

Electronic Supplementary Information

**Covalent organic framework-LZU1@PEI@Fe₃O₄-based magnetic
dispersive micro-solid phase extraction of tetracyclines from
environmental water prior to HPLC analysis**

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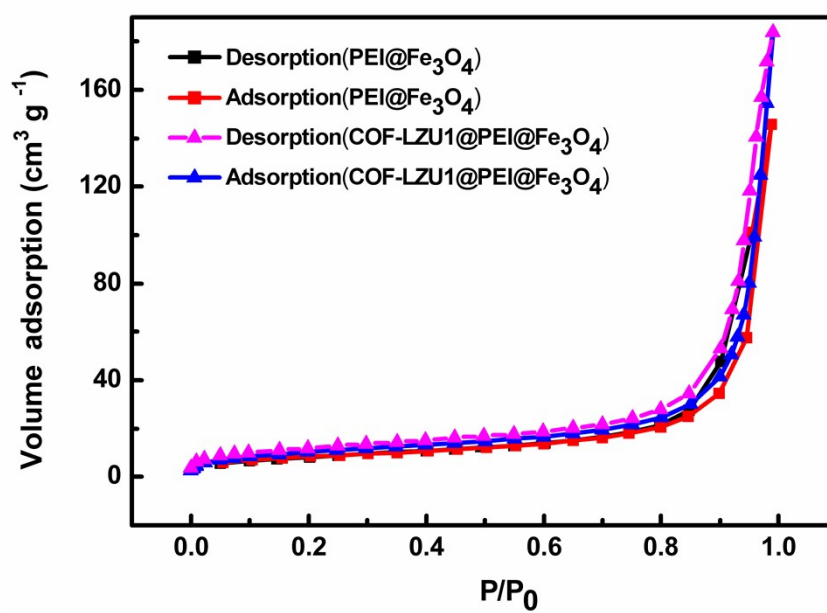


Fig. S1 Nitrogen adsorption and desorption isotherms of PEI@Fe₃O₄ and COF-LZU1@PEI@Fe₃O₄.

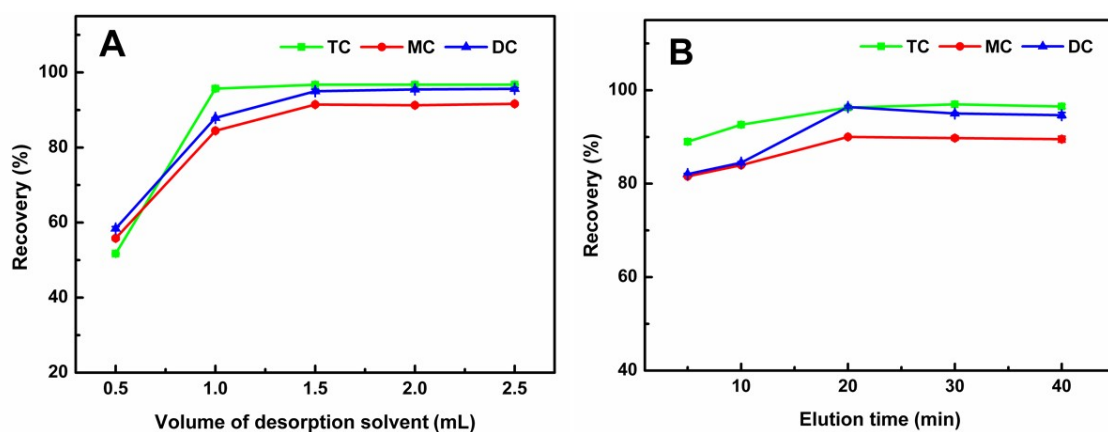


Fig. S2 Effect of desorption conditions on the extraction efficiency. (A) Volume of elution solvent; (B) Elution time, 1.50 mL elution solvent. Other conditions: amount of adsorbent, 5.0 mg; extraction time, 30 min; sample volume, 10.00 mL; sample pH, 7.0; extraction temperature, 30 °C.

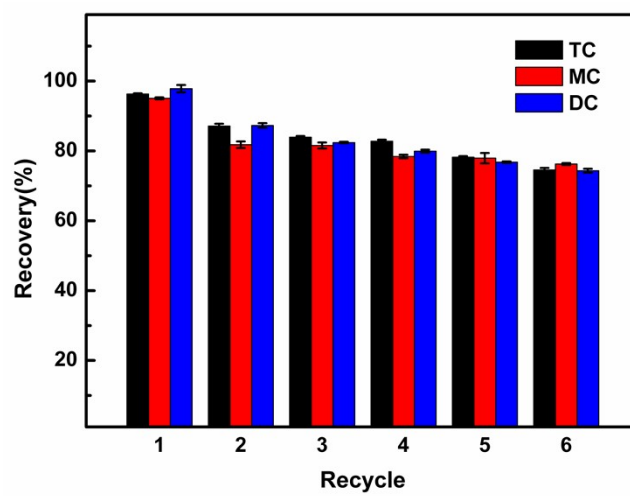


Fig. S3 Reusability of COF-LZU1@PEI@Fe₃O₄.

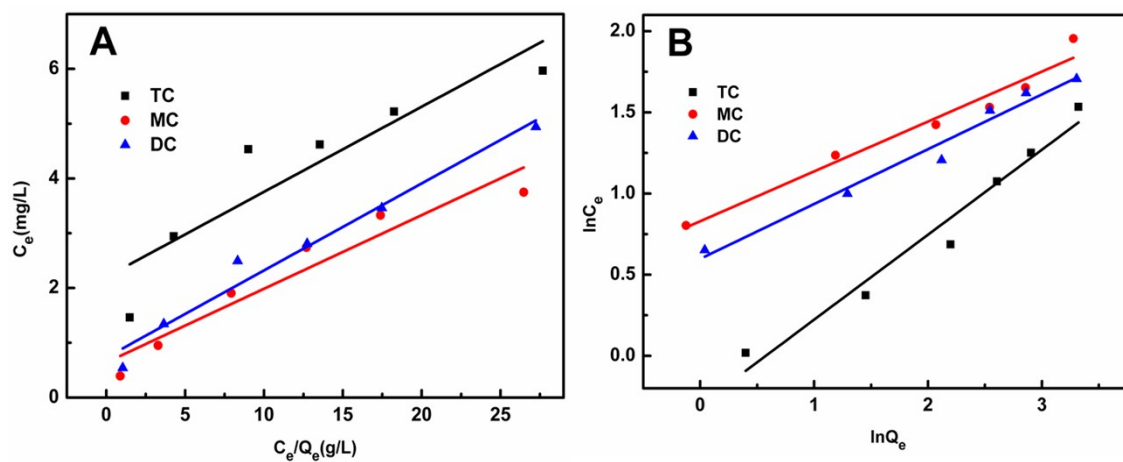


Fig. S4 Adsorption isotherms of TCs on COF-LZU1@PEI@Fe₃O₄ fitted by (A) Langmuir model; (B) Freundlich model.

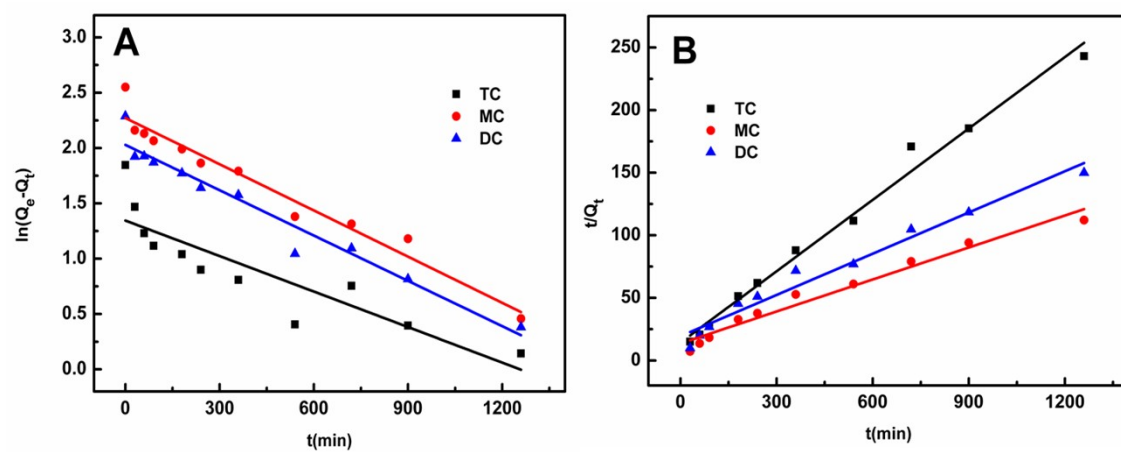


Fig. S5 Adsorption kinetic model of COF-LZU1@PEI@Fe₃O₄ to TCs. (A) pseudo-first-order kinetics; (B) pseudo-second-order kinetics.

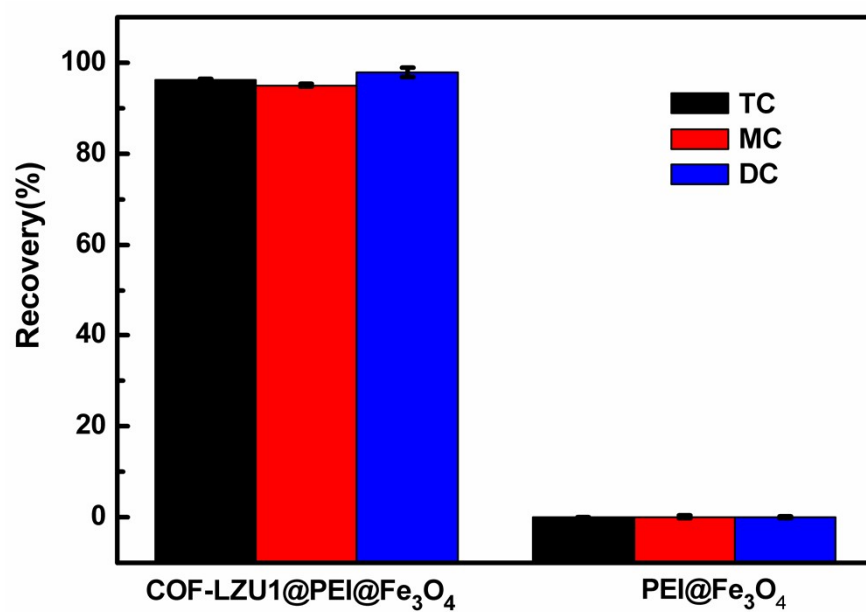


Fig. S6 COF-LZU1@PEI@Fe₃O₄ and PEI@Fe₃O₄ performance comparison.

Table S1 Inter-batch precision of COF-LZU1@PEI@Fe₃O₄

<u>Analytes</u>	<u>Recovery(%)</u>			<u>RSD(%)</u>
	<u>1</u>	<u>2</u>	<u>3</u>	
<u>TC</u>	<u>94.6</u>	<u>96.9</u>	<u>95.8</u>	<u>1.2</u>
<u>MC</u>	<u>90.2</u>	<u>92.0</u>	<u>91.1</u>	<u>1.5</u>
<u>DC</u>	<u>97.6</u>	<u>94.1</u>	<u>96.2</u>	<u>1.9</u>

Table S2 Experimental data of the thermodynamics studies of TCs on COF-LZU1@PEI@Fe₃O₄ (303 K).

	<u>TC</u>	<u>MC</u>	<u>DC</u>
<u>C_e (mg mL⁻¹)</u>	<u>1.49</u>	<u>0.88</u>	<u>1.04</u>
	<u>4.27</u>	<u>3.28</u>	<u>3.64</u>
	<u>9.01</u>	<u>7.92</u>	<u>8.33</u>
	<u>13.54</u>	<u>12.69</u>	<u>12.73</u>
	<u>18.25</u>	<u>17.39</u>	<u>17.48</u>
	<u>27.68</u>	<u>26.47</u>	<u>27.24</u>
<u>Q_e (mg g⁻¹)</u>	<u>1.02</u>	<u>2.23</u>	<u>1.92</u>
	<u>1.45</u>	<u>3.44</u>	<u>2.72</u>
	<u>1.99</u>	<u>4.16</u>	<u>3.34</u>
	<u>2.93</u>	<u>4.63</u>	<u>4.53</u>
	<u>3.50</u>	<u>5.22</u>	<u>5.05</u>
	<u>4.64</u>	<u>7.06</u>	<u>5.51</u>

Table S3 Parameters of adsorption isotherms for TCs on COF-LZU1@PEI@Fe₃O₄ (303 K).

Analytes	Q _e (mg g ⁻¹)	Langmuir			Freundlich		
		Q _{max} (mg g ⁻¹)	K _L (L mg ⁻¹)	R ²	K _F (mg g ⁻¹)	N	R ²
TC	4.64	6.44	0.71×10^{-1}	0.8339	0.74	1.91	0.9648
MC	7.06	7.44	2.09×10^{-1}	0.9242	2.29	3.25	0.9652
DC	5.51	6.29	2.17×10^{-1}	0.9721	1.82	2.96	0.9743

Table S4 Experimental data of the kinetics studies of TCs on COF-LZU1@PEI@Fe₃O₄ (303 K).

<u>Time (min)</u>	<u>Q_t (mg g⁻¹)</u>		
	<u>TC</u>	<u>MC</u>	<u>DC</u>
<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>
<u>30</u>	<u>2.00</u>	<u>4.14</u>	<u>3.02</u>
<u>60</u>	<u>2.92</u>	<u>4.39</u>	<u>3.00</u>
<u>90</u>	<u>3.28</u>	<u>4.93</u>	<u>3.37</u>
<u>180</u>	<u>3.51</u>	<u>5.50</u>	<u>3.98</u>
<u>240</u>	<u>3.88</u>	<u>6.38</u>	<u>4.71</u>
<u>360</u>	<u>4.10</u>	<u>6.83</u>	<u>5.02</u>

Table S5 Parameters of adsorption kinetic for TCs on COF-LZU1@PEI@Fe₃O₄ (303 K) .

Analytes	Q _e (mg g ⁻¹)	pseudo-first-order			pseudo-second-order		
		K ₁ (min ⁻¹)	Q _{e,cal} (mg g ⁻¹)	R ²	K ₂ (g mg ⁻¹ min ⁻¹)	Q _{e,cal} (mg g ⁻¹)	R ²
TC	6.34	1.10×10 ⁻³	3.84	0.7782	2.54×10 ⁻³	5.26	0.9885
MC	12.83	1.40×10 ⁻³	9.70	0.9563	0.54×10 ⁻³	11.74	0.9714
DC	9.83	1.40×10 ⁻³	7.60	0.9555	0.62×10 ⁻³	9.12	0.9717

Table S6 Results of sample analysis for the determination of TCs.

	Added ($\mu\text{g L}^{-1}$)	Shapan reservoir			Jinhua river			Qingxikou reservoir		
		Found ($\mu\text{g L}^{-1}$)	Recovery (%)	RSD (%)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)	RSD (%)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)	RSD (%)
TC	0	--	--	--	--	--	--	--	--	--
	<u>5</u>	<u>4.5</u>	<u>89.3</u>	<u>2.6</u>	<u>4.8</u>	<u>95.6</u>	<u>3.1</u>	<u>5.1</u>	<u>101.4</u>	<u>1.7</u>
	<u>10</u>	<u>9.9</u>	<u>98.6</u>	<u>0.9</u>	<u>9.8</u>	<u>98.4</u>	<u>0.6</u>	<u>10.0</u>	<u>100.2</u>	<u>1.4</u>
	30	27.5	91.7	0.4	30.1	100.3	0.4	30.6	102.0	1.1
	50	48.0	96.0	3.9	43.5	87.0	5.1	44.1	88.2	1.7
	100	93.5	93.5	1.6	89.8	89.8	0.8	94.8	94.8	0.4
MC	0	--	--	--	--	--	--	--	--	--
	<u>5</u>	<u>4.8</u>	<u>95.4</u>	<u>2.3</u>	<u>4.8</u>	<u>97.0</u>	<u>2.2</u>	<u>4.8</u>	<u>95.4</u>	<u>2.3</u>
	<u>10</u>	<u>9.6</u>	<u>96.4</u>	<u>1.1</u>	<u>10.8</u>	<u>108.2</u>	<u>1.4</u>	<u>9.9</u>	<u>98.9</u>	<u>4.6</u>
	30	32.7	109.0	0.8	31.8	106.0	0.4	31.8	106.0	0.4
	50	56.9	113.8	1.5	49.1	98.2	1.7	53.3	106.6	1.6
	100	111.0	111.0	1.2	105.6	105.6	1.2	108.3	108.3	0.8
DC	0	--	--	--	--	--	--	--	--	--
	<u>5</u>	<u>4.5</u>	<u>90.6</u>	<u>2.9</u>	<u>4.6</u>	<u>91.5</u>	<u>1.5</u>	<u>4.9</u>	<u>98.1</u>	<u>2.7</u>
	<u>10</u>	<u>8.7</u>	<u>86.8</u>	<u>2.2</u>	<u>9.6</u>	<u>96.4</u>	<u>1.3</u>	<u>9.7</u>	<u>97.3</u>	<u>1.3</u>
	30	27.9	93.0	0.6	27.5	91.7	2.5	28.3	94.3	1.2
	50	49.3	98.6	1.2	47.3	94.6	4.9	47.7	95.4	3.7
	100	94.7	94.7	0.6	96.3	96.3	4.2	94.7	94.7	3.1