The synergetic effect of structure-engineered mesoporous SiO_2-ZnO composite for doxycycline adsorption

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1. Preparation of mesoporous SiO_2

6 g CTAB and 0.18 g TEA dissolved in 60 g H_2O at 60 °C for 1 h and simultaneously stirred at 150 rpm using a heater/magnetic stirrer. After that, a mixed solution of 16 mL of cyclohexane and 4.2 g of TEOS was added to the above solution and stirred at 60 °C for 15 h. The resulting solution was transferred into a Teflon-lined stainless-steel autoclave, which was sealed and heated at 100 °C for 10 h and naturally cooled to room temperature. The white particles were collected and washed with ethanol and deionized water, and dried under vacuum at 60 °C for 8 h. Finally, to remove PVP and obtain the adsorbent mesoporous SiO_2, the as-prepared powder was calcined at 550 °C for 6 h with a heating rate of 5 °C min^{-1}.

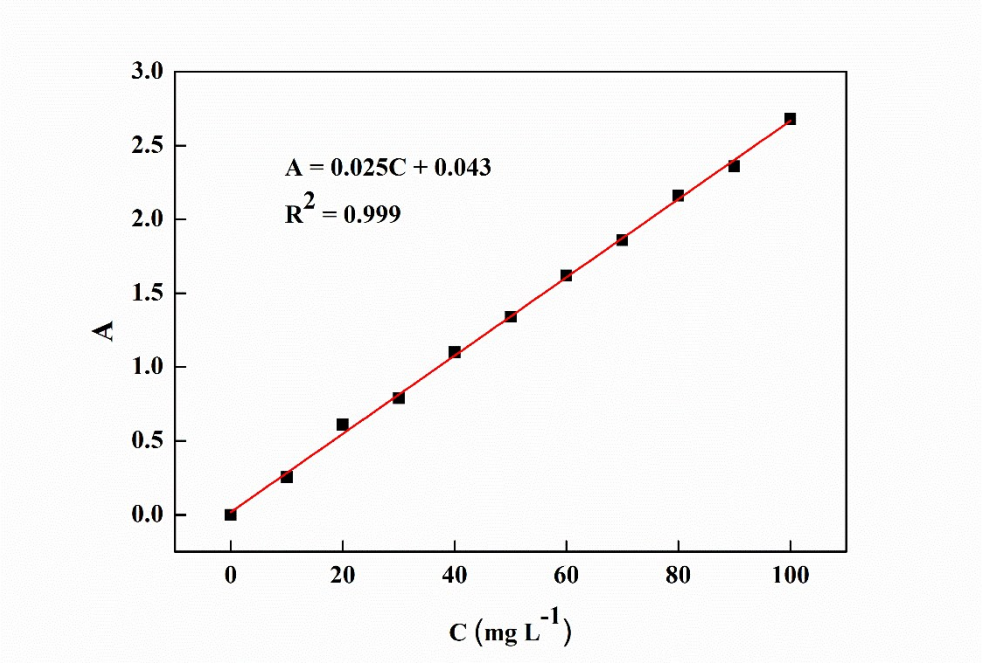

Fig. S1 Standard curve of DOX.

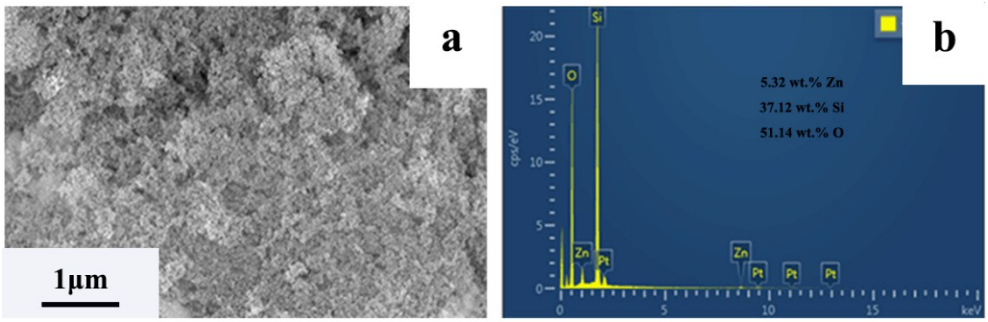

Fig. S2 SEM image (a) and EDS spectra (b) of mesoporous SiO_2-ZnO.

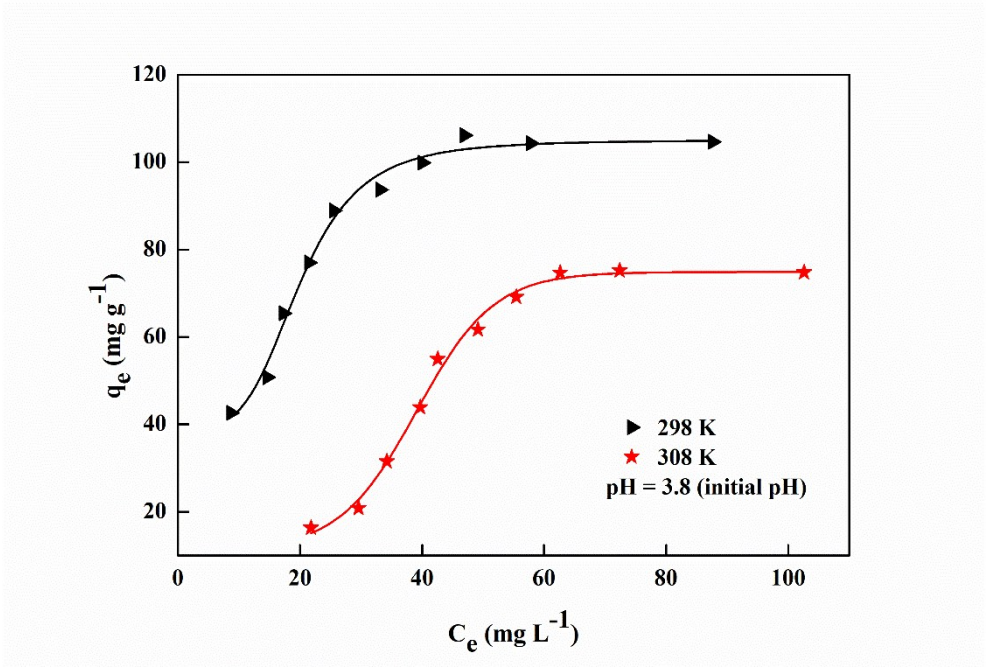

Fig. S3 DOX sorption isotherms with mesoporous SiO_2-ZnO at two different temperatures.

($m_{sorbent}$ = 10 mg, V = 20 mL, $C_{0(DOX)}$ = 10-100 mg L^{-1}, t = 24 h)

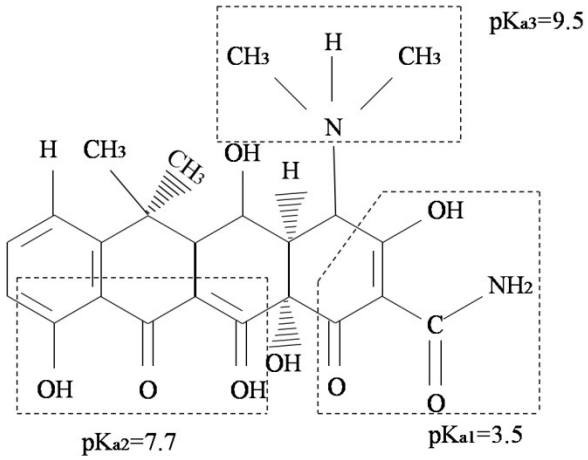

Fig. S4 Molecular structure and physicochemical properties of DOX.

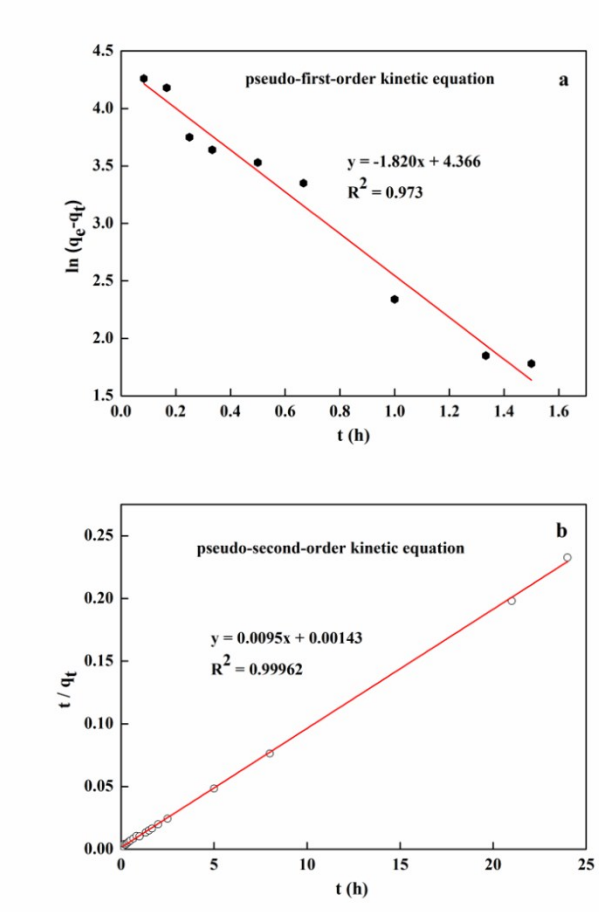

Fig. S5 Fitting results of pseudo-first-order (a) and pseudo-second-order (b) models for DOX sorption on mesoporous SiO_2-ZnO.

($m_{sorbent}$ = 100 mg， $V_{(DOX)}$ = 200 mL, $C_{0(DOX)}$ = 100 mg L^{-1}, T = 298 K, initial pH)

Table S1 Capacities of doxycycline hydrochloride onto various adsorbents.

Adsorbents	Adsorption conditions	Qe (mg g^{-1})	References
GO-MP 298K	initial pH	35.3	[53]
MIP-HCM	298K,	58.2	[54]
SBC@β-FeOOH	298K, pH=2	15.1	[55]
RH700	318K, pH=6	85.2	[56]

The Langmuir, Freundlich, Temkin and D-R isotherm equations are shown below:

Langmuir models:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

Freundlich models:

$$q_e = K_F C_e^{1/n} \quad (2)$$

Temkin model:

$$q_e = B \ln A_T + B \ln C_e \quad (3)$$

Dubinin-Radushkevich models:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (4)$$

$$\varepsilon = RT\ln\left(1 + {}^{1}\!/_{C_e}\right) \quad (5)$$

$$E = (2\beta)^{-{}^{1}\!/_{2}} \quad (6)$$

Where q_m (mg g^{-1}) is the maximum adsorption capacity, n is a dimensionless number related to surface heterogeneity, K_F (mg^{1-n} L^n g^{-1}) is Freundlich affinity

coefficient and K_L (L mg^{-1}) is the Langmuir fitting parameter, β is a constant related to sorption energy; ε is Polanyi sorption potential, related to the sorption energy E required to move one molecule of solute from infinity to the surface of adsorbents. R is the ideals gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K).

Model evaluation parameters

Coefficient of determination: R^2 (COD)

Degree-of-freedom adjusted coefficient of determination: Adj. R^2

Sum of squared residuals:

$$SSE = \sum_{i=1}^{n} (y_{experiment} - y_{fitting})^2 \quad (7)$$

Root mean squared error:

$$Root - MSE = \sqrt{\frac{SSE}{n}} = \sqrt{\frac{1}{n}\sum_{i=1}^{n} (y_{experiment} - y_{fitting})^2} \quad (8)$$

The pseudo-first-order kinetic, pseudo-second-order kinetic, intra-particle diffusion and liquid-film diffusion equations are shown below:

The pseudo-first-order kinetic model:

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (9)$$

The pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

The intra-particle diffusion model:

$$q_e = k_d t^{\frac{1}{2}} + C \quad (11)$$

The liquid-film diffusion model:

$$\ln\left(1-\frac{q_t}{q_e}\right) = -k_f t + A \tag{12}$$

Where t is the adsorption time (h), q_e and q_t (mg g^{-1}) are the absorption capacity at equilibrium and time t. k_1 (h^{-1}), k_2 (g mg^{-1} h^{-1}), k_d (g mg^{-1} $h^{-0.5}$) and k_f (h^{-1}) are adsorption rate constant of the pseudo-first-order kinetic, pseudo-second-order kinetic, intraparticle diffusion and liquid-film diffusion models, respectively. C is the thickness of boundary layer and A is liquid-film diffusion constant.