New Journal of Chemistry
Electronic Supplementary Information

Hierarchically porous zeolitic imidazole framework-8/cellulose membrane installed in filter as sorbent for microextraction in packed syringe towards trace tetracyclines in water samples

Lin Li[1] · Sijia Zhang[2] · YingyingLi[1] · Ting Wang[2] · Xiaohong Hou[2*]

[1] *School of Pharmacy, Shenyang Pharmaceutical University, Shenyang 110016, Liaoning Province, People's Republic of China.*

[2] *School of Pharmaceutical Engineering, Shenyang Pharmaceutical University, Shenyang 110016, Liaoning Province, People's Republic of China.*

_____

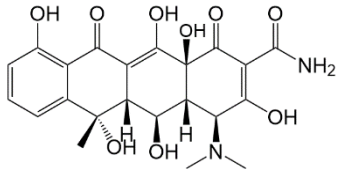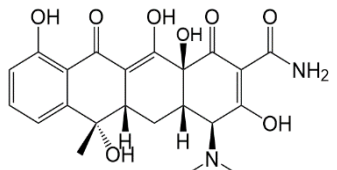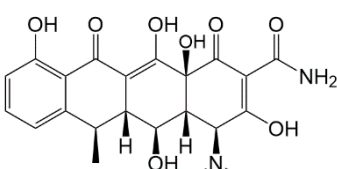*Corresponding author. Tel: +86-024-43520212; Fax: +86-024-43520212.

E-mail address:syphu_houxiaohong@163.com

Content list

1. Chemical properties and structures of target TCs

Table S1 Chemical properties and structures of target TCs

Analyte	Molecular formula	Molecular mass	Chemical structure	pK_a^{1-2}
Oxytetracycline (OTC)	$C_{22}H_{24}N_2O_9$	460.43		3.3, 7.3, 9.1
Tetracycline (TC)	$C_{22}H_{24}N_2O_8$	444.43		3.3, 7.7, 9.3
Doxycycline (DC)	$C_{22}H_{24}N_2O_8$	444.43		3.5, 7.7, 9.5

2. Reagents and materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 2-methylimidazole were obtained from Aladdin Industrial Corporation (Shanghai, China). Methanol and acetonitrile were acquired from Yuwang Group (Shandong, China). Cotton linter was provided by Hubei Chemical Fiber Group (Wuhan, China). Ultrapure water was produced by SZ-93A auto Redistilled water system (Shanghai, China). All other reagents and chemicals used in the experiments were from Damao Chemical Reagent Factory (Tianjin, China).

3. Instrumentation and analytical conditions

Chromatographic separation and determination of TCs were achieved on a Shimadzu LC-20 AT liquid chromatography tandem SPD-20A ultraviolet detector (Shimadzu, Japan) with a Diamonsil C18 analytical column (250 mm×4.6 mm, i.d. 5 μm) (Dikma, China). The mobile phase was constituted of 0.02 mol L^{-1} oxalic acid aqueous solution and acetonitrile (73:27, v/v). The detection wavelength was 360 nm. The flow rate was 1 mL min^{-1}. The column temperature was maintained at $30^{o}C$ and the injection volume was 20 μL.

Other main equipment used are as follows: X-ray diffraction (XRD) measurements were performed with a D8 ADVANCE diffractometer (Bruker, Germany). The morphology of CM and ZIF-8/CM was observed by Gemini SEM 300 scanning electron microscopy (SEM) (ZEISS, Germany). Thermal gravimetric analysis (TGA) was tested by thermal gravimetric analyser (METTLER TOLEDO, America) with a heating rate of $10^{o}C$ min^{-1} from 30 to $700^{o}C$ under nitrogen atmosphere. The nitrogen physisorption isotherms were carried out with a SA-3100 surface area and pore analyzer instrument (Bekman Coulter, USA).

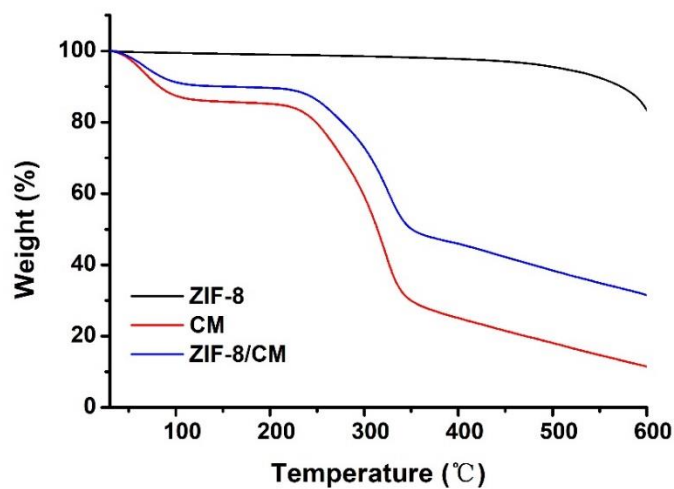## 4. The schematic diagram of ZIF-8/CM synthesis procedure
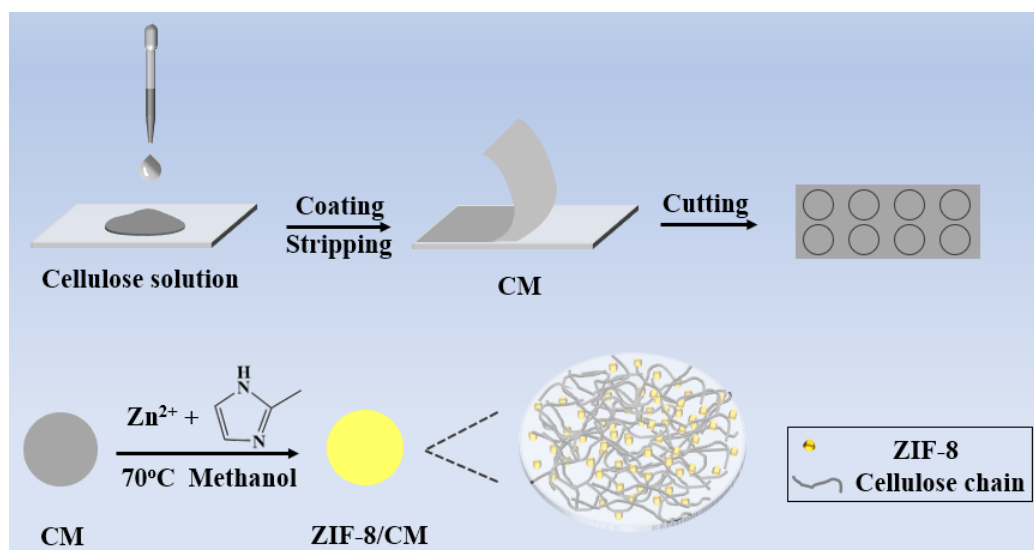
Fig. S1 Schematic diagram of ZIF-8/CM synthesis procedure

5. The schematic diagram of MEPS device and procedure
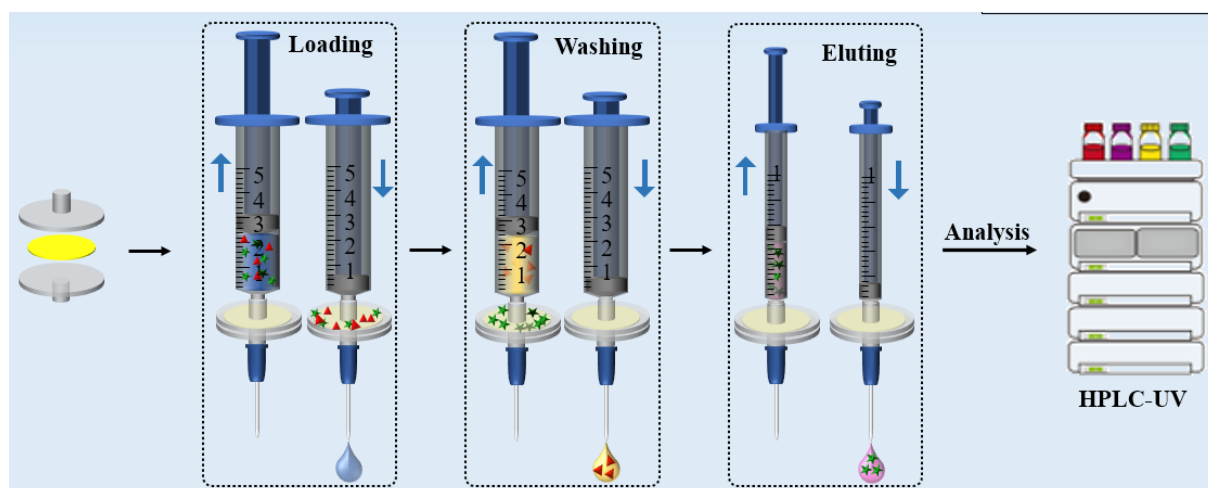
Fig. S2 Schematic diagram of MEPS device and procedure

6. TGA curves and the determination of ZIF-8 content in ZIF-8/CM

Fig. S3 TGA curves for ZIF-8, CM and ZIF-8/CM

$$Measured\ content\ (\%) = \frac{ash\ content_{ZIF\text{-}8/CM} - ash\ content_{CM}}{ash\ content_{ZIF\text{-}8} - ash\ content_{CM}} \times 100$$

where ash content$_{ZIF\text{-}8/CM}$ is the ash content of ZIF-8/CM, ash content$_{CM}$ is the ash content of CM and ash content $_{ZIF\text{-}8}$ is the ash content of ZIF-8.

Table S2 Measured content of ZIF-8 in the ZIF-8/CM

	Ash content	Measured content
ZIF-8	83.46%	
CM	11.46%	27.86%
ZIF-8/CM	31.52%	

7. Recovery results of four original samples

Table S3 Recovery of three TCs in different water samples (n = 3)

Sample	Spiked level	OTC		TC		DC	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Bottle water	Low[a]	75.3	4.7	77.9	5.1	81.0	8.7
	Middle[b]	79.4	5.9	86.1	3.9	85.8	4.5
	High[c]	87.4	2.9	85.3	2.8	91.0	3.8
Tap water	Low	82.1	8.4	73.2	4.8	84.3	9.2
	Middle	88.9	7.2	95.2	7.8	77.6	8.9
	High	96.4	5.8	87.1	6.5	82.4	4.2
River water 1	Low	77.5	4.7	72.9	6.6	75.8	7.8
	Middle	88.3	3.9	95.8	2.9	81.4	5.3
	High	91.5	2.4	93.4	3.4	83.7	3.5
River water 2	Low	84.2	4.7	77.8	7.1	83.1	5.4
	Middle	90.4	8.1	87.3	4.7	84.1	8.3
	High	97.6	3.8	89.9	4.5	83.3	4.4

[a]2 μg L^{-1} OTC, 4 μg L^{-1} TC and 12.5 μg L^{-1} DC

[b]20 μg L^{-1} OTC, 40 μg L^{-1} TC and 125 μg L^{-1} DC

[c]32 μg L^{-1} OTC, 64 μg L^{-1} TC and 200 μg L^{-1} DC

8. Analytical results of original samples

Table S4 Analytical results of original samples

Sample	Concentration ($\mu g\ L^{-1}$) (n=3)		
	OTC	TC	DC
Bottle water	ND[d]	ND	ND
Tap water	ND	ND	ND
River water 1	ND	ND	ND
River water 2	< LOQ	ND	ND

[d] Not detected

9. References

1 A. Y. Udalova, S. G. Dmitrienko, S. V. Natchukc, V. V. Apyari and Y. A. Zolotov, J. *Anal. Chem.*, 2015, **70**, 292-297.

2 R. L. Wang, C. Li, Q. L. Li, Q. L. Li, S. X. Zhang, F. Lv and Z. M. Yan, *J. Chromatogr. A*, 2020, **1622**, 461098.