Supporting Information

Removal and Detection of Phenols through SPE-HPLC Method Using Microporous Organic Networks as Adsorbent

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Reagents, Materials, and Instrumentation

The poly (4-styrene sulfonic acid-co-maleic acid, SS: MA = 3:1) sodium salt (PSSMA 3:1, Mw 20000), 2,4,6-Trichlorophenol (99%), (EG, 99.0%) were purchased from Aladdin Biochemistry Technology Co. (Shanghai, China). $FeCl_3 \cdot 6H_2O$ (98%), Copper(I) iodide (99 %) was purchased from Anhui Science Technology Co. (Anhui, China), Sodium acetate anhydrous (99%), Sodium Chloride (NaCl 99.5%), Sodium hydroxide (NaOH 96%) was supplied by Tianjin Chemical Reagent Factory (Tianjin, China). 2,4-dichlorophenol (98%), 4-Nitrophenol (99%), Bis(triphenylphosphine)- palladium-dichloride ($Pd(PPh_3)_2Cl_2$, 98%), 2,4,6-Tris(4-bromophenyl)-1,3,5-triazine (98%), 1,3,5-Triethylbenzen, 2,4,6-Tris(4-bromophenyl)-1,3,5-triazine (98%), Triethylamine (99.5%) Tetrakis (4-bromophenyl) methane and 4-4'-Diehylbiphenyl) were purchased from Energy Chemical Technology Co. (Shanghai, China). Dichloromethane (99.5%), Methanol anhydrous (99.5%), and Acetonitrile (99%) were purchased from Chengdu Kelong Chemical Co. (Chengdu, China). Ethanol was purchased from Tianjin Fuyu Fine Chemical Co. (Tianjin China), and Humic acid, Toluene (99.5%) Hydrochloric acid were purchased from Xilong Scientific Co. (Guangdong, China).

Nitrogen adsorption-desorption experiments are recorded on ASAP 2020 Plus surface area and pore analyzer (Micromeritics, USA) using Nitrogen at 77K. Thermogravimetric analysis (TGA) was recorded on an STA PT 1600 (TG-DSC) thermal gravimetric analyzer (Linseis, Germany) from room temperature to 700 °C. The scanning electron microscope (SEM) images are recorded on a Thermofisher Apreo 2 S scanning electron microscope (USA). Transmission electron microscopy (TEM) images were recorded on a Protochips Atmosphere 200 (USA). The water

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contact angle measurements are recorded on an SUNZERN-CAMBI contact angle measuring device (Shanghai, China). The FT-IR spectra were recorded on a Nicolet iS 5 FTIR spectrometer (Nicolet, USA). The X-ray diffraction spectrometry (XRD) patterns were measured on a PANalytical Aeris diffractometer (Netherlands). The magnetic hysteresis loops were measured on an EV9 vibrating sample magnetometer (VSM) (MicroSense Technologies, USA). The ultraviolet absorption (UV) spectra were recorded on a UV-VIS spectrophotometer-T7 (Persee,China). Zeta potential were measured on Zeta potential and laser particle size analyser (NanoBrook 90 Plus Pals, Brookhaven, USA) and Fluorescence spectra were measured on Fluorescence Spectrometer (RF-5301pc,15 Kyoto, Japan) and slit widths were 10 nm and 10 nm.

The analytes were subjected to HPLC-UV analysis before and after performing the adsorption on both MONs. The supernatants were separated and analyzed by a UHPLC (Ultimate-3000 model) using a C-18 column 4.6×250 mm, I.D. 5 μm. The determination of wavelengths were set at 230 nm for TCP, DCP, 2-NT, and 4-NP. The mobile phase consisted of methanol: water (85:20, v/v) for TCP, methanol: water (60:40, v/v) for 2-NT, methanol: water (80:20, v/v) for 4-NP, and acetonitrile: water (52:48, v/v) was used for 2,4-DCP at a flow rate of 1.0 mL min^{-1}.

Synthesis of Fe_3O_4 Microspheres

Briefly, 0.81 g of $FeCl_3 \cdot 6H_2O$ and 0.7 g of PSSMA were separately dissolved with 10 mL of EG by ultrasound for 15 min at room temperature. These two solutions were then mixed in a 50 mL beaker and followed by adding 1.8 g of sodium acetate. Afterward, the suspension was transmitted to a 30 mL Teflon-lined stainless-steel autoclave and kept at 200 °C for 10 h. Subsequently, the resulting black product was gathered by a magnet, washed 3 times with water and ethanol, and finally dried at 60°C overnight.

Equations

The pseudo-first-order kinetic model (eq. S1) and pseudo-second-order kinetic model (eq. S2) were further used to study the adsorption behavior of TCP on the two MONs.

$$\ln (Q_e - Q_t) = \ln Q_e - \frac{k_1}{2.303} \quad \text{(S1)}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q^2} + \frac{t}{Q_e} \quad \text{(S2)}$$

where Q_e and Q_t are the adsorption capacity (mg g^{-1}) at equilibrium and t is time (min). The k is the adsorption rate constant (g mg^{-1} min^{-1}).

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad \text{(S3)}$$

$$\ln Q_e = \ln K_F + \frac{1}{n}(\ln C_e) \quad \text{(S4)}$$

where C_e (mg L^{-1}) is the equilibrium concentration of TCP, Q_0, and Q_e (mg g^{-1}) are the maximum and equilibrium adsorption capacity, respectively, b (L mg^{-1}) is the Langmuir constant. K_F and n are related to the adsorption capacity and intensity, respectively.

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta S}{RT} \quad \text{(S5)}$$

$$\Delta G = -RT \ln b \quad \text{(S6)}$$

where b (L mol^{-1}) is the constant of the Langmuir model, T is the absolute temperature and R (8.314 J mol^{-1} K^{-1}) is the universal gas constant. The values of ΔS and ΔH can be calculated from ln b versus 1/T relation (Figure S4) for both MONs.

Figures and Tables

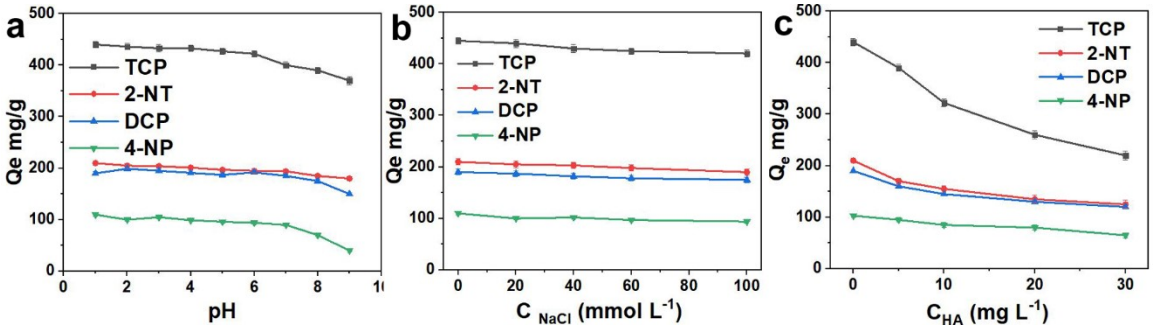

Fig. S1. Effects of (a) pH, (b) ionic strength, and (c) HA on the adsorption of TCP, DCP, 4-NP, and 2-NT on TTMON

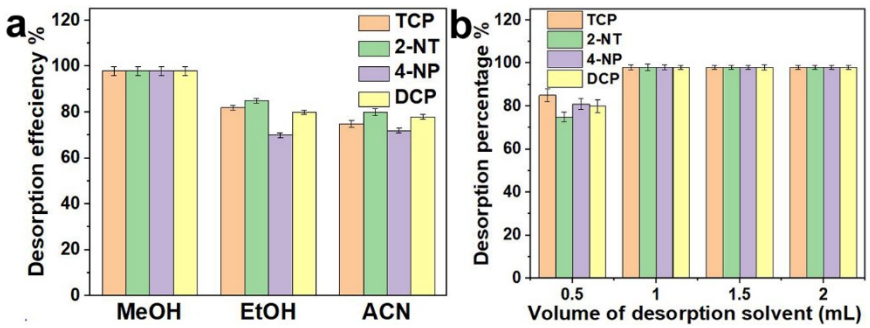

Fig. S2. Effect of desorption solvents (a) and desorption solvent volume (b) on the desorption efficiency of TCP, 2-NT, 4-NP, and DCP from TTMON

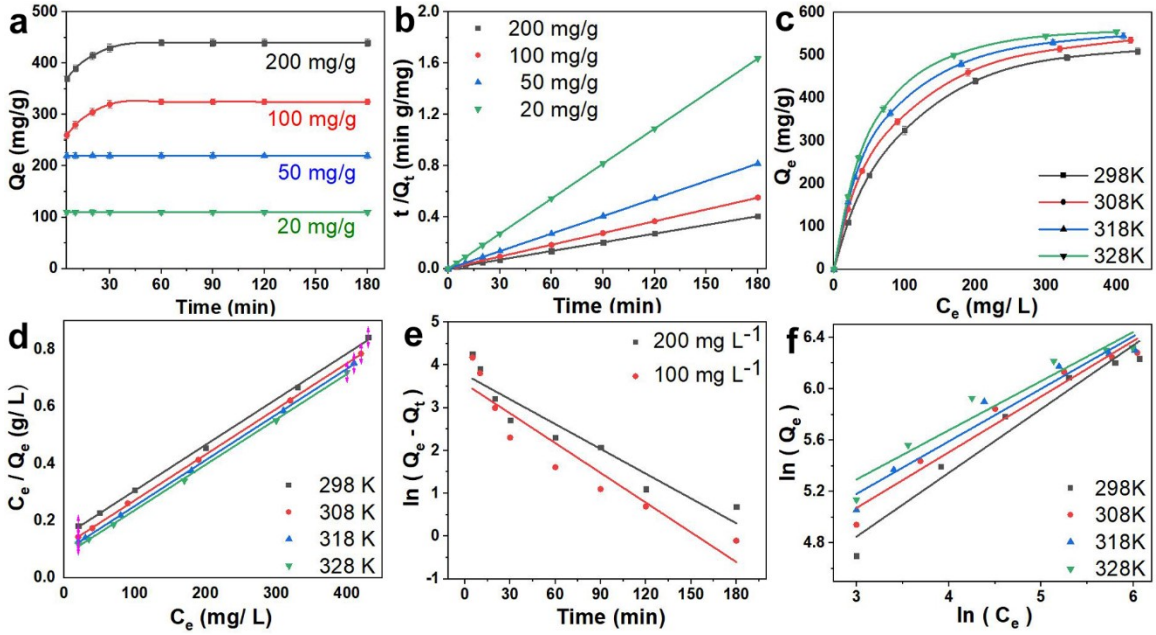

Fig. S3. (a) Time-dependent adsorption of TCP, and (b) the plots of pseudo-second-order kinetics for the adsorption of TCP at different initial concentrations on TTMON at 25°C. (c) Adsorption isotherms, and (d) their corresponding Langmuir plots for the adsorption of TCP on TTMON at the temperature range 25−55°C. (e) Pseudo-first-order kinetics for TCP adsorption on TTMON, and (f) Freundlich curves for TCP adsorption on TTMON.

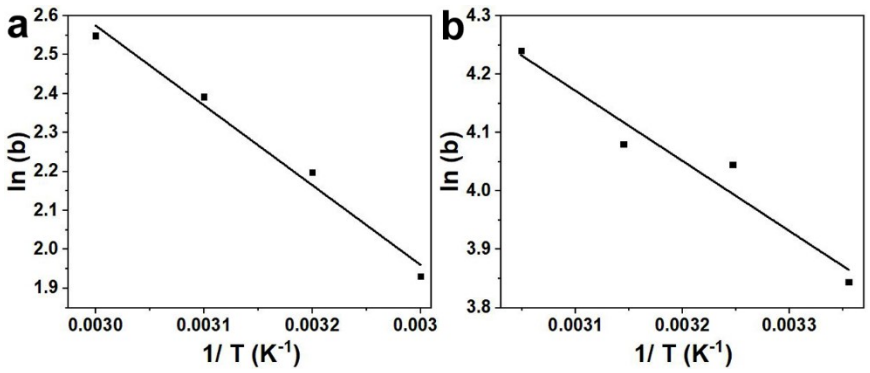

Fig. S4. Van't Hoff plot for TCP adsorption on (a) TDMON, and (b) TTMON

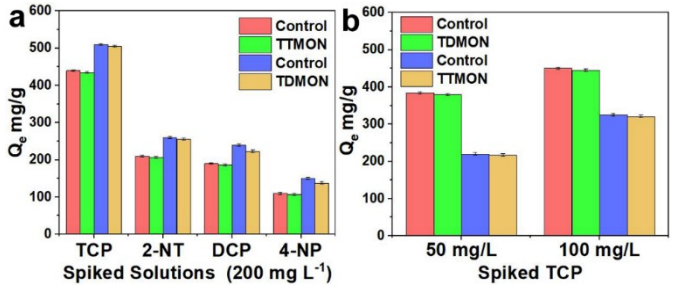

Fig. S5. (a) The adsorption equilibrium for spiked (200 mg L-1) analytes TCP, 2-NT, DCP, and 4-NP in yellow river water using TTMON and TDMON, (b) the adsorption equilibrium for spiked TCP in real water samples using TTMON and TDMON

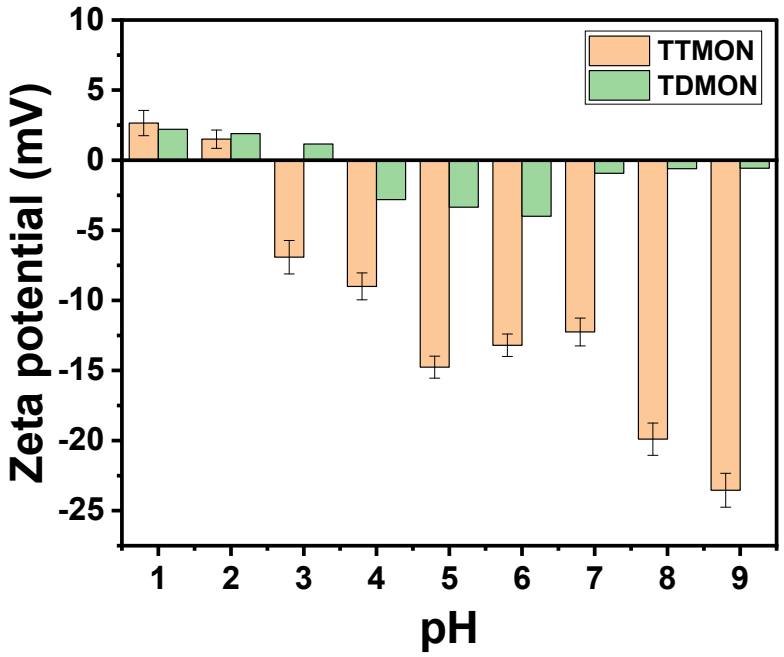

Fig. S6. Zeta potential of TTMON and TDMON

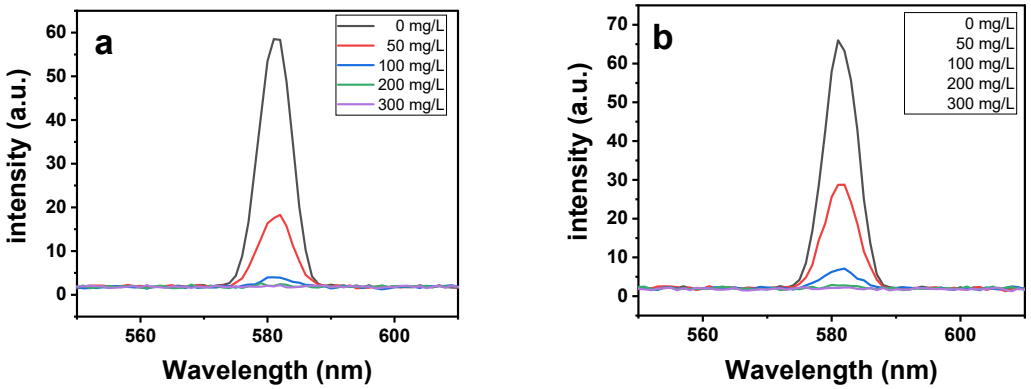

Fig. S7. Fluorescence spectra of MONs after addition of different amount of TCP.

a for TTMON and b for TDMON.

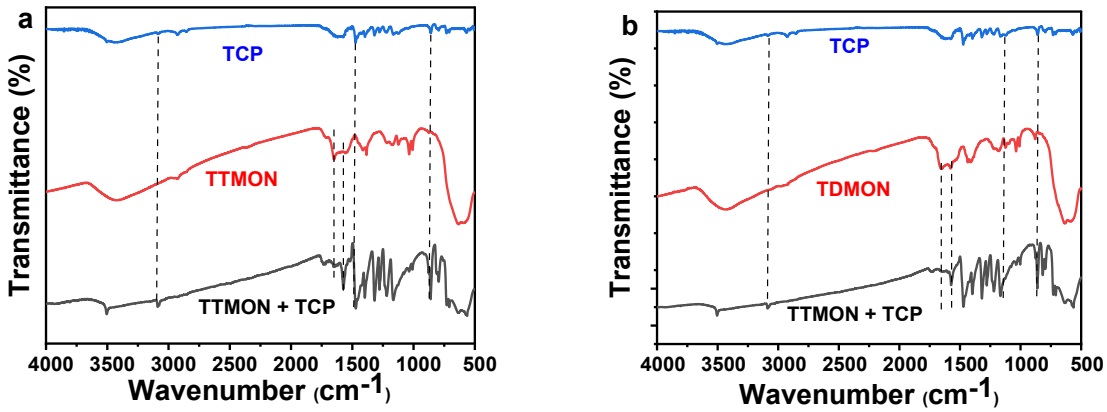

Fig. S8. FT-IR spectra of TTMON, TDMON and TCP

Table S1. Pseudo-second-order kinetic parameters for the adsorption of TCP on MONs

C_0 (mg L^{-1})	$q_{e,\,exp}$ (mg g^{-1})	$q_{e,\,cal}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2
pseudo-second-order kinetic model for TTMON				
20	110	110	-	0.999
50	220	220	-	0.999
100	325	327.2	2.46 x 10-^{3}	0.999
200	440	442.3	2.40 x 10^{-3}	0.999
pseudo-second-order kinetic model for TDMON				
20	283	283	-	0.999
50	384	384	-	0.999
100	450	451.9	2.89 x 10^{-3}	0.999
200	510	513.8	1.46 x 10^{-3}	0.999

Table S2. Pseudo-first-order kinetic parameters for the adsorption of TCP on MONs

pseudo-first-order kinetic model for TTMON				
C_0 (mg L^{-1})	$q_{e,\ exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2
20	-	-	-	-
50	-	-	-	-
100	325	43.2	2.6×10^{-6}	0.9
200	440	51.8	1.6×10^{-6}	0.88
pseudo-first-order kinetic model for TDMON				
20	-	-	-	-
50	-	-	-	-
100	450	57.8	1.8×10^{-6}	0.9
200	510	47.6	1.1×10^{-6}	0.95

Table S3. The Langmuir and thermodynamic parameters for the adsorption of TCP on MONs

The adsorption of TCP on TTMON						
Langmuir parameters				Thermodynamic parameters		
T(°C)	R^2	q_0 (mg g^{-1})	b (L mol^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
25	0.999	510	6.90	-1.63	17.04	72.49
35	0.999	535	9.01	-2.02	-	-
45	0.999	545	10.94	-2.31	-	-
55	0.999	555	12.80	-2.55	-	-
The adsorption of TCP on TDMON						
25	0.999	520	46.7	-9.5	9.95	65.54
35	0.999	530	57.1	-10.4	-	-
45	0.999	570	59.2	-10.8	-	-

55	0.999	605	69.4	-11.6	-	-

Table S4. Freundlich parameters for the adsorption of TCP on both MONs

The adsorption of TCP on TTMON			
Temperature	**Freundlich parameters**		
T (K)	**K_F (mg g^{-1})(L mg^{-1})$^{1/n}$**	**n**	**R^2**
298	28.7	2.02	0.931
308	43.4	2.31	0.953
318	51.9	2.45	0.961
328	62.8	2.62	0.956
The adsorption of TCP on TDMON			
298	179.5	5.35	0.873
308	208.5	6.06	0.874
318	225.9	6.13	0.915
328	284.3	7.58	0.901

Table S5. Adsorption of different organic pollutants from aqueous solution using TDMON and TTMON

Sr. No.	**Organic Pollutant**	**Adsorption Qe (mg/g)**	
		TDMON	**TTMON**
1	Benzene	120	114
2	2-Chlorophenol	80	90
3	3-Chlorophenol	70	60
4	4-Chlorophenol	60	30
5	2-Nitrophenol	100	90
6	3-Nitrophenol	70	60

N.A = No Adsorption