Supporting information

Facile Synthesis of Magnetic Fe_3O_4/$CeCO_3OH$ Composites with Excellent Adsorption Capability for Small Cationic Dyes

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Adsorption kinetics

The kinetics of Fe4Ce1 was analyzed using two commonly used kinetic models, namely, the pseudo-first-order[1] and pseudo-second-order kinetic models[2], which can be expressed as equations (1) and (2), respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (1)$$

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

where q_t (mg g^{-1}) is the adsorption uptake at time t (min); q_e (mg g^{-1}) is the adsorption capacity at adsorption equilibrium; and k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the kinetic rate constants for the pseudo-first-order and the pseudo-second-order models, respectively. The adsorption kinetic data were fitted to the above two models by linear fitting of $\ln(q_e – q_t)$ versus t and (t/q_t) versus t, respectively. The fitting plots are shown in Fig. S1 and the calculated kinetic parameters are listed in Table S1. The results (the correlation coefficients R^2 listed in Table S1) clearly indicate that the adsorption kinetics closely follows the pseudo-second-order kinetic model rather than the pseudo-first-order kinetic model. Compared to the pseudo-first-order model, the calculated q_e based on the pseudo-second-order model is consistent well with the experimental q_e, which supports our conclusion that the kinetic data are followed by the pseudo-second-order model.

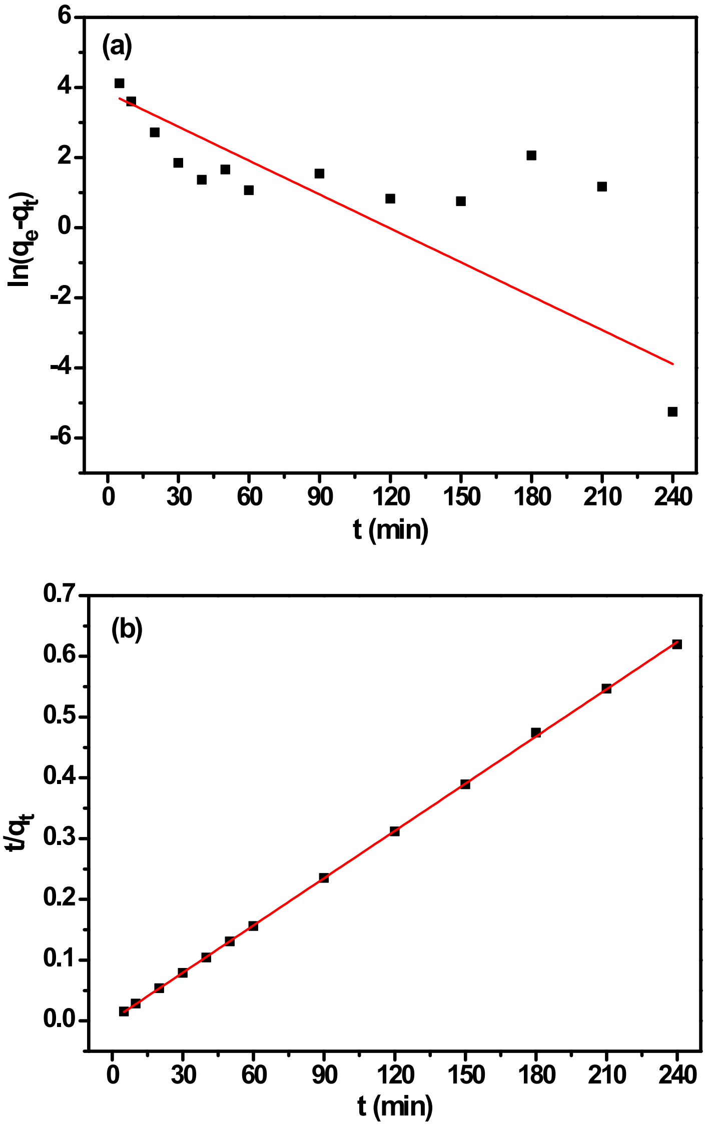


Fig. S1 Plots of pseudo-first-order (a) and pseudo-second-order (b) kinetics for the adsorption of MB on Fe4Ce1.

Table S1 Kinetic parameters for the adsorption of MB on Fe4Ce1.

Pseudo-first-order model			Pseudo-second-order model		
k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
0.0322	46.9	0.3949	0.0039	386.1	0.9999

Adsorption isotherms

The Langmuir[3] and Freundlich[4] isotherm models were used to analyze the equilibrium adsorption data, and their linear forms can be expressed as equations (3) and (4), respectively:

$$\frac{C_e}{q_e} = \frac{1}{K_l q_{\max}} + \frac{C_e}{q_{\max}} \tag{3}$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{4}$$

where C_e (mg L^{-1}) is the equilibrium concentration of MB; q_e (mg g^{-1}) is the amount of MB adsorbed per unit mass of adsorbent; q_{max} (mg g^{-1}) represents the maximum adsorption capacity of MB per unit mass of adsorbent; K_l (L mg^{-1}) is the Langmuir constant related to the energy of adsorption, K_f is the Freundlich constant related to the adsorption capacity (mg$^{1-1/n}$ L$^{1/n}$/g), and n is a dimensionless parameter related to the adsorption intensity. The adsorption isotherms of MB on Fe4Ce1 fitted with the linearized Langmuir and Freundlich models are shown in Fig. S2, and the fitting parameters on the basis of experimental data for MB adsorption isotherms are listed in Table S2. For the adsorption of MB on Fe4Ce1, the Langmuir model fits better with the adsorption data than the Freundlich model. On the basis of the Langmuir equation, the value of q_{max} was calculated to be 671.1 mg g^{-1} for MB adsorption, consistent well with the experimental value of 666.2 mg g^{-1}.

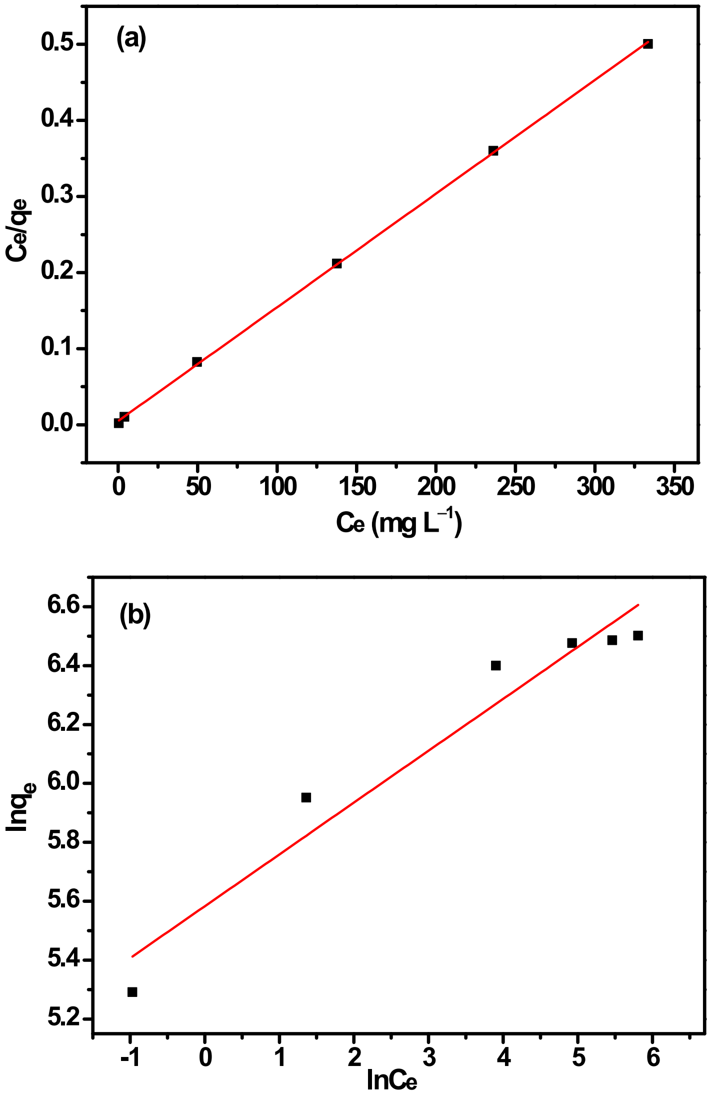
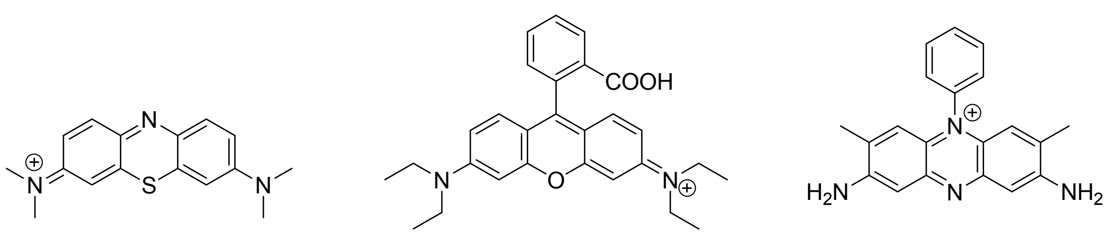


Fig. S2 Langmuir plot (a) and Freundlich plot (b) of isotherms for the adsorption of MB on Fe4Ce1.

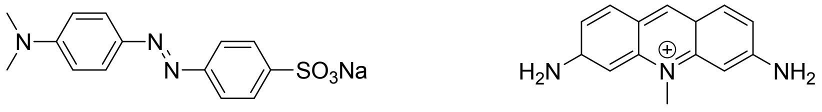
Table S2 Adsorption isotherm constants for the adsorption of MB on Fe4Ce1.

Langmuir constants			Freundlich constants		
q_{max} (mg g^{-1})	K_l (L mg^{-1})	R^2	K_f (mg$^{1-1/n}$ L$^{1/n}$/g)	n	R^2

671.1	0.2986	0.9998	265.8148	5.6818	0.9327



Methylene Blue (MB) **Rhodamine B (RhB)** **Basic Red 2 (BR2)**



Methyl Orange (MO) **Acriflavine Hydrochloride (AH)**

Fig. S3 Molecular structure of dyes used in the experiments.

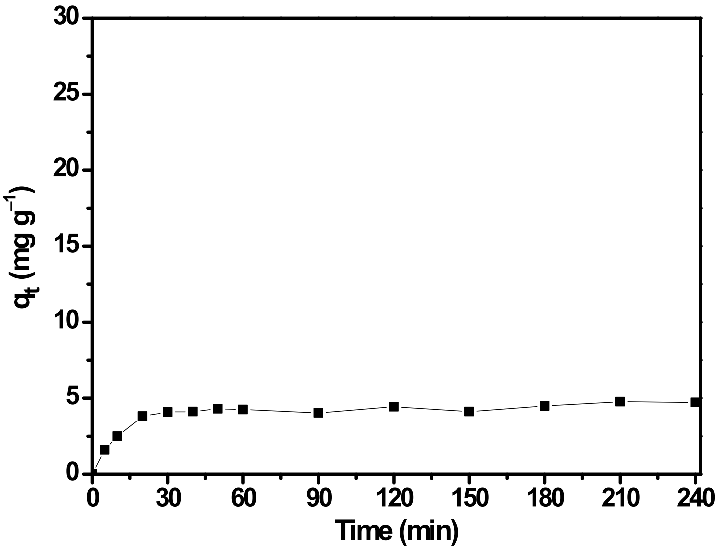


Fig. S4 Adsorption amount of Fe4Ce1 prepared without addition of PAAS versus contact time for MB.

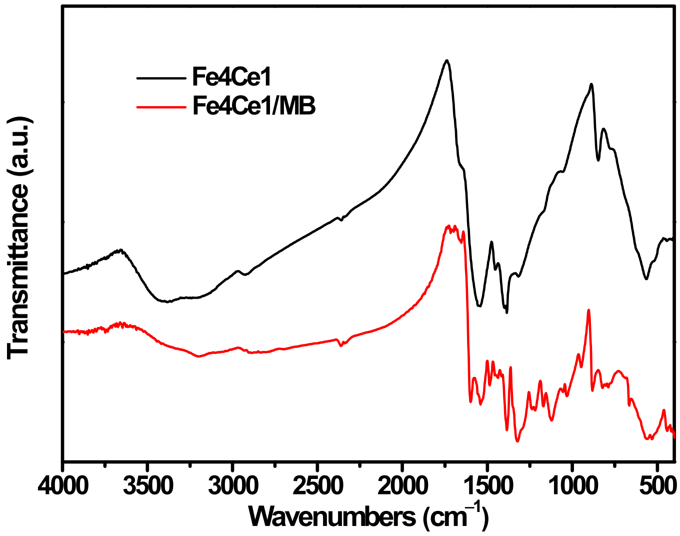


Fig. S5 FTIR spectra of Fe4Ce1 before and after MB adsorption.

Table S3 Weight losses of Fe5Ce0, Fe4Ce1, Fe1Ce1, Fe1Ce4 and Fe0Ce5 at different stages.

Adsorbent	25–200 °C (%)	200–550 °C (%)	$CeCO_3OH^*$ (%)	Carboxylic groups (%)
Fe5Ce0	2.6	7.6	0	7.6
Fe4Ce1	12.3	24.5	6.2	18.3
Fe1Ce1	9.5	26.1	11.0	15.1
Fe1Ce4	7.7	25.4	13.4	12.0
Fe0Ce5	5.2	20.6	14.7	5.9

[*] The weight loss of $CeCO_3OH$ decomposition for Fe4Ce1, Fe1Ce1 and Fe1Ce4 was calculated by multiplying the weight loss of $CeCO_3OH$ decomposition for Fe0Ce5 (14.7 %) by the weight percentage of $CeCO_3OH$ in the Fe-Ce composites. The weight percentages of $CeCO_3OH$ in Fe4Ce1, Fe1Ce1 and Fe1Ce4 are 41.9 %, 75.1 % and 91.2 %, respectively.

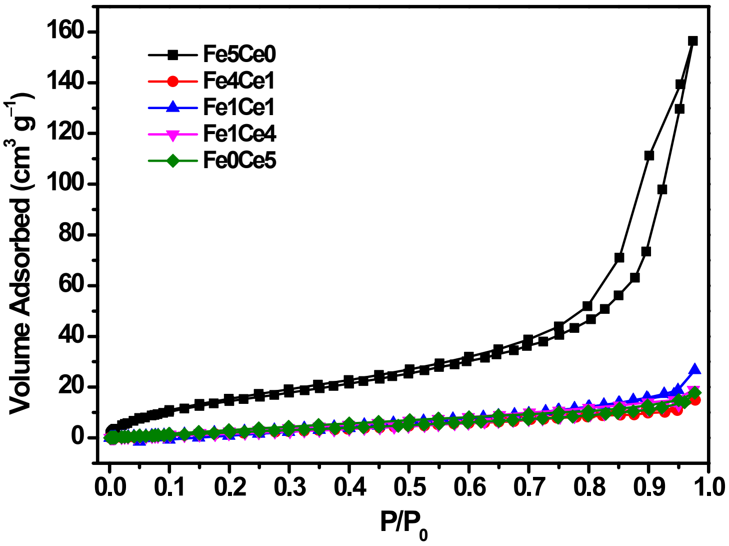


Fig. S6 Ar adsorption/desorption isotherms of Fe5Ce0, Fe4Ce1, Fe1Ce1, Fe1Ce4 and Fe0Ce5.

Table S4 BET surface areas of the samples.

Samples	Fe5Ce0	Fe4Ce1	Fe1Ce1	Fe1Ce4	Fe0Ce5
S_{BET} (m^2 g^{-1})	54.0	12.4	14.8	16.2	13.3

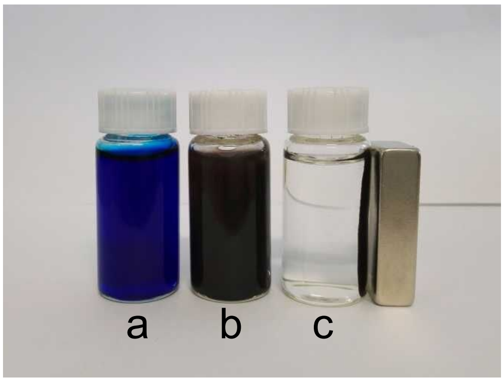


Fig. S7 Photographs for MB solution before (a), after adsorption by adding Fe4Ce1 (b) and after being separated using an outer magnet (c).

References

(1) S. Lagergren, *K. Sven. Vetenskapsakad. Handl.*, 1898, 24, 1.

(2) K. Periasamy, K. Srinivasan and P. R. Muruganan, *J. Environ. Health*, 1991, 33, 433.

(3) I. Langmuir, *J. Am. Chem. Soc.*, 1918, 40, 1361.

(4) H. M. F. Freundlich, *Z. Phys. Chem.*, 1906, 57, 385.