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Electronic Supplementary Material

Three-dimensional adamantane-based microporous organic network for removal of trazodone in environmental aqueous samples

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Chemicals, reagents and instruments

All chemicals and reagents used were at least of analytical grade. 1,3,5,7-Tetrakis(4-bromophenyl)adamantane was purchased from Chengdu Tongchuangyuan Pharmaceutical Co., Ltd. (Chengdu, China) and 1,4-diethynylbenzene (DEB) was bought from Yanshen Technology Co., Ltd. (Jilin, China). Cuprous iodide (CuI) was provided by Sigma-Aldrich Co., Ltd. (Shanghai, China). Bis(triphenylphosphine)palladium dichloride (>98%) was supplied by Shanghai Shengen Chem-Tech Co., Ltd. (Shanghai, China). Toluene，triethylamine (TEA), methanol, anhydrous ethanol, isopropanol and acetonitrile were from Tianjin Fuyu Fine Chemical Co., Ltd. (Tianjin, China). Formic acid, trazodone (TRZ) and ammonia were purchased from Shanghai Titan Scientific Co., Ltd. (Shanghai, China). Acetic acid was purchased from Concord Technology Co., Ltd. (Tianjin, China). HCl and sodium hydroxide were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Humic Acid (HA) was provided by Yuanye Bio-Technology Co., Ltd. (Shanghai, China). Sodium chloride was provided by Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Ultrapure water was purchased from Wahaha Group Co., Ltd. (Jinan, China). Zeolite was provided by Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Commercial C18 was from Tianjin Bojianhe Chromatography Technology Co., Ltd. (Tianjin, China).

Instruments

Fourier transform infrared spectroscopy (FT-IR) were obtained using Agilent Cary 630 FT-IR spectrometer (Agilent, USA). Solid-state ^{13}C nuclear magnetic resonance

(^{13}C NMR) experiments were performed on an AVANCE III HD 400 MHz spectrometer (Bruker, Germany). N_2 adsorption-desorption isotherms (N_2, 77 K) were measured using ASAP 2460 specific surface area and pore size analyzer (Micromeritics, USA). Thermogravimetric analysis (TGA) data acquisition from room temperature to 700 °C was performed using PerkinElmer TGA 8000 (PerkinElmer, USA). Water contact angle tests were measured by OCA150pro optical contact angle measurement device (Beijing Eastern-Dataphy, China). The x-ray photon energy spectrometer (XPS) was recorded on KRATOS Axis Ultra DLD (KRATOS Analytical, UK).

Preparation of Ad-MON+TRZ for XPS analysis

10 mL TRZ standard solution (50 mg L^{-1}) with 5 mg Ad-MON were conducted to prepare the Ad-MON+TRZ under a natural pH. After staying for 1 h, the supernatant was separated, and pre-adsorbed Ad-MON was dried for XPS analysis.

Comparison of the adsorption performance with commercial C18 and zeolite

Commercial C18, zeolite, and Ad-MON (5 mg) was separately dispersed with 10 mL trazodone standard solution (50 mg L^{-1}). After staying for 1 h under a natural pH at 25 ℃, the supernatant was filtered and determined by HPLC.

Adsorption kinetics

The amount of trazodone adsorbed on Ad-MON could be calculated from Eq. (S1):

$$q_t = \frac{(C_0 - C_t)v}{m} (S1)$$

Where C_0 and C_t (mg L^{-1}) are the concentrations of TRZ at start and t. Respectively, q_t (mg g^{-1}) is the amount of TRZ adsorbed at time t, and v (mL) is the

volume of the TRZ solution, and *m* (mg) is the amount of Ad-MON.

For the intraparticle diffusion model, the adsorption process can be expressed as Eq. (S2):

$$q_t = K_i t^{0.5} + c \ (S2)$$

Where K_i (mg g^{-1} min$^{-0.5}$) is the intra-particle diffusion constant, and c (mg g^{-1}) is a constant proportional to the boundary layer thickness.

Adsorption thermodynamics and isotherms

Eq. (S3) converts the Langmuir constant b (dimensional) to the thermodynamic equilibrium constant Ko Eq (dimensionless):

$$K_{Eq}^{o} = \frac{b \times M_W \times C_{Adsorbate}^{o} \times 10^3}{\gamma_{Adsorbate}} \ (S3)$$

The thermodynamic free energy change (ΔG, kJ mol^{-1}), enthalpy change (ΔH, kJ mol^{-1}) and entropy change (ΔS, J mol^{-1} K^{-1}) associated with the adsorption process can be calculated from Eqs. (S4) and (S5):

$$\Delta G = - RT ln(K_{Eq}^{o}) \quad (S4)$$

$$ln(K_{Eq}^{o}) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \ (S5)$$

Where R (J mol^{-1} K^{-1}) is the universal gas constant, T (K) is the absolute temperature and is Ko Eq the Langmuir constant.

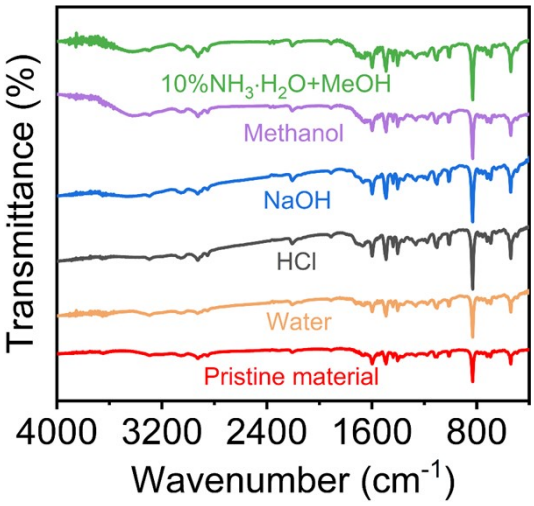


Fig. S1. Study on structural stability of Ad-MON.

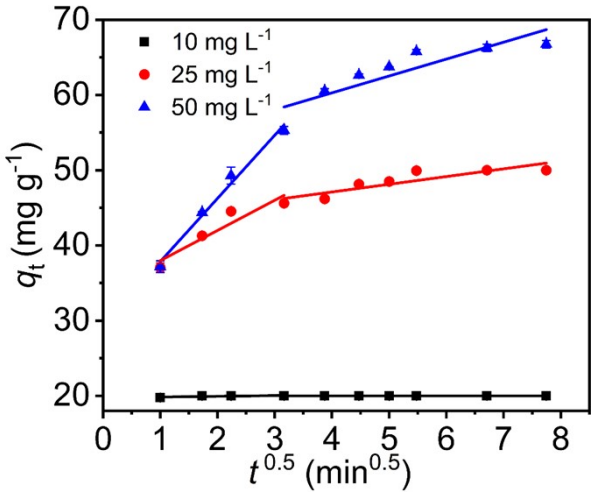


Fig. S2. Intraparticle diffusion model plots for the adsorption of TRZ on Ad-MON.

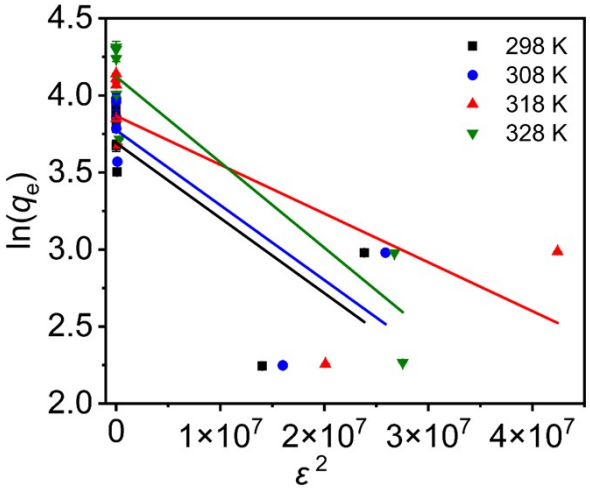


Fig. S3. Dubinin-Radushkevich plots for the adsorption of TRZ on Ad-MON.

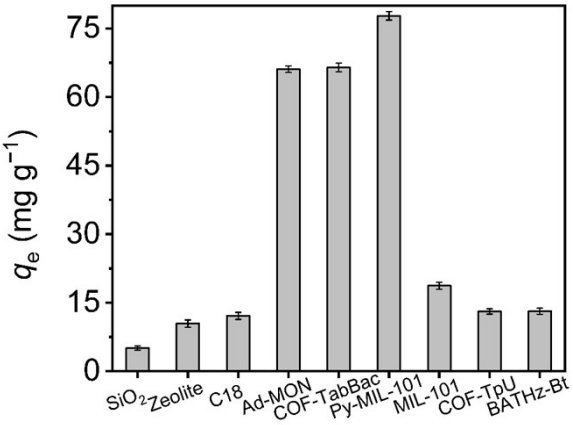


Fig. S4. Comparison of the adsorption capacities for TRZ (50 mg L^{-1}) on different adsorbents.

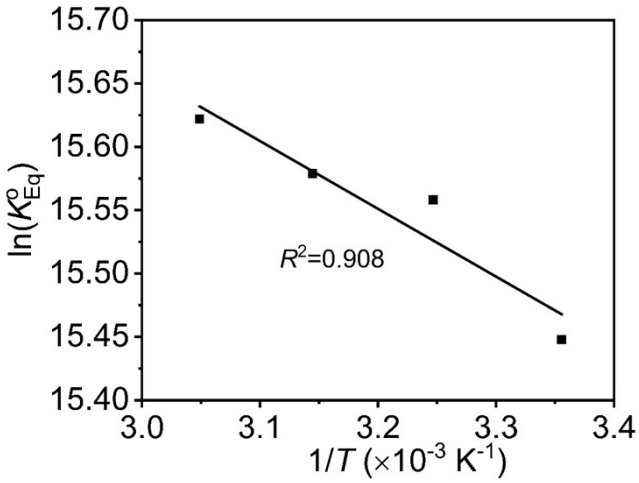


Fig. S5. Van't Hoff plots for the adsorption of TRZ on Ad-MON.

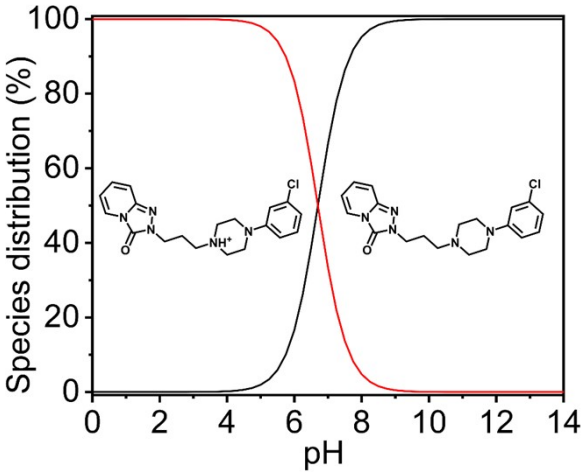


Fig. S6. TRZ speciation with the pH.

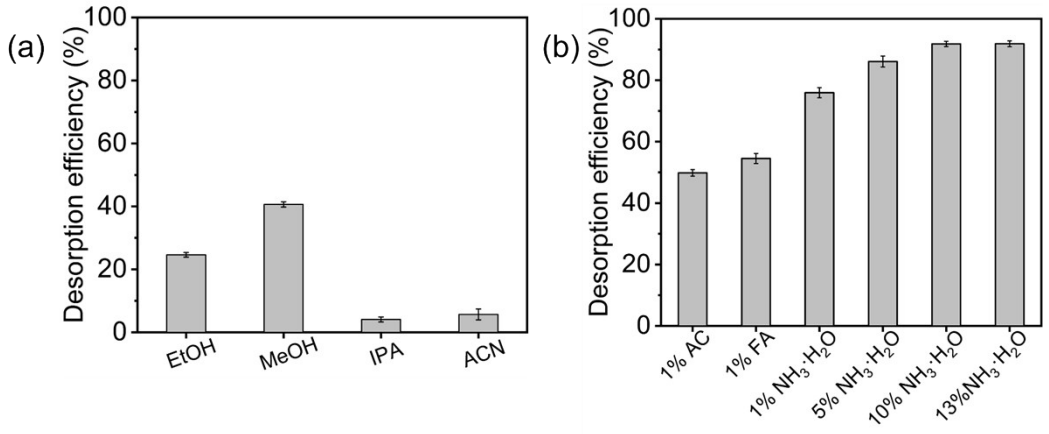


Fig. S7. Effects of types of desorption (a) common desorption agents and (b) optimize MeOH by adjusting the pH.

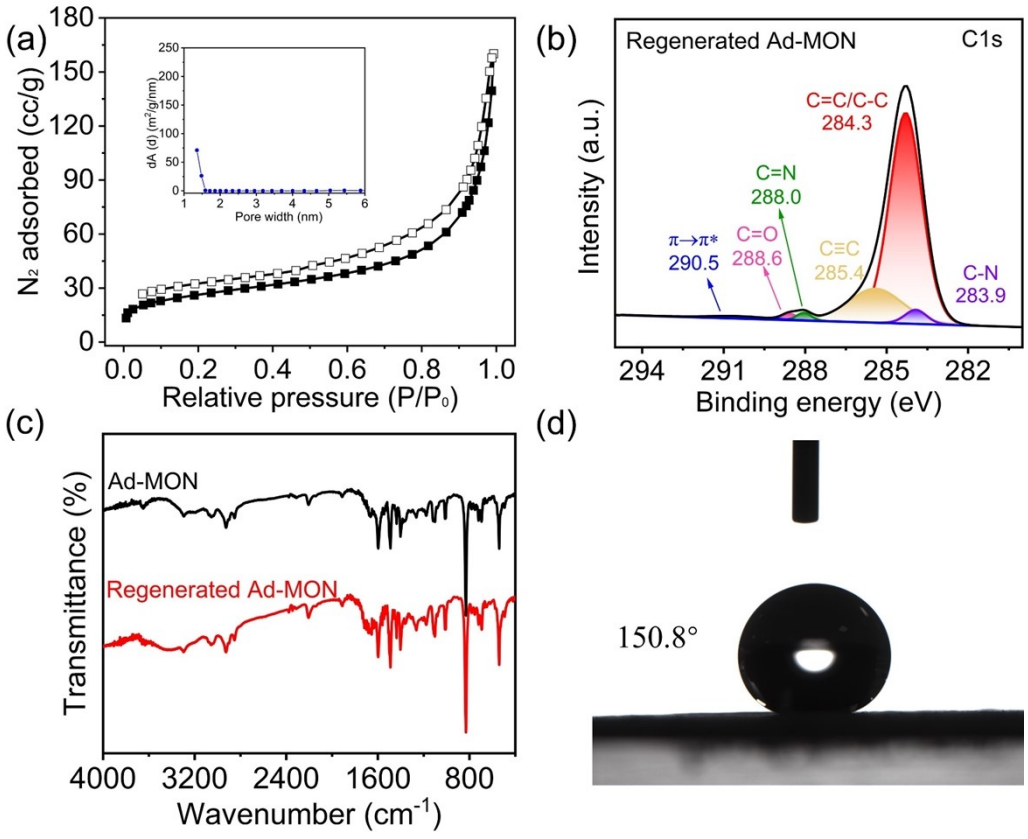


Fig. S8. (a) N_2 adsorption-desorption isotherms, (b) C1s XPS spectra, (c) FT-IR spectra and (d) water contact angle of regenerated Ad-MON.

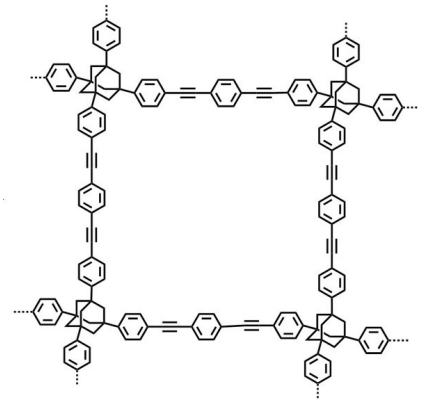


Fig. S9. Structure of Ad-MON.

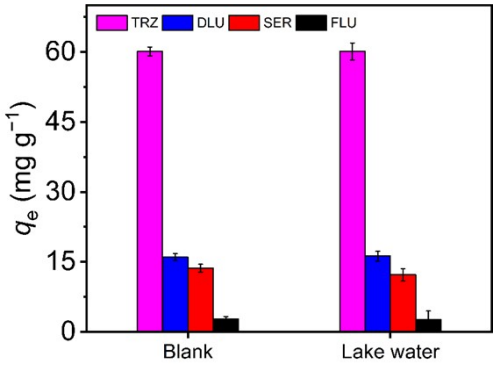


Fig. S10. Selective adsorption experiment of Ad-MON.

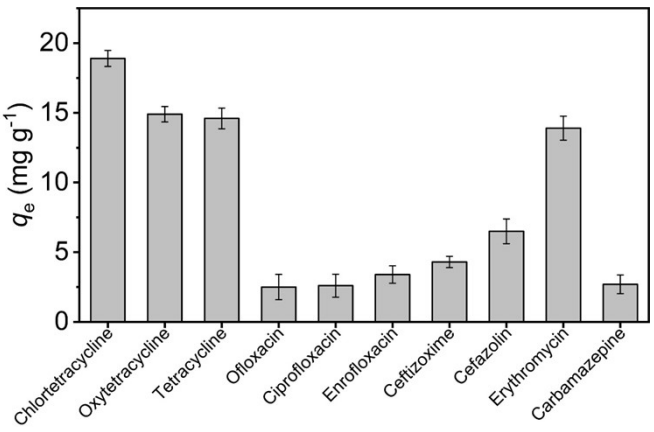


Fig. S11. Adsorption of Ad-MON to other drug contaminants.

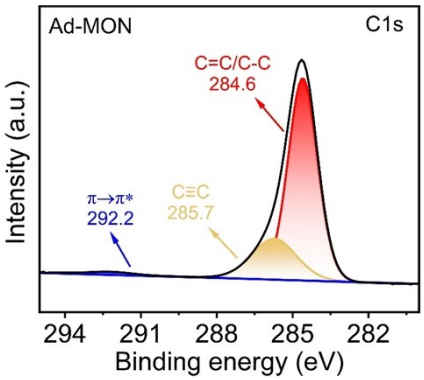


Fig. S12. C1s XPS spectra of Ad-MON.

Table S1. The adsorption kinetic constants and corresponding linear correlation coefficients for the TRZ adsorption on Ad-MON.

Model	Parameters				
Pseudo-first-order	C_0 (mg L^{-1})	R^2	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	K_1 (min^{-1})
$\ln(q_e-q_t) = -K_1t+\ln(q_e)$	10	0.297	19.9	1.5×10^{-3}	6.6×10^{-2}
	25	0.909	50.0	35.6	2.1×10^{-1}
	50	0.890	66.7	22.6	7.9×10^{-2}
Pseudo-second-order	C_0 (mg L^{-1})	R^2	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})
$\frac{t}{q_t}=\frac{t}{q_e}+\frac{1}{K_2q_e^2}$	10	0.999	19.9	20.0	25.0
	25	0.999	50.0	50.8	2.3×10^{-2}
	50	0.999	66.7	68.5	8.4×10^{-3}
Elovich	C_0 (mg L^{-1})	R^2	α (mg g^{-1} min^{-1})	β (g mg^{-1})	
$q_t=\frac{1}{\beta}\ln(t)+\frac{1}{\beta}\ln(\alpha\beta)$	10	0.477	—	25.38	
	25	0.964	3.9×10^{5}	0.31	
	50	0.977	8.5×10^{2}	0.13	

Table S2. Intraparticle diffusion constants for different original TRZ concentrations on Ad-MON.

C_0 (mg L^{-1})	Intraparticle diffusion					
	$q_t = K_i\,t^{0.5}+c$					
	K_{i1} (mg g^{-1} $min^{-0.5}$)	c_1	R^2	K_{i2} (mg g^{-1} $min^{-0.5}$)	c_2	R^2
10	1.00	19.74	0.576	5.0×10^{-5}	20.00	0.911
25	4.01	32.96	0.896	1.02	43.04	0.796
50	8.40	29.46	0.988	2.24	51.30	0.783

Table S3. The values of R_L calculated from the Langmuir isotherm.

C_0 (mg L^{-1})	5	10	25	50	100	200	300
298 K	0.470	0.307	0.151	0.081	0.042	0.022	0.015
308 K	0.442	0.284	0.137	0.074	0.038	0.019	0.013
318 K	0.437	0.280	0.135	0.072	0.037	0.019	0.013
328 K	0.427	0.271	0.130	0.069	0.036	0.018	0.012

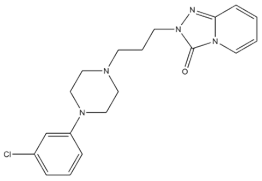
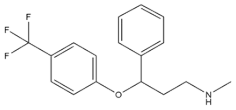
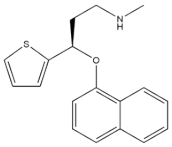
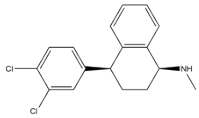
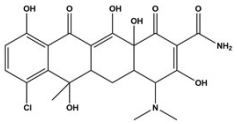
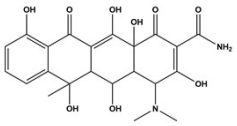
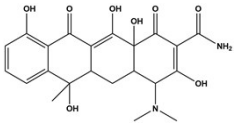
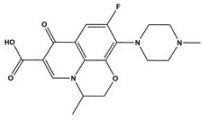
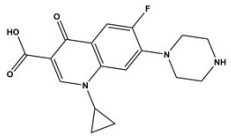
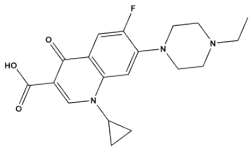
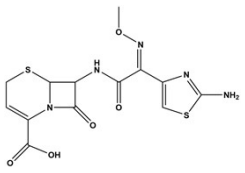
Table S4. The Freundlich parameters for the adsorption of TRZ on Ad-MON.

Freundlich parameters			
T (K)	K_F (mg^{1-n} L^n g^{-1})	n	R^2
298	19.37	5.42	0.821
308	20.15	5.14	0.829
318	22.56	4.91	0.831
328	22.99	4.11	0.900

Table S5. The Tempkin and Dubinin-Radushkevich parameters for the adsorption of TRZ on Ad-MON.

Tempkin parameters				Dubinin-Radushkevich parameters			
T (K)	A_T (L mg^{-1})	b_T (J mg^{-1})	R^2	q_s (mg g^{-1})	K_{ad} (mol^2 J^{-2})	E (kJ mol^{-1})	R^2
298	96.44	501.74	0.938	40.12	5.0×10^{-8}	3.16	0.592
308	79.70	468.28	0.947	43.57	5.0×10^{-8}	3.16	0.640
318	76.23	411.73	0.945	47.82	3.0×10^{-8}	4.08	0.546
328	31.56	318.56	0.983	61.67	6.0×10^{-8}	2.89	0.874

Table S6. Names and structure of drugs.

Drugs name	Structure of drugs	Aromatic conjugated system
Trazodone		3
Fluoxetine		2
Duloxetine		2
Sertraline		2
Chlortetracycline		1
Oxytetracycline		1
Tetracycline		1
Ofloxacin		2
Ciprofloxacin		2
Enrofloxacin		2
Ceftizoxime		1

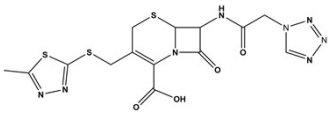
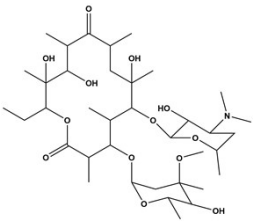
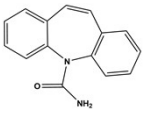
Cefazolin		2
Erythromycin		0
Carbamazepine		3

Table S7. Comparison of adsorption capacity of TRZ on various adsorbents.

Adsorbents	*T* (℃)	Adsorption capacity	*t* (min)	C_0	*V* (mL)	References
EB		9.5 mg g^{-1}				
HB	20	4.6 mg g^{-1}	5	2 mg L^{-1}	250	[1]
GB		5.4 mg g^{-1}				
GCE/B-rGO/MnO NPs	—	131.3 mg g^{-1}	90	100 mg L^{-1}	50	[2]
AC-PS[a]	30	1.0 ng g^{-1}	50	10.8 ng L^{-1}	25	[3]
Ad-MON	25	78.1 mg g^{-1}	30	50 mg L^{-1}	50	This work

[a] Under multi-component conditions

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