t*-test and *p* values less than 0.05 ($p<0.05$) were accepted as significant. *p* values more than 0.05 ($p>0.05$) were considered as no statistically significant difference.

Otherwise, the parameters of imprinting factor (α), distribution coefficients (K_d), selectivity coefficients (K) and relative selectivity coefficient (K') were used to evaluate the selectivity of dt-MIPs [1]. The imprinting factor (α) can be calculated by Equation (S1),

$$\alpha = \frac{Q_{MIP}}{Q_{NIP}} \qquad (S1)$$

where Q_{MIP} and Q_{NIP} are the adsorption capacity of the template or their analogues on dt-MIPs and NIPs, respectively.

Distribution coefficient (K_d) can be calculated by Equation (S2),

$$K_d = \frac{Q_e}{C_e} \qquad (S2)$$

where K_d represents the distribution coefficient (mL g^{-1}), Q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_e (mg L^{-1}) is the equilibrium concentration.

The selectivity coefficient (K) of dt-MIPs can be calculated by Equation (S3),

$$K = \frac{K_{d\,(tem)}}{K_{d(ana)}} \qquad (S3)$$

where $K_{d(tem)}$ and $K_{d(ana)}$ are the distribution coefficients of template and structurally related compounds, respectively.

The relative selectivity coefficient (K') can be defined as Equation (S4),

$$K' = \frac{K_{MIP}}{K_{NIP}} \qquad (S4)$$

where K_{MIP} and K_{NIP} are the selectivity coefficient of dt-MIPs and NIPs, respectively, the higher value of K', the greater the difference between dt-MIPs and NIPs.

Experimental S2. *Enrichment factor and extraction recovery*

For this study, the value of enrichmen factor (EF) and extraction recovery (ER) for NOR and ENR were calculated at the concentration of 50 μg L^{-1} individual. And, EF was defined as the ratio between the concentration after extraction (C_{final}) and the initial concentration ($C_{initial}$) for an analyte [1-4], which can be calculated by Equation S5,

$$EF = \frac{C\text{final}}{C\text{initial}} \qquad (S5)$$

where C_{final} and $C_{initial}$ are the concentrations after extraction and the initial sample solution, respectively.

Extraction recovery (ER, %) can be calculated by Equation S6,

$$ER = \frac{n\text{final}}{n\text{initial}} \times 100 = EF \times \frac{V\text{e}}{V\text{s}} \times 100 \qquad \text{(S6)}$$

where n_{final} and $n_{initial}$ are the final and initial mole numbers in the extraction solvent and sample solution, respectively; V_s is the volume of the sample solution; and V_e is the volume of the extraction solvent.

References

[1] M. Hemmati, M. Rajabi, A. Asghari, A twin purification/enrichment procedure based on two versatile solid/liquid extracting agents for efficient uptake of ultra-trace levels of lorazepam and clonazepam from complex bio-matrices, J. Chromatogr. A, 1524 (2017) 1–12.

[2] S. Nojavan, M. Yazdanpanah, Micro-solid phase extraction of benzene, toluene, ethylbenzene and xylenes from aqueous solutions using water-insoluble beta-cyclodextrin polymer as sorbent, J. Chromatogr. A, 1525 (2017) 51–59.

[3] K. Mandrah, G.N.V. Satyanarayana, S.K. Roy, A dispersive liquid-liquid microextraction based on solidification of floating organic droplet followed by injector port silylation coupled with gas chromatography-tandem mass spectrometry for the determination of nine bisphenols in bottled carbonated beverages, J. Chromatogr. A, 1528 (2017) 10–17.

[4] K. Wang, X. Xie, Y. Zhang, Y. Huang, S. Zhou, W. Zhang, Y. Lin, H. Fan, Combination of microwave-assisted extraction and ultrasonic-assisted dispersive liquid-liquid microextraction for separation and enrichment of pyrethroids residues in Litchi fruit prior to HPLC determination, Food Chem., 240 (2018) 1233–1242.

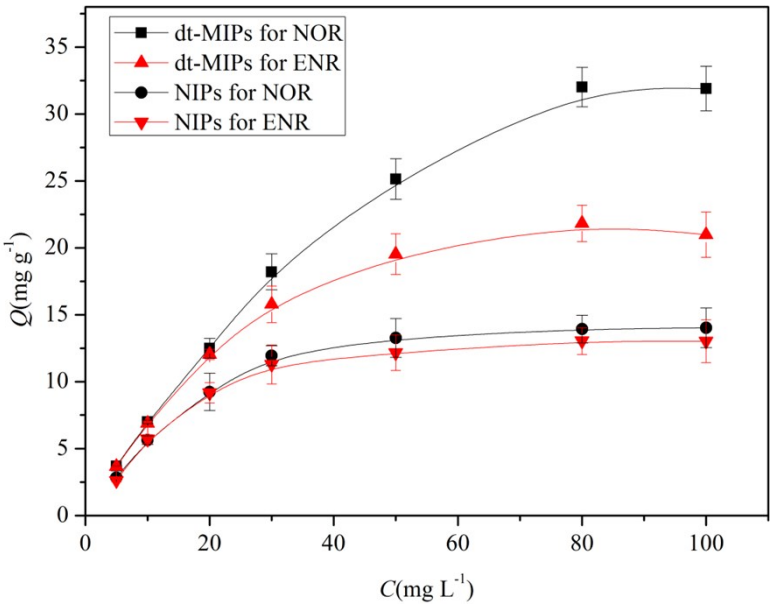
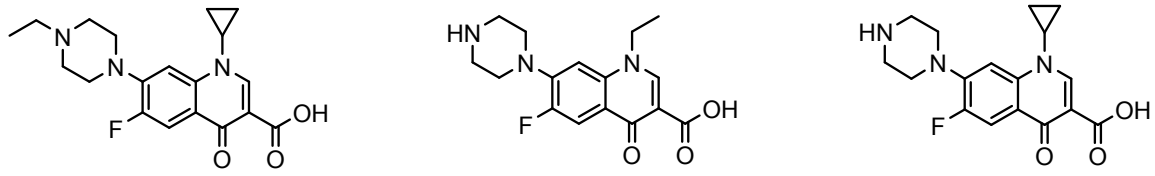


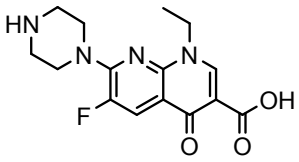
Fig. S1. Binding isotherms of dt-MIPs and NIPs for NOR and ENR. Experimental conditions: volume, 4.0 mL; mass of polymer, 5.0 mg; adsorption time, 24 h; room temperature.



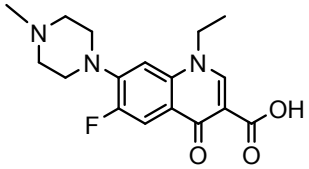
Enrofloxacin(ENR)

Norfloxacin(NOR)

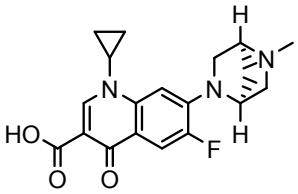
Ciprpfloxacin(CIP)



Enoxacin(ENO)



Pefloxacin(PEF)



Danofloxacin(DAN)

Fig. S2. Chemical structures of the used FQs in this study.

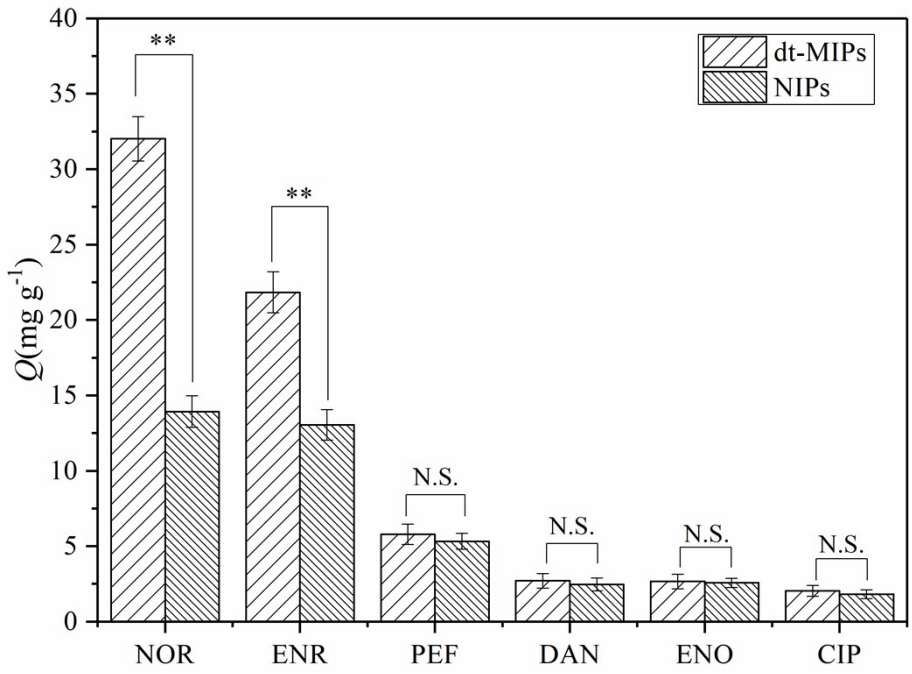


Fig. S3. Binding selectivity tests of dt-MIPs and NIPs for NOR and ENR and four structurally related compounds with the concentration of 80 mg L^{-1} individual. Experimental conditions are the same as that described in Fig. S1. N.S. stands for no statistically significant difference (p>0.05), and double stars (**) stands for highly significant difference (p<0.01).

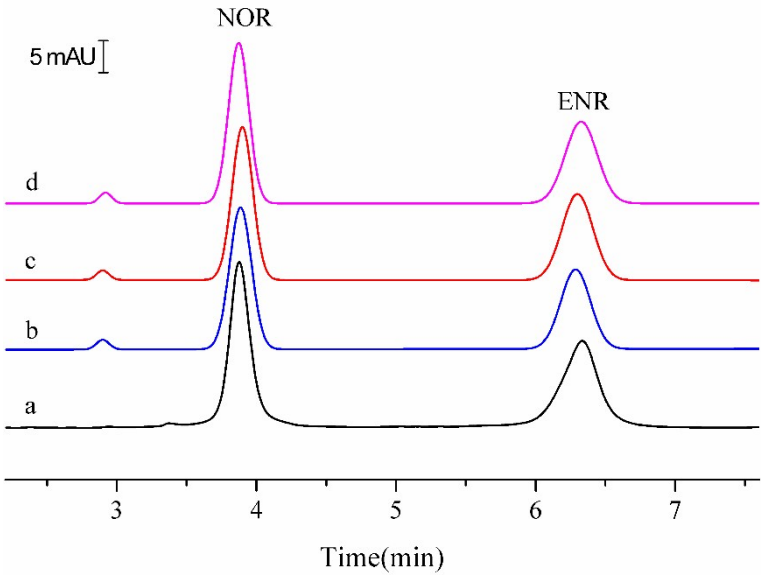


Fig. S4. Chromatograms of FQs after dt-MIPs-DSPE monitored at 280 nm in distilled water (i.e., ultrapure water standard solution) (a), lake water (b), sea water (c) and tap water (d) samples spiked with 50 μg L^{-1} NOR and ENR individual. HPLC conditions: mobile phase, H_2O (containing 0.05% formic acid)-acetonitrile (85:15, v/v); flow rate, 1 mL min^{-1}; injection volume, 20 μL; column temperature, 30 ºC.

Table S1. Selectivity parameters of NOR and ENR on dt-MIPs and NIPs to the other four analogues

Analytes	α	K_d (mL g^{-1})		K		K'
		MIPs	NIPs	MIPs	NIPs	
NOR	2.30	400	174	—	—	—
PEF	1.09	72.4	66.5	5.52	2.62	2.11
DAN	1.10	33.8	30.8	11.8	5.65	2.09
ENO	1.03	33.2	32.1	12.0	5.42	2.22
CIP	1.13	25.6	22.7	15.6	7.68	2.04
ENR	1.67	273	163	—	—	—
PEF	1.09	72.4	66.5	3.77	2.45	1.54
DAN	1.10	33.8	30.8	8.07	5.29	1.52
ENO	1.03	33.2	32.1	8.21	5.07	1.62
CIP	1.13	25.6	22.7	10.67	7.19	1.48

Table S2. Comparisons of the developed dt-MIPs-DSPE-HPLC method with published MIPs-SPE-HPLC methods for FQs determination.

FQs	Template	Polymerization method	Pretreatment technique	Detection technique	Adsorption capacity (mg g^{-1})	LODs	Recovery (%)	Sample	Ref
NOR, CIP, DAN, ENR	CIP	Precipitation Polymerization	SPE	HPLC-UV	—	0.04–0.35 μg kg^{-1}	75.2–103.5	Soil	[28]
LEV, ENR, CIP, GAT	LEV	Bulk Polymerization	SPE	HPLC-UV	36.1	0.3–0.5 ng g^{-1}	82.4–98.3	Lake water, milk	[29]
GAT	GAT	Surface imprinting	MSPE	HPLC-UV	192.7	6 ng mL^{-1}	74.3–89.5	Serum	[47]
PEF, ENR	PEF	Surface imprinting	SPE	HPLC-UV	107.6	0.8, 1.5 ng mL^{-1}	92.04–98.31	Milk	[56]
NOR, OFL, CIP	NOR	Surface imprinting	SPE	HPLC-UV	135.1	2.65–3.65 μg kg^{-1}	69.3–102.8	Fish	[57]
NOR, ENR	NOR and ENR	Precipitation polymerization	DSPE	HPLC-UV	32.0, 21.8	0.22, 0.36 ng mL^{-1}	80.9–101.0	Lake, sea, tap water	This study

Abbreviations: CIP, ciprofloxacin; DAN, danofloxacin; LEV, levofloxacin; GAT, gatifloxacin; PEF, pefloxacin; OFL, ofloxacin; MSPE, magnetic solid phase extraction