

Supporting Information

Oleic acid tailored geopolymer microspheres with tunable porous structure for enhanced removal of tetracycline in saline wastewater

Xiaoyun Wang, Zheng Zhang, Yuanyuan Ge*

School of Chemistry & Chemical Engineering, Guangxi Key Lab of Petrochemical Resource Processing and Process Intensification Technology, Guangxi University,

Nanning 530004, China

*Corresponding author: geyy@gxu.edu.cn

1. Experimental Procedure

The equations of the pseudo-first-order, the pseudo-second-order, and intra-particle diffusion model were presented as follows:

The pseudo-first-order dynamics model:

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

The pseudo-second-order dynamics model:

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

Intra-particle diffusion model:

$$Q_t = k_i t^{1/2} + C \quad (\text{S3})$$

Where, Q_e and Q_t ($\text{mg} \cdot \text{g}^{-1}$) are respectively the adsorption capacity of MM on TC at adsorption equilibrium and at contact time t (min), respectively; k_1 (min^{-1}) and k_2

$(g \cdot (mg \cdot min)^{-1})$ are the rate constants; $k_i (mg \cdot (g \cdot min^{1/2})^{-1})$ is the diffusion rate constant in particles. C is a constant related to the thickness of the reaction boundary layer.

The parameters in the dynamic adsorption process are calculated by the following formulas.

$$m_{ad,t} = m_{in,t} - m_{out,t} \quad (S4)$$

$$m_{in,t} = c_0 q t \quad (S5)$$

$$m_{out,t} = c_0 q \int_0^t \left(\frac{c_t}{c_0} \right) dt \quad (S6)$$

$$Q_f = \frac{m_{ad,t}}{m} = \frac{c_0 q \int_0^t \left(1 - \frac{c_t}{c_0} \right) dt}{m} \quad (S7)$$

$$Y = \frac{m_{ad,t}}{m_{in,t}} \times 100\% \quad (S8)$$

Where, $m_{in,t}$ is the total content of TC flowing into the fixed bed at time t , $mg \cdot g^{-1}$; $m_{out,t}$ is the total TC content flowing out of the fixed bed at time t , $mg \cdot g^{-1}$; c_0 is the TC concentration flowing into the fixed bed, $mg \cdot L^{-1}$; c_t is the TC concentration flowing out of the fixed bed, $mg \cdot L^{-1}$; q is the flow rate of TC solution in the fixed bed, $L \cdot h^{-1}$; t is the contact time between TC solution and the fixed bed, h ; t_b is breakthrough time when $c_t/c_0 = 0.1$, min ; t_s is saturation time when $c_t/c_0 = 0.9$, min ; Q_f is adsorption capacity, $mg \cdot g^{-1}$; m is the quality of adsorbent in fixed bed, g ; Y is adsorption rate that is the ratio of the total amount of TC absorbed by the adsorbent to the total amount of TC flowing into the fixed bed.

Langmuir and Freundlich isotherm models were expressed as follows.

Langmuir isotherm model:

$$\frac{c_e}{Q_e} = \frac{1}{Q_m K_l} + \frac{c_e}{Q_m} \quad (S9)$$

Freundlich isotherm model:

$$\ln Q_m = \ln K_F + \frac{1}{n} \ln c_e \quad (S10)$$

Where c_e ($\text{mg}\cdot\text{L}^{-1}$) is the concentration of TC at adsorption equilibrium; K_L ($\text{L}\cdot\text{mg}^{-1}$) is Langmuir constant; Q_m ($\text{mg}\cdot\text{g}^{-1}$) is the theoretical maximum adsorption capacity of MM3; K_F ($(\text{mg}\cdot\text{g}^{-1})(\text{L}\cdot\text{mg}^{-1})^{-1/n}$) is Freundlich constant; n is the constant of adsorption strength. It is generally believed that it is easy to adsorb when n is greater than 2.

The thermodynamic parameters were obtained by the following formulas.

$$\Delta G = \Delta H - T\Delta S \quad (\text{S11})$$

$$\ln K_e = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (\text{S12})$$

$$K_e = \frac{(1000 \cdot K_L \cdot \text{molecular weight of adsorbate}) \cdot [\text{Adsorbate}]}{\gamma} \quad (\text{S13})$$

Where ΔG ($\text{KJ}\cdot\text{mol}^{-1}$) is Gibbs free energy of adsorption; ΔH ($\text{KJ}\cdot\text{mol}^{-1}$) is the enthalpy change; T (K) is the absolute temperature; ΔS ($\text{J}\cdot(\text{mol}\cdot\text{K})^{-1}$) is entropy change; R ($8.314 \text{ J}\cdot(\text{mol}\cdot\text{K})^{-1}$) is the ideal gas constant; K_e is the thermodynamic equilibrium constant; K_L is the Langmuir equilibrium constant; γ is the coefficient of activity.

2. Results

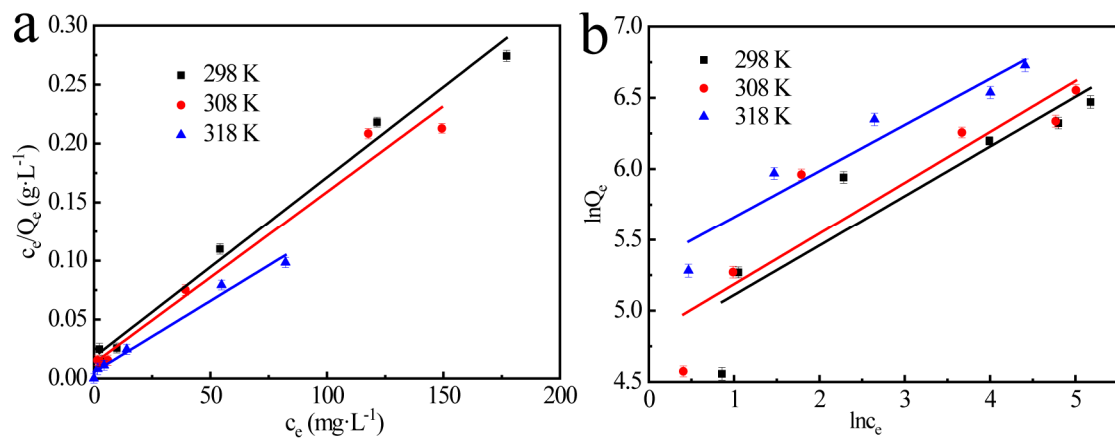


Figure S1. (a) Langmuir and (b) Freundlich adsorption isotherms ($m_{\text{MM3}}=0.01 \text{ g}$; $\text{pH}=4$;

$V = 20 \text{ ml}$; $t=12 \text{ h}$).

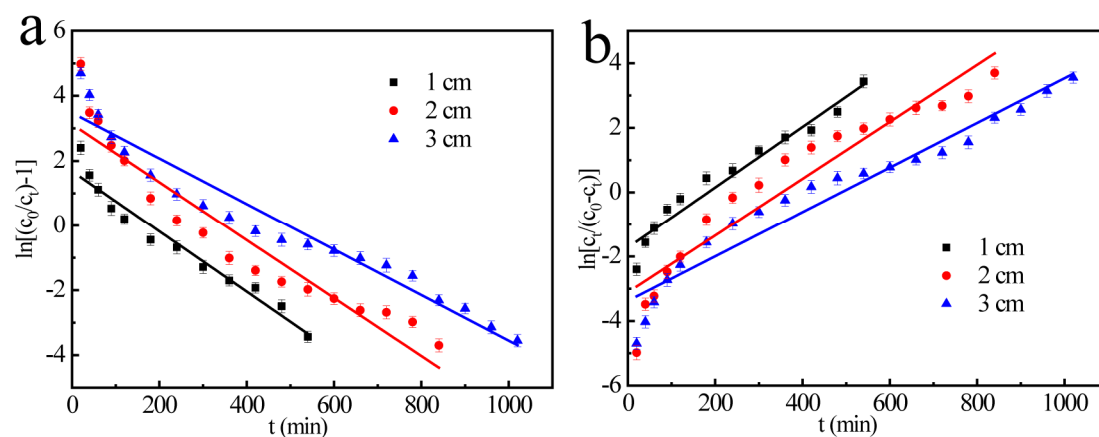


Figure S2. Linear plots of (a) Thomas and (b) Yoon-Nelson model.

Table S1. Porosity parameters of MM with different dosage of oleic acid.

Adsorbent	BET specific	Total pore	Average
	surface area $\text{m}^2 \cdot \text{g}^{-1}$	volume	pore size
	1	$\text{cm}^3 \cdot \text{g}^{-1}$	nm
MM0	24.23	0.09	14.42
MM1	24.62	0.10	16.32
MM2	39.42	0.17	15.47
MM3	40.09	0.15	14.39
MM4	30.11	0.15	18.80
MM5	25.88	0.14	21.61

Table S2. The element composition in XPS.

Name	Atomic%	
	MM3	TC@MM3
Al 2p	6.09	4.76
Si 2p	15.13	14.37
O 1s	42.78	39.03
C 1s	33.37	38.16