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Supplementary Materials: Fabrication of Water-Compatible Molecularly Imprinted Resin in a Hydrophilic Deep Eutectic Solvent for the Determination and Purification of Quinolones in Wastewaters

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1. HPLC Conditions

HPLC was performed using YL9110 equipment from Younglin Co. Ltd. (Daegu, Korea), which included a YL9110 quaternary pump, YL9101 vacuum degasser, YL9131 column compartment, and YL9120 ultraviolet-visible dual channel detector. The analysis was conducted on a Chromatography Data System Autochro-3000 (Younglin Co. Ltd., Daegu, Korea) using an Optima pak C_{18} column (5 μm, 250 × 4.6 mm, RS Tech Corporation, Daejeon, Korea). The mobile phase was a 0.02 mol/L TMAB-ACN-TFA (90:10:0.06, v/v/v) solution with a flow rate of 1.0 mL/min. The injection volume was 10μL and the detection wavelength was set to 280 nm. The column temperature was set to 25 °C.

2. Synthesis of DES-based MIR

First, a 30 mmol resorcinol and 60 mmol formaldehyde solution (37%) was added to 6 mL of the DES (DES-1, DES-2, or DES-3) as the reaction solvent at 40 °C with stirring (bottle #1). Subsequently, 10 mmol melamine and 30 mmol formaldehyde were dissolved in 6 mL of DES and stirred at 80 °C until the solution became transparent (bottle #2). Bottle #2 was then allowed to cool to room temperature. The solution in bottle #2 was poured into bottle #1 with stirring. The next step was achieved by adding 0.25 mmol template (OFL) into bottle #1 for self-assembly for 1h at 40 °C. Subsequently, bottle #1 was heated to 80 °C for 24 h. The resulting solid was collected by suction filtration and washed several times with ultrapure water to remove the un-reacted reagents and DES. The obtained solid particles were eluted with methanol-water-acetic acid (8/1/1, v/v/v) until the elution did not contain the template, which was then checked by HPLC. Finally, the DES-MIR was washed with methanol to neutrality and dried at 50 °C for 24 h

Table S1. Properties of the adsorbents.

Specimens	N content (wt%)	Br or Cl content (wt%)
MIR	12.48	-
DES^1-MIR	11.04	14.40(Cl)
DES^2-MIR	7.34	36.13(Br)
DES^3-MIR	8.21	25.42(Cl)

Table S2. Calibration equation, linear ranges, LOD and LOQ for the OFL and CIP with DES[1]-MIR-SPE method.

Compound	Calibration equation (μg/mL)	Linear range (μg/mL)	LOD (μg/mL)	LOQ (μg/mL)	R^2
OFL	y = 56.3x + 13.8	0.1–100	0.012	0.040	0.9995
CIP	y = 48.5x + 8.2	0.1–100	0.018	0.060	0.9989

Table S3. Intra-day and inter-day precision, accuracy and recovery of OLF and CIP at three different concentrations (n = 3) with DES[1]-MIR-SPE method.

Analyts	Spiked (μg/mL)	Intra-day		Inter-day		Method Recovery(%)
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	-
OLF	1	93.4	3.3	91.7	3.1	92.3
	10	94.5	2.4	93.2	2.4	93.9
	100	93.5	1.9	94.5	2.2	94.0
CIP	1	89.2	3.7	91.5	4.6	90.4
	10	92.6	2.5	94.4	3.4	93.5
	100	91.4	2.1	88.7	3.0	90.1

Table S4. Comparison of the present method with previously reported methods.

Adsorbents	Sample	Linearity (μg/mL)	Recovery (%)	LOD (μg/mL)	RSD (%)	Ref.
MIP	Serum	0.35–150	90.7-101.2	0.07	2.9-4.1	Qiao et al[1]
Hybrid-MIP	Tilapia	0.05–25	87.3-100.6	0.0072	1.9-2.5	Yan et al[2]
Magnetic graphene	Food (Egg)	0.2–2	96.5-98.0	0.2	2.3-3.0	Wang et al[3]
MIP particle	Milk	0.02–1	78.3-97.7	0.01	2.4	Wang et al[4]
DES-MIR	Wastewater	0.1–100	90.1-94.0	0.012	1.9-4.6	This study

Table S5. Extraction and determination of OLF and CIP in real water sample from local environment with DES[1]-MIR-SPE method (n=3).

Sample	Analytes	Concentration before SPE (μg/mL)	Concentration after SPE (μg/mL)	Recovery (%)	RSD (%)
Sample[a]	OLF	*	*	*	*
	CIP	*	*	*	*
Sample[b]	OLF	0.35	*	93.0	2.6
	CIP	0.45	*	*	*
Sample[c]	OLF	0.91	0.850	93.4	2.0
	CIP	1.32	1.21	91.8	1.5

a: tap water; b: lake water; c: seafood market water; *: not detected.

References

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