Supporting information

Adsorption Behaviors of Organic Micropollutants on Zirconium Metal-Organic Framework UiO-66: Analysis of Surface Interactions

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Section S1.

Langmuir model

To our knowledge, the Langmuir isotherm is more suitable for monolayer uniform adsorption, while Freundlich isotherm is used for heterogeneous surface of adsorption. Many of the removal process of pollutants from water can be illustrated by Langmuir adsorption isotherm[1], and the equation is given as shown below:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L \times Q_m} \quad (1)$$

Where Q_m（mg/g）is the theoretical maximum adsorption capacity, K_L is Langmuir constants that are related to the affinity between the adsorbent and the adsorbate. Both Q_m and b can be calculated from the slope and intercept of C_e/Q_e for a simple line graph of Ce, respectively. C_e and Q_e are the equilibrium concentrations and equilibrium adsorption capacities.

Freundlich model

The Freundlich equation [2-4] indicated below:

$$\ln q_e = lnK_f + \frac{1}{n} lnC_e \quad (2)$$

Where q_e (mg/g) is equilibrium adsorption capacity. K_f is the Freundlich constant; 1/n is the adsorption index. K_f is a parameter related to the adsorption capacity of the adsorbent, and n is a parameter related to the effect of the adsorbent on the surface of the adsorbent. The values of K_f and 1/n can be obtained from the slope and intercept of the Freundlich equation.

Section S2.

Pseudo-first-order and pseudo-second-order kinetics models

In order to better understand the situation of adsorption kinetic experiments. The data of adsorption were fitted using the pseudo first order and second order rate models. The pseudo first order and second order rate laws are showed as the following equation respectively:

The adsorption pseudo-first order kinetic model was calculated by Lagergren equation [5]:

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \quad (3)$$

We can obtain the Equation (4) by the integration of Equation (3) from t = 0 to t> 0 (q = 0 to q> 0):

$$\ln\left(q_{e,exp} - q_t\right) = lnQ_{e,cal} - k_1 t \quad (4)$$

Where $q_{e,exp}$ (mg g^{-1}) is the maximum amount of our experiment, $Q_{e,cal}$ and k_1 (min^{-1}) are the theoretical equilibrium adsorption capacity and the first-order adsorption rate constants respectively, which can gain by the intercept and slope of $\ln(q_{e,exp}-q_t)$ for a linear graph of t, respectively. q_t (mg g^{-1}) is the amount of adsorption when time is t (min).

The adsorption pseudo-second order kinetic model can be described by the McKay equation[6]. The second order kinetic equation is based on the rate control step that is a chemical reaction or chemical adsorption through electron sharing or electron gain or loss:

$$\frac{dQ_t}{d_t} = k_2(q_e - q_t)^2 \quad (5)$$

We can obtain the Equation (6) by the integration of Equation (5) from t = 0 to t> 0 (q = 0 to q> 0):

$$\frac{t}{q_t} = \frac{1}{k_2 Q_{e,cal}{}^2} + \frac{1}{Q_{e,cal}} t \quad (6)$$

Where $Q_{e,cal}$ and k_2 [g (mg·min) $^{-1}$] are theoretical equilibrium adsorption capacity and the pseudo second order kinetic constant, respectively, which can be acquired by the intercept and slope of t/q_t for a simple line graph of t, respectively. q_t (mg/g) is the amount of adsorption when time is t,

Section S3.

Thermodynamic studies.

Thermodynamic parameters of the adsorption of CBZ and TC on UiO-66 just like free energy change (ΔGº), enthalpy change (ΔHº) and entropy (ΔSº) were calculated using the Eq. (8) [7]and van't Hoff (Eq. (9))[8]:

$$\Delta G° = -RT\ln K_p \quad (8)$$

$$\ln K_p = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (9)$$

Where K_p is thermodynamic equilibrium constant calculated by plotting ln(Qe/Ce) vs Qe and extrapolating to zero Qe. Qe is the adsorption capacity of the origin contaminants on UiO-66 (mmol/g) and Ce is the equilibrium concentration targeted contaminants. A plot of ln K_p as a function of 1/T yielded a straight line (Figure S1).

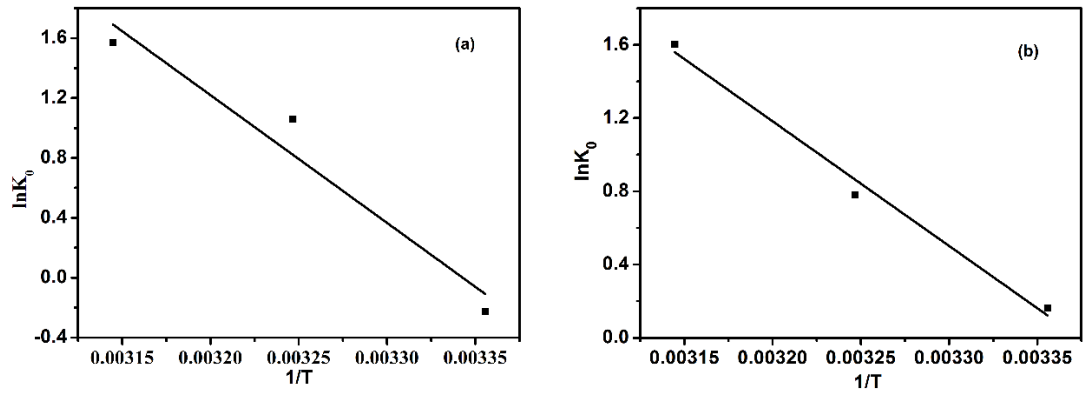

Figure S1. van't Hoff plot for the adsorption of CBZ (a) and TC (b) by UiO-66.

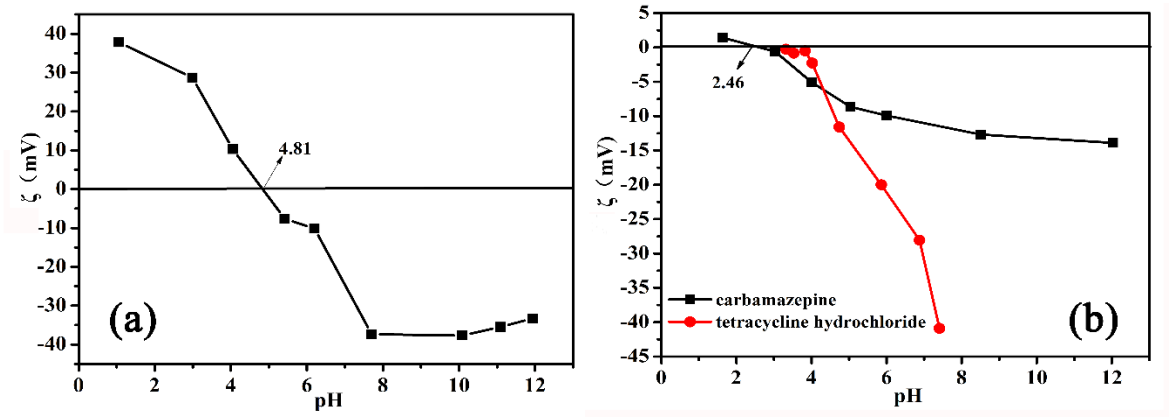

Figure S2. (a) The zeta potential of UiO-66 (b) The zeta potential of CBZ and TC.

Table S1. Thermodynamic parameters for the adsorption CBZ and TC by UiO-66.

	Temperature(℃)	ΔG°(kJ/mol)	ΔH°(kJ/mol)	ΔS°(J/(mol·K))
CBZ	25℃	0.56	70.9	0.24
	35℃	-2.71		
	45℃	-4.15		
TC	25℃	-0.40	56.6	0.19
	35℃	-2.00		
	45℃	-4.24		

Table S2. The intensity ratios of main diffraction peaks for UiO-66 before and after CBZ and TC adsorption

	$I_{(200)}/I_{(111)}$	$I_{(222)}/I_{(111)}$	$I_{(400)}/I_{(111)}$	$I_{(442)}/I_{(111)}$	$I_{(711)}/I_{(111)}$
UiO-66	0.400	0.037	0.121	0.250	0.136
UiO-66 after adsorption of CBZ	0.267	0.049	0.061	0.124	0.064
UiO-66 after adsorption of TC	0.179	0.042	0.054	0.108	0.079

Table S3. Atomic ratio of UiO-66 and after adsorption of CBZ and TC.

	Zr 3d (%)	O 1s (%)	C 1s (%)	N 1s (%)
UiO-66	6.39	25.93	67.02	0.66
UiO-66 after adsorption of CBZ	3.88	23.36	72.32	0.45
UiO-66 after adsorption of TC	4.27	23.60	71.15	0.98

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