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Supplementary Information

Zeolitic imidazolate framework-8/graphene oxide/magnetic chitosan nanocomposite for efficient removal of Congo red from aqueous solution

Xuefeng Tong, Jingjing Zhang, Qibin Chen*, Honglai Liu

State Key Laboratory of Chemical Engineering and School of Chemistry & Molecular Engineering, East China University of Science and Technology, Shanghai, 200237, P.R. China

*Corresponding author E-mail: qibinchen@ecust.edu.cn

1. Procedure for preparing materials

Graphene oxide/magnetic chitosan (GMCS) was prepared by using a cross-linking method. In brief, 0.9 g chitosan powder (CS) was dissolved in 50 mL acetic acid solution (2%, w/w). Then, 0.5 g Fe_3O_4 and 120 mL graphene oxide (GO) dispersion (2 mg/mL) were added and stirred for 1 h. After that, 0.5 mL glutaraldehyde solution (25 wt%) was added and stirred until the gel was formed. At last, the gel was dried at 70 °C for 16 h and GMCS was obtained after washing and drying.

For comparison, magnetic chitosan (MCS) was also synthesized using the same method without adding GO at the beginning.

ZIF-8-GMCS contains four components: Fe_3O_4, chitosan (CS), graphene oxide (GO) and ZIF-8. Compared with the other three components, ZIF-8 has the highest adsorption capacity toward Congo red (CR). Therefore, the effect of the ratio of ZIF-8 in ZIF-8-GMCS on the adsorption performance was explored. Since the amount of $ZnSO_4 \cdot 7H_2O$ used was directly related to the content of ZIF-8 in ZIF-8-GMCS, four samples were synthesized via varying the amount of $ZnSO_4 \cdot 7H_2O$, while remaining the other conditions the same.

As shown in Figure S1, the increase in the amount of $ZnSO_4 \cdot 7H_2O$ gives rise to the incremental proportion of ZIF-8 in ZIF-8-GMCS, thus yielding the increasing adsorption capacity. However, the adsorption capacity obviously levels off when ZIF-8-GMCS is prepared using a higher amount of $ZnSO_4 \cdot 7H_2O$.

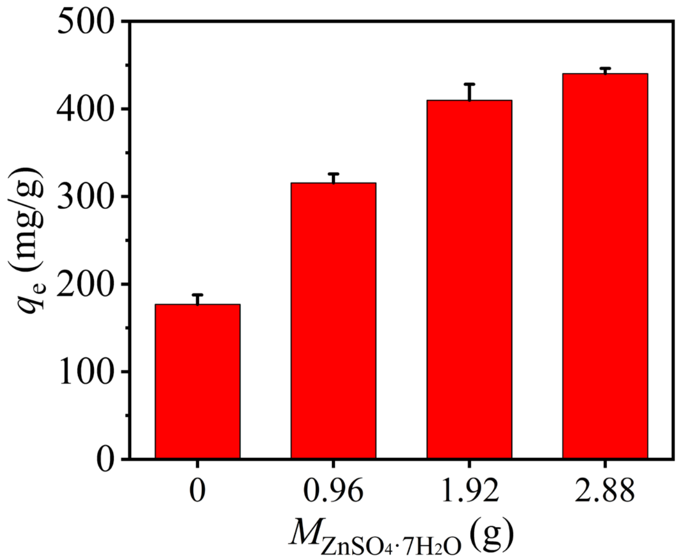

Figure S1. Effect of the mass of $ZnSO_4 \cdot 7H_2O$ employed on the adsorption capacity toward CR: C_{CR} = 200 mg/L, t = 24 h and T = 303.15 K.

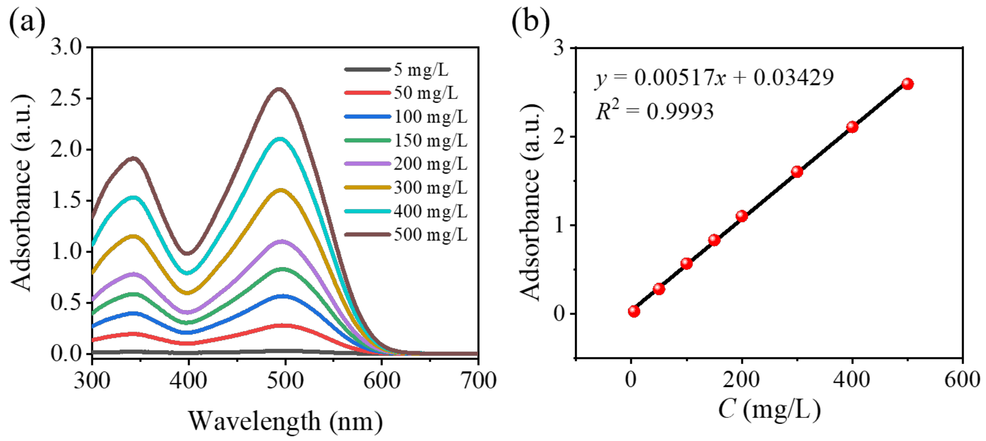

Figure S2. UV-vis spectra of different concentration aqueous solution of Congo red (a); UV-vis standard curve of Congo red solution (b).

In order to explore the effect of other anionic dyes on the adsorption process of Congo red (CR), methyl blue (MB) as the interfering substance. Since MB is also a type of the anionic dye, the competitive adsorption might happen between MB and CR. Therefore, the effect of varying MB concentration, while holding the CR concentration unchanged was examined.

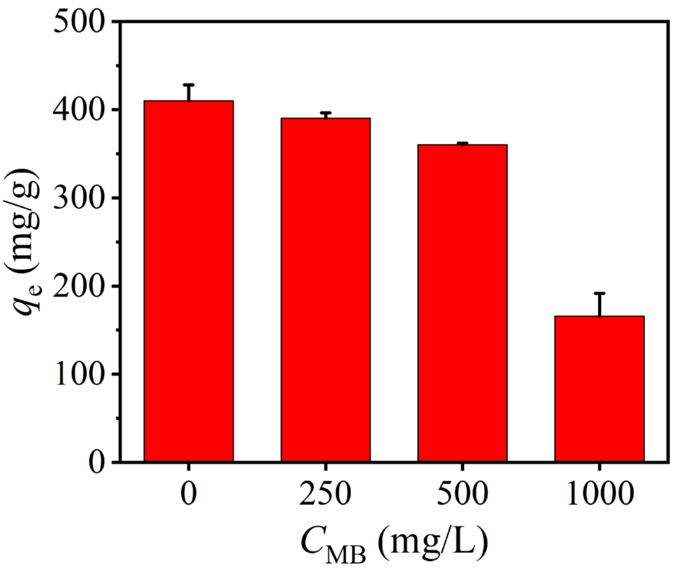

Figure S3. Effect of methyl blue on the adsorption performance, experimental conditions: C_{CR} = 250 mg/L, t = 24 h and T = 303.15 K.

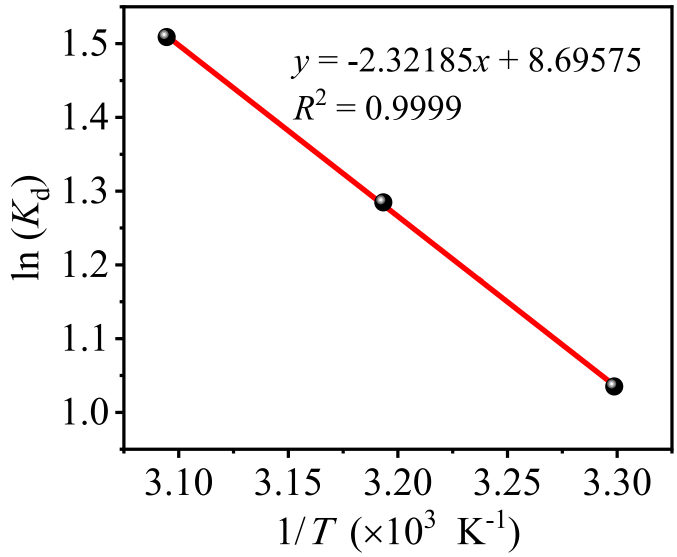

Figure S4. Effect of adsorption temperature on the CR adsorption relationship curve between ln (K_d) and $1/T$.

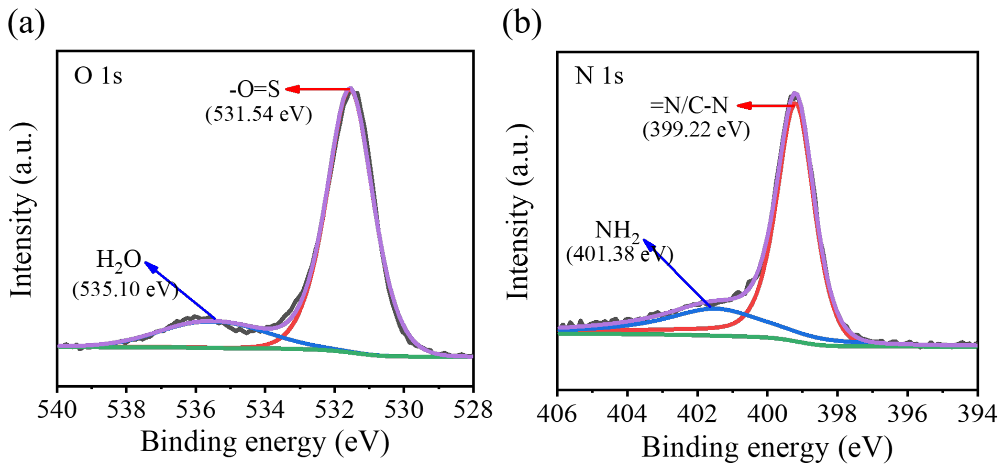

Figure S5. High resolution scans of O 1s (a) and N 1s (b) spectra of Congo red.

Table S1

Kinetic parameters of the adsorption of Congo red with ZIF-8-GMCS.

	pseudo-first-order model			pseudo-second-order model		
T (K)	q_e (mg/g)	k_1 (h^{-1})	R^2	q_e (mg/g)	$k_2 \times 10^3$ ($g \cdot h^{-1} \cdot mg^{-1}$)	R^2
303.15	179.93	0.213	0.9784	301.20	2.06	0.9998
313.15	245.96	0.196	0.9853	381.68	1.24	0.9999
323.15	231.91	0.177	0.9715	400.00	1.39	0.9997

Table S2

The Constants and Correlation Coefficients of Langmuir and Freundlich model.

	Langmuir model			Freundlich model		
T (K)	q_m (mg/g)	K_L (L/mg)	R^2	K_L (L/mg)	n	R^2
303.15	476.19	0.052	0.9963	70.76	2.63	0.9174
313.15	512.82	0.105	0.9978	117.01	3.18	0.8216
323.15	571.43	0.135	0.9970	140.74	3.22	0.7863

Table S3

Comparison of the maximum adsorption capacity for Congo red from the Langmuir model with other adsorbents.

Adsorbents	q_m (mg/g)	Temperature (K)	Ref.
Magnetic chitosan grafted MgO	401.60	303.15	[1]
Metal oxide $Fe_xCo_{3-x}O_4$	160.3	Room temperature	[2]
Amine functionalized magnesium ferrite	71.4	298.15	[3]
Magnetic peanut husk grafted aluminum and iminodiacetic acid	62.5	303.15	[4]
Triethylenetetramine cross-linked magnetic chitosan	583.11	298.15	[5]
Magnetic zeolitic imidazolate framework	210.5	298.15	[6]
Iron oxide nanoparticles	418.41	298.15	[7]
magnetic $CuFe_2O_4$ nanocomposites	434.78	298.15	[8]
Magnetite intercalated bentonite	48.0	298.15	[9]
$ZnFe_2O_4/SiO_2$/Tragacanth gum magnetic nanocomposite	159.90	298.15	[10]
ZIF-8/GO/chitosan/Fe_3O_4 composite	476.19	303.15	This work

Table S4

Thermodynamic parameters of CR adsorption with ZIF-8-GMCS.

T (K)	K_d	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS ($J \cdot K^{-1} \cdot mol^{-1}$)
303.15	2.82	-2.37		
313.15	3.61	-3.18	22.17	80.94
323.15	4.52	-3.99		

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