Supporting Information

One-step construction of magnetic biochar with a hierarchical porous structure and its adsorption properties

Morigen Bao[a], Morigejile[a], Hongye Zhao[a], Siqin Zhao[a,b,c], Sin Asuha[a,b]

[a] *Chemistry & Environmental Science College, Inner Mongolia Normal University, Inner Mongolia, 81 Zhaowudalu, Hohhot,* 010022, China

[b] *Key Laboratory of Physics and Chemistry of Functional Materials, Inner Mongolia, 81 Zhaowudalu, Hohhot,* 010022, China

[c] *Collaborative Innovation Center for Water Environment Security, Inner Mongolia, 81 Zhaowudalu, Hohhot,* 010022, China

*To whom correspondence should be addressed. E-mails: zhaosq@imnu.edu.cn (S. Zhao)

Table S1 D-spacing (Å) of the synthesized samples and those of γ-Fe_2O_3 and Fe_3O_4 from JCPDS files.

Sample	Crystalline plane (hkl)				
	220	311	400	511	440
MBC-20	2.9545	2.5249	2.0930	1.6115	1.4797
γ-Fe_2O_3 [a]	2.9530	2.5177	2.0866	1.6073	1.4758
Fe_3O_4 [b]	2.9670	2.5320	2.0993	1.6158	1.4845

a JCPDS file No. 39–1346.

b JCPDS file No. 19–0629.

Standard working curve of Rhodamine B solution

Rhodamine B solution with different mass concentrations was prepared respectively. The absorbance of Rhodamine B solution was determined by Ultraviolet-visible spectrophotometer at 553 nm wavelength. The standard working curve was drawn by linear regression method, as shown in Fig. S1.

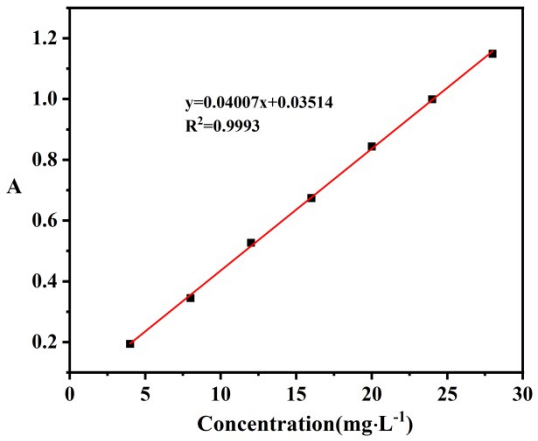

Fig. S1 Standard working curve of Rhodamine B solution

The concentration-absorbance formula obtained from the standard working curve is:

$$y=0.04007x+0.03514 \quad (1)$$

Where, x is the mass concentration of Rhodamine B solution (mg·L^{-1}); y is absorbance; R^2=0.9993, that is, there is a good linear relationship between the mass concentration of Rhodamine B solution and absorbance.

The concentration of Rhodamine B solution after adsorption can be calculated from the above standard working curve. The adsorption quantity q_e (mg·g^{-1}) and adsorption rate η (%) of adsorbent could be calculated according to the following formula:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

$$\eta = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (3)$$

Where, C_0 is the initial mass concentration of Rhodamine B solution (mg·L^{-1}); C_e is the mass concentration of Rhodamine B solution after adsorption (mg·L^{-1}); V is the volume (L) of Rhodamine B solution; m is the amount of magnetic biochar composite material (g).

Adsorption kinetics

The adsorption behavior of hierarchical porous magnetic biochar on Rhodamine B belongs to the solid-liquid adsorption process, and the adsorption kinetics of MBC-20 on Rhodamine B can be analyzed using the quasi first-order kinetic model and quasi second-order kinetic model.[1]

Quasi-first-order dynamic equation:

$$\log(q_e - q_t) = \log(q_{e,1}) - \frac{k_1}{2.303}t \quad \text{……linear form}$$

$$q_{t=}q_e(1\text{-}e^{-k1t}) \quad \text{……non-linear form}$$

Where, q_e is the adsorption amount of the adsorbent at the adsorption equilibrium (mg·g^{-1}), q_t is the adsorption amount of adsorbent at time t (mg·g^{-1}), $q_{e,1}$ is the theoretical equilibrium adsorption amount (mg·g^{-1}) obtained by fitting the quasi-first-order kinetics equation, k_1 is the quasi-first-order adsorption rate constant (min^{-1}). With t as the horizontal coordinate and ln(q_e-q_t) as the vertical coordinate, the slope and intercept of the fitted equation were used to calculate the values of $q_{e,1}$ and k_1, respectively.

Quasi-second-order kinetics equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{1}{q_{e,2}}t \quad \text{……linear form}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad \text{……non-linear form}$$

Where, $q_{e,2}$ is the theoretical equilibrium adsorption amount (mg·g^{-1}) obtained by fitting the quasi-secondary kinetic equation; k_2 is the quasi-second-order adsorption rate constant (min^{-1}). With t as the horizontal coordinate and t/q_t as the vertical coordinate, a regression line can be obtained, and the slope and intercept of the fitted equation were used to calculate the values of $q_{e,2}$ and k_2, respectively.

Isothermal adsorption

The commonly used isothermal adsorption models include Langmuir and Freundlich isothermal adsorption models. The Langmuir model was based on the completely homogeneous monolayer adsorption of the adsorbent, while the Freundlich model is more applicable to the inhomogeneous adsorption of the adsorbent.[2]

Langmuir isothermal adsorption model:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_\infty} + \frac{C_e}{q_\infty} \quad \text{……linear form}$$

$$q_e = \frac{k_L q_\infty C_e}{1 + k_L C_e} \quad \text{……non-linear form}$$

Where: k_L is Langmuir adsorption equilibrium constant (L·mg^{-1}); C_e is the concentration of solution after equilibrium adsorption (mg·L^{-1}); q_e is the maximum saturated adsorption capacity (mg·g^{-1}) of the adsorbent after the adsorption reaches equilibrium; q_∞ is the theoretically calculated limit adsorption capacity (mg·g^{-1}).

Freundlich isothermal adsorption model:

$$lnq_e = lnk_F + \frac{1}{n} lnC_e \quad \text{……linear form}$$

$$q = k \times C_e^{\wedge}\left(\frac{1}{n}\right) \quad \text{……non-linear form}$$

Where: k_F is Freudlich adsorption equilibrium constant (L·mg^{-1}). A regression line can be obtained by taking lnC_e as abscissa and lnq_e as ordinate; The slope and intercept of the fitted equation are used to calculate the value of 1/n and k_F, respectively.

Adsorption thermodynamics

Adsorption thermodynamics focuses on the extent to which the adsorption process proceeds by calculating the standard reaction Gibbs free energy change (ΔG^θ, kJ·mol^{-1}), the standard reaction enthalpy change (ΔH^θ, kJ·mol^{-1}), the standard reaction entropy change (ΔS^θ, kJ·mol^{-1}·K^{-1}), and other thermodynamic parameters of the adsorption reaction.[3]

$$K_c = \frac{q_e}{C_e} \quad (6)$$

$$\Delta G^\theta = -RTlnK_C \quad (7)$$

$$lnK_c = -\frac{\Delta H^\theta}{RT} + \frac{\Delta S^\theta}{R} \quad (8)$$

Where, K_c is the adsorption partition coefficient; q_e is the maximum saturated

adsorption capacity ($mg \cdot g^{-1}$) of the adsorbent at adsorption equilibrium; C_e is the concentration of solution at adsorption equilibrium ($mg \cdot L^{-1}$); R is the ideal gas constant, 8.314 $J \cdot (mol \cdot K^{-1})^{-1}$; T is the absolute temperature (K). Using the abscissa as $1/T$ and $\ln K_c$ as the ordinate, a regression line could be obtained, and the values of ΔH^{θ} and ΔS^{θ} could be calculated from the slope and intercept of the fitted equation, respectively.

The relationship between the reaction proceeding and ΔH^{θ}, ΔS^{θ} and ΔG^{θ}.

(1) $\Delta H^{\theta}>0$, the reaction belongs to endothermic reactio; $\Delta H^{\theta}<0$, the reaction belongs to exothermic reaction.

(2) $\Delta S^{\theta}>0$, the reaction belongs to the process of system disorder increase; $\Delta S^{\theta}<0$, the reaction belongs to the process of system disorder reduction.

(3) $\Delta G^{\theta}>0$, the reaction was non-spontaneous; $\Delta G^{\theta}<0$, the reaction the reaction was spontaneous.

Table S2 Specific surface area, pore size and pore volume of different samples

Samples	Specific surface areas/$m^2 \cdot g^{-1}$	Integrable aperture/nm	Specific pore volume/$cm^3 \cdot g^{-1}$
BC-400	4.1	3.409	0.027
γ-Fe_2O_3	18.6	3.822	0.080
MBC-10	18.3	3.817	0.054
MBC-15	18.4	3.829	0.030
MBC-20（before）	117.1	3.831	0.094
MBC-20（after）	35.0	1.916	0.063
MBC-25	48.4	3.833	0.040

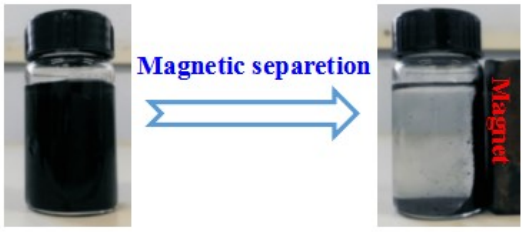

Fig.S2 The magnetic recovery of MBC-20

We have conducted relevant experiments to evaluate the effectiveness of MBC-20. We adsorbed two cationic dyes methylene blue and Congo red (Fig. S3a and 3b), and two anionic dyes acid chrome Blue K and weakly acidic dark blue (Fig. S3c and 3d) with MTC-20, and real wastewater obtained from washing clothes that are prone to fading, including two water samples without and after detergent addition (Fig. S3e and 3f). The adsorption conditions and experimental procedures were consistent with the adsorption conditions for Rhodamine B in this paper. 20 mL of each of the above solutions were taken, 100 mg MBC-20 was added, the oscillation rate was 150 $r \cdot min^{-1}$, and the supernatant was centrifuged for 30 min. Then the supernatant was compared with the original solution. The results showed that MBC-20 had good adsorption effect on different dyes and real sewage.

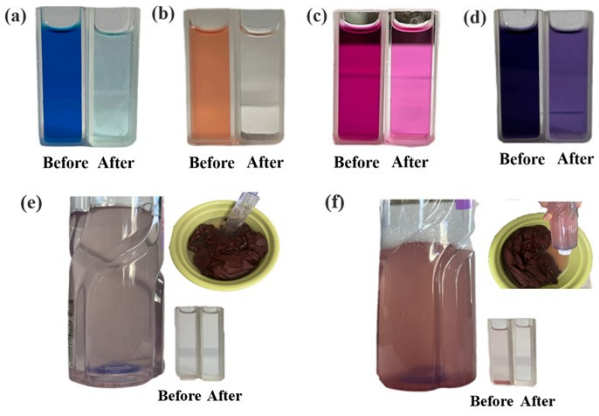

Fig.S3 Adsorption effect of MBC-20 on different cationic dyes and different anionic dyes (a) methylene blue, (b) congo red, (c) acid chromium Blue K, (d) weakly acidic deep blue, (e) sewage samples without adding detergent, and (f) sewage sample after adding detergent.

References

[1] J. T. Nwabanne, O. C. Iheanacho, C. C. Obi and C. E. Onu, *Applied Water Science* **12** (2022) 91, https://doi.org/10.1007/s13201-022-01635-1.

[2] P. Ganguly, R. Sarkhel and P. Das, *Surfaces and Interfaces* **20** (2020) 100616, https://doi.org/10.1016/j.surfin.2020.100616.

[3] M. Jain, S. A. Khan, A. Sahoo, P. Dubey, K. K. Pant, Z. M. Ziora and M. A. Blaskovich, *Bioresour.Technol.* **352** (2022) 127030, https://doi.org/10.1016/j.biortech.2022.127030.