

Electronic Supplementary Information

for

Ultrafast synthesis of magnetic hollow carbon nanospheres for the adsorption of quinoline from coking wastewater

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Supplementary equations.

The adsorption capacity q_t (mg g⁻¹) and q_e (mg g⁻¹) were determined, the equations are as follows:

$$q_t = V(C_0 - C_t)/m \quad (S-1)$$

$$q_e = V(C_0 - C_e)/m \quad (S-2)$$

where C_0 (mg L⁻¹), C_t (mg L⁻¹) and C_e (mg L⁻¹) are the concentrations of Q solution at time 0, time t and equilibrium, respectively. V (L) represents the volume of Q solution; m (g) is the weight of adsorbent.

Kinetic models :

The pseudo-first-order kinetic model (Eq. (S3)) and pseudo-second-order kinetic model (Eq. (S4)) can be described by the following equations:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (S-3)$$

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (S-4)$$

where q_t (mg g⁻¹) and q_e (mg g⁻¹) are the amounts of quinoline adsorbed on MHCNSs at time t (min) and at equilibrium, respectively. k_1 (min⁻¹) represents the pseudo-first-order kinetic rate constant; k_2 (g mg⁻¹ min⁻¹) represents the pseudo-second-order kinetic rate constant.

Isotherm models :

The Langmuir model (Eq. (S5)), Freundlich model (Eq. (S6)) and Langmuir–Freundlich model (Eq. (S7)) can be described by the following equations:

$$C_e/q_e = C_e/q_m + 1/(q_m K_L) \quad (S-5)$$

$$\ln q_e = \ln C_e/n + \ln K_F \quad (S-6)$$

$$q_e/q_m = (K_{L-F}C_e)^n / (1 + (K_{L-F}C_e)^n) \quad (S-7)$$

where C_e (mg L^{-1}) represents the equilibrium concentration of quinoline in solution. q_e (mg g^{-1}) represents the adsorption capacity of quinoline on MHCNSs at equilibrium. q_m (mg g^{-1}) is the maximum adsorption capacity. K_L is Langmuir constant; K_F is Freundlich constant; K_{L-F} is Langmuir–Freundlich constant. n represents the empirical constant.

Thermodynamic parameters :

The thermodynamic parameters including standard enthalpy ΔH^θ , standard entropy ΔS^θ and standard Gibbs free energy ΔG^θ are acquired by the following equations:

$$\Delta G^\theta = -RT \ln K_c \quad (S-8)$$

$$\ln K_c = \Delta S^\theta / R - \Delta H^\theta / (RT) \quad (S-9)$$

where K_c is the thermodynamic equilibrium constant, obtained by Langmuir equation. T (K) and R ($\text{J mol}^{-1} \text{K}^{-1}$) represent the absolute temperature and ideal gas constant, respectively. ΔH^θ and ΔS^θ can be achieved from the linear plots of $\ln K_c$ versus $1/T$.

Supplementary figures.

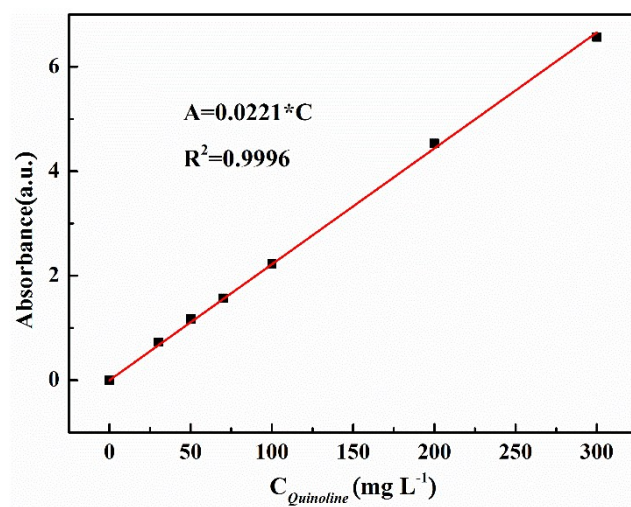


Figure S1. Standard curve of quinoline in water.



Figure S2. Photograph of coking wastewater after biological pretreatment.

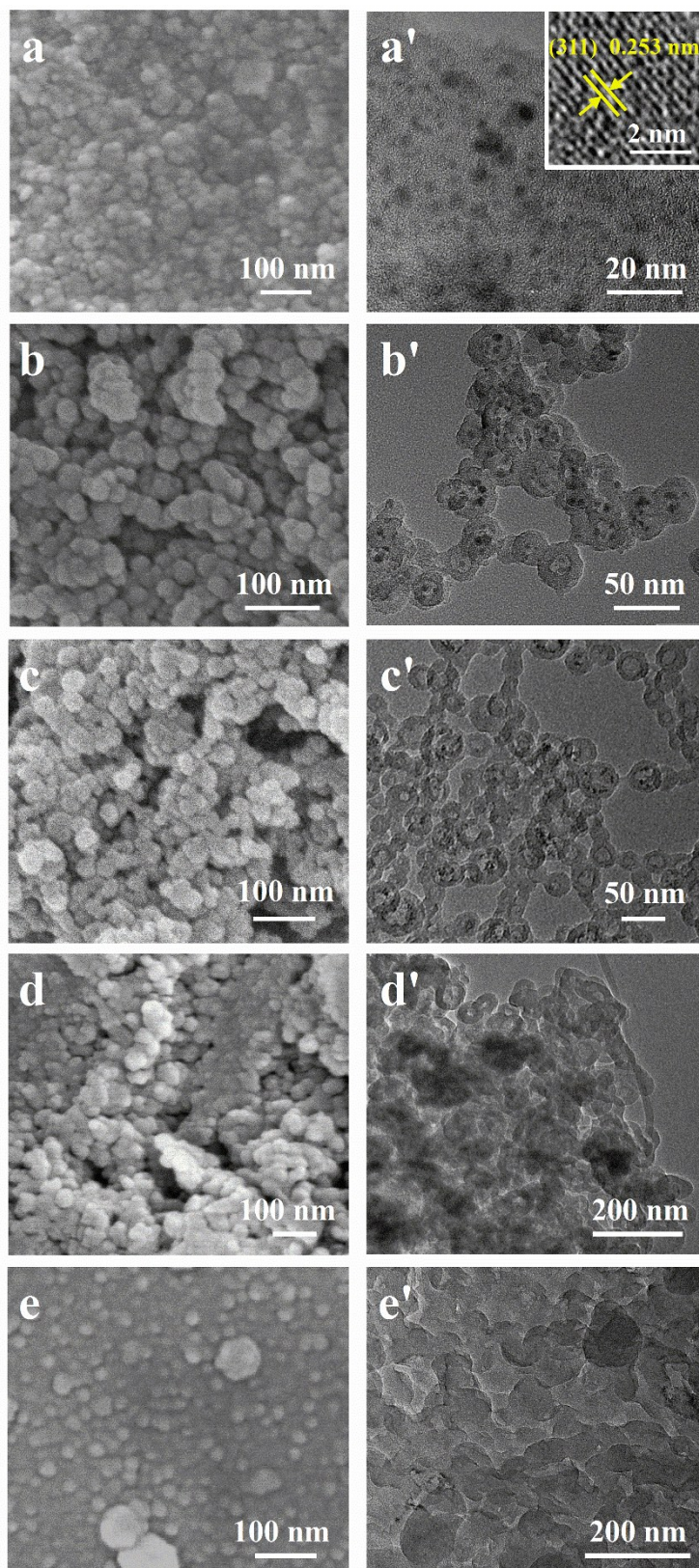


Figure S3. (a–e) FESEM images and (a'–e') TEM images of CNSs with different reaction conditions: (a, a') CNSs-1, (b, b') CNSs-2, (c, c') CNSs-3, (d, d') CNSs-4 and (e, e') CNSs-5.

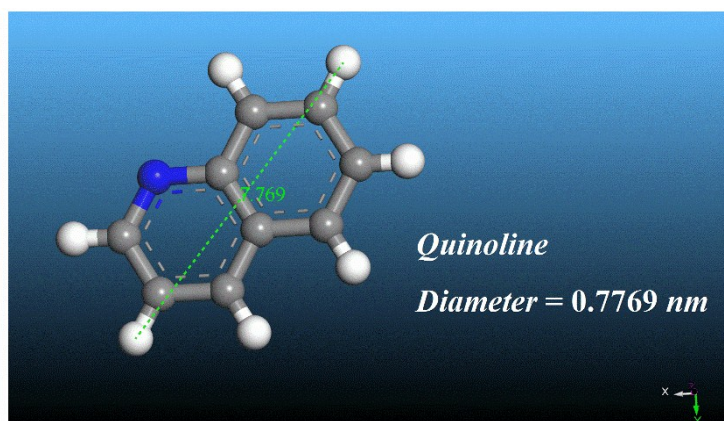


Figure S4. Molecular diameter of quinoline.

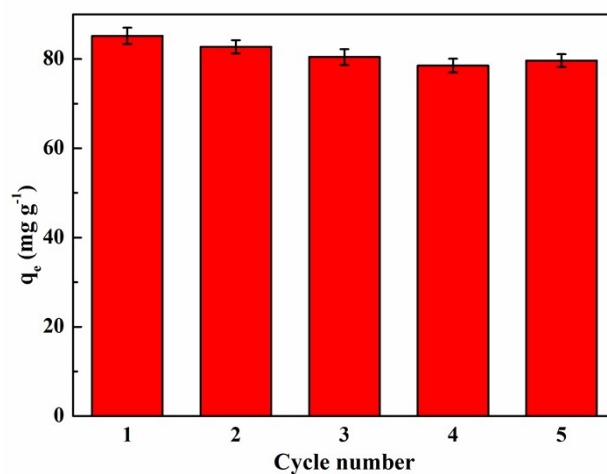


Figure S5. Regeneration tests of MHCNSs.

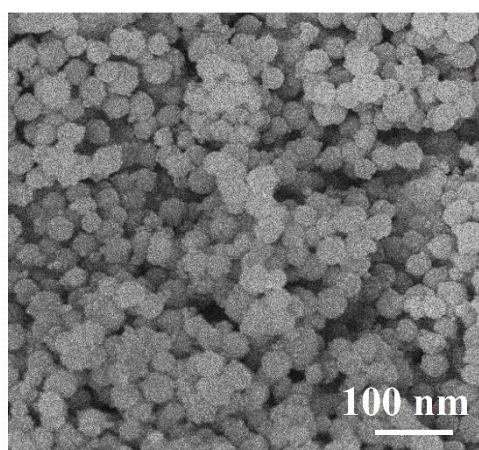


Figure S6. FESEM image of the regenerated MHCNSs.

Supplementary tables.

Table S1. Textural properties of MHCNSs.

Adsorbent	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{micro} ($\text{m}^2 \text{g}^{-1}$)	S_{meso} ($\text{m}^2 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	D_p (nm)
MHCNSs	386.26	309.60	76.66	0.53	0.16	1.61

Table S2. Kinetic parameters on quinoline adsorption.

T (K)	Pseudo-first-order				Pseudo-second-order		
	$q_{\text{e,exp}}$ (mg g^{-1})	$q_{\text{e,cal}}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{\text{e,cal}}$ (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
288	94.48	90.30	0.2375	0.9568	96.78	0.0041	0.9913
MHCNSs 298	85.19	80.49	0.2522	0.9704	86.95	0.0046	0.9926
308	78.21	74.01	0.1735	0.9510	80.24	0.0034	0.9924

Table S3. Comparison of different adsorbents for quinoline removal from water.

Adsorbent	Adsorbent synthesis time	Adsorption capacity (mg g^{-1})	Equilibrium time (min)	Reference
Granular activated carbon	–	160.03	500	[14]
Bagasse fly ash	–	31.18	500	[14]
Bamboo charcoal	5–8 d	32.50	1440	[15]
Magnetic carbon nanospheres	24 h	99.43	115	[49]
Modified agricultural waste	1 h	35.03	180	[56]
MHCNSs	80 s	155.23	65	This work

Table S4. Isotherm parameters on quinoline adsorption.

	T (K)	Langmuir			Freundlich			Langmuir–Freundlich			
		q_m	K_L	R^2	n	K_F	R^2	q_m	K_{L-F}	n	R^2
		(mg g ⁻¹)						(mg g ⁻¹)			
	288	145.46	0.87	0.9523	8.26	83.12	0.8274	153.43	0.87	0.70	0.9812
MHCNSs	298	151.50	0.17	0.9946	5.46	58.99	0.8769	156.76	0.21	0.85	0.9995
	308	155.43	0.08	0.9821	4.26	43.76	0.8376	148.66	0.05	1.23	0.9852

Table S5. Thermodynamic parameters on quinoline adsorption.

	T (K)	ΔG^θ	ΔH^θ	ΔS^θ
		(kJ mol ⁻¹)	(kJ mol ⁻¹)	(J mol ⁻¹ K ⁻¹)
	288	-37.45		
MHCNSs	298	-34.73	-88.08	-176.85
	308	-33.95		

References

1. J. Du, L. Liu, Y.F. Yu, Y. Zhang and A.B. Chen, *Chinese Chemical Letters*, 2019, **30**, 1423–1427.
2. C. Dong, Z.H. Li, L. Zhang, G.H. Li, H.C. Yao, J.S. Wang, Q.C. Liu and Z.J. Li, *Diamond and Related Materials*, 2019, **92**, 32–40.
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