Facile preparation of core-shell magnetic Fe_3O_4@ZIF-8-PSS for organic dyes adsorption

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1. Adsorption experiment of dye

1.1 Adsorption isotherm

Adsorption isotherm experiments were performed by adding 20 mg of adsorbent to 20 ml of CV aqueous solutions at three different temperatures (298, 308, 318 K). The initial concentration of CV aqueous solution is (250, 300, 350, 400, 450, 500, 550, and 600 mg/L), respectively, and the pH = 6. These solutions were fixed on an automatic shaker (SUZHOU NINENBO, model NG-3) and shaken at 200 rpm for 24 h. After magnetic separation, 1 mL of dye solution was extracted and diluted to measure the concentration of CV. The concentration of each diluted CV was measured and repeated three times.

The adsorption capacity of the Fe_3O_4@ZIF-8-PSS was calculated by the

following equation Eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e (mg/g) is the capacity of adsorption at equilibrium, C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of dye, respectively; V (L) is the volume of dye solution, m (g) is the mass of the adsorbent.

The results of isothermal adsorption experiments were fitted using the Langmuir (Eq. (2)), Freundlich (Eq. (3)), and Temkin models (Eq. (4)) [1].

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \quad (2)$$

$$\ln q_e = \frac{\ln C_e}{n} + \ln k_F \quad (3)$$

$$q_e = B \ln A + B \ln C_e \quad (4)$$

$$B = \frac{RT}{b}$$

where q_m (mg/g) is the maximum adsorption amount, k_L (L/mg) is the Langmuir adsorption constant; k_F (L/g) is the Freundlich binding constant, and 1/n is a constant related to the surface heterogeneity; A (L/g) is the equilibrium binding constant, B (J/mol) is the constant associated with the heat of adsorption, R (8.314 J/mol K) is the ideal gas constant and T is the adsorption temperature.

1.2. Adsorption thermodynamics parameters

The thermodynamic parameters, including enthalpy change (ΔH^o), entropy change (ΔS^o) and free energy (ΔG^o) are obtained by the following equations (Eq. (5-6)) [1]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

$$\ln k_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

where T (K) is the absolute temperature at the time of the experiment, R (8.314 J mol^{-1} K^{-1}) is the gas constant, k_c is the thermodynamic equilibrium constant obtained by plotting $\ln(q_e/C_e)$.

1.3. Adsorption kinetics

The kinetics experiments were carried out to 298 K, where 200 mg adsorbent were added to 200 mL CV solution at a concentration of 500 mg/L. The solution was shocked in a gas bath thermostatic shaker (SUZHOU NINENBO, model NG-3), followed by the taking out of 1 mL of the solution at a time at various times, diluting and measuring until adsorption equilibrium.

Adsorption kinetic data are often analysed by fitting pseudo-first-order, pseudo-second-order. The following are expressions for the two classical kinetic models [2].

Kinetic equations of pseudo-first-order (Eq. (7))

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (7)$$

Kinetic equations of pseudo- second-order (Eq. (8))

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (8)$$

Kinetic equations of Elovich model (Eq. (9))

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad (9)$$

where q_t (mg/g) is the amounts of adsorption at time t (min), respectively. k_1 (min^{-1}) and k_2 (mg/g/min) are the linear first-and second-order rate constants, respectively. α and β are Elovich coefficients.

2. Characterization of samples

The powder X-ray diffraction (XRD) data was collected with the D8 Advanced X-ray Diffractometer (Bruker) and recorded over an angular range of 5° - 60°. The morphologies of samples were obtained by Scanning Electron Microscope (SEM, S-4800, Hitachi, Working distance: 8 mm for non-magnetic materials and 15 mm for magnetic materials) equipped with Energy-Dispersive X-ray spectroscopy (EDX, Quantax 200, Bruker). The core-shell structure of the samples was observed under the Field Emission Transmission Electron Microscopy (TEM, Tecnai G^2-S-Twin, FEI). The magnetic properties of the samples were studied by a Magnetic Property Measurement System (MPMS, XL-7, Quantum Design) at room temperature. Infrared absorption spectroscopy was acquired by Fourier Transform Infrared Spectrometer (FTIR, VERTEX 70, Bruker). The nitrogen adsorption-desorption isotherms were measured using an Automatic Surface Area and Porosimetry Analyzer (ASAP 2020M, Micromeritics) at liquid nitrogen temperature (77 K). The specific surface area was estimated by the Brunauer-Emmett-Teller (BET) method. The total pore volume was calculated by the t-plot method, and the pore size distribution was assessed by the supplied DFT software package. Thermogravimetric analyses were performed in

nitrogen at a heating rate of 10 ℃/min on a Simultaneous Thermal Analysis (TG-DSC, STA 449 F3, Netzsch). The concentration of the dye solution was determined by using the Ultraviolet-visible Spectrophotometer (UV-1750, Shimadzu) at the maximum absorption wavelength λ_{max} = 591 nm.

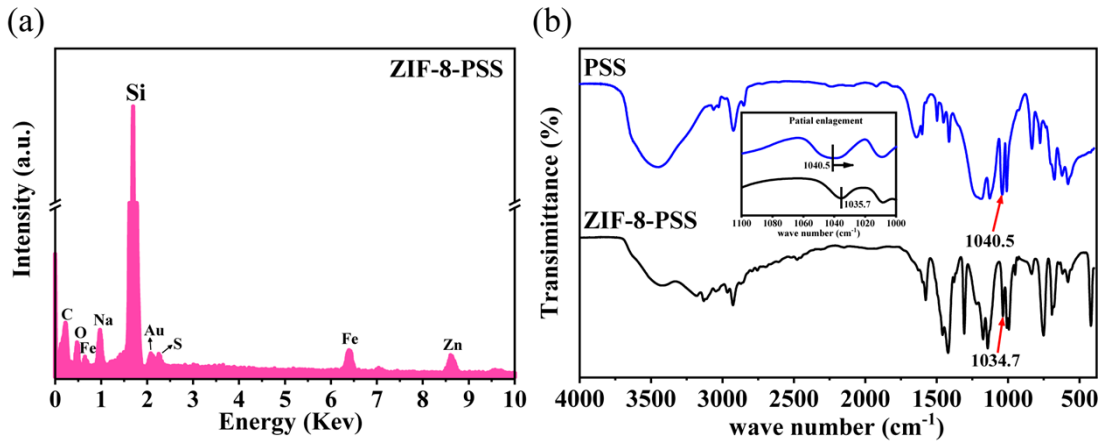

Fig. S1. (a) EDX energy spectrum of ZIF-8-PSS, (b)FT-IR spectra of ZIF-8-PSS and PSS.

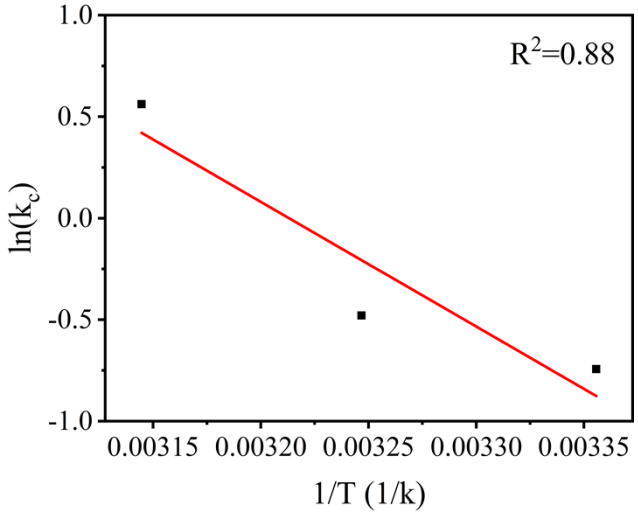

Fig. S2. The relationship between $\ln k_c$ with 1/T.

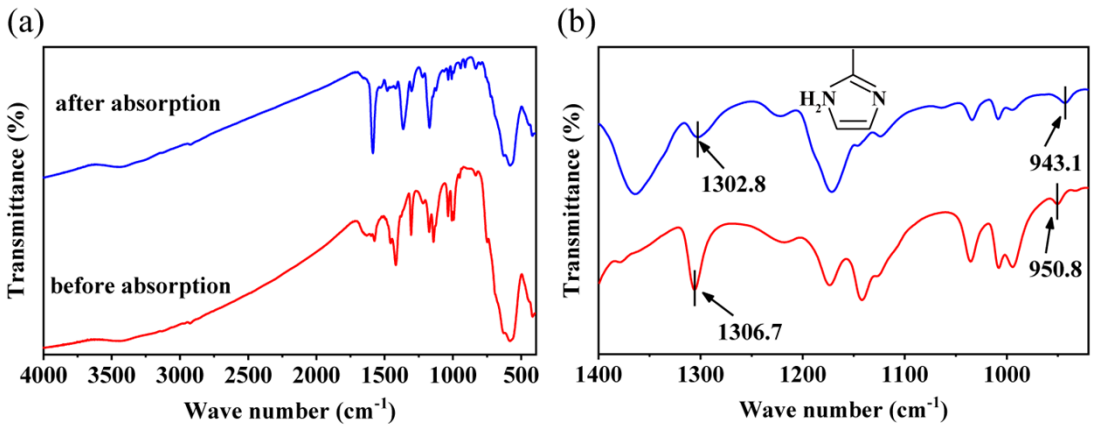

Fig. S3. FT-IR spectra of Fe_3O_4@ZIF-8-PSS before and after adsorption of CV.

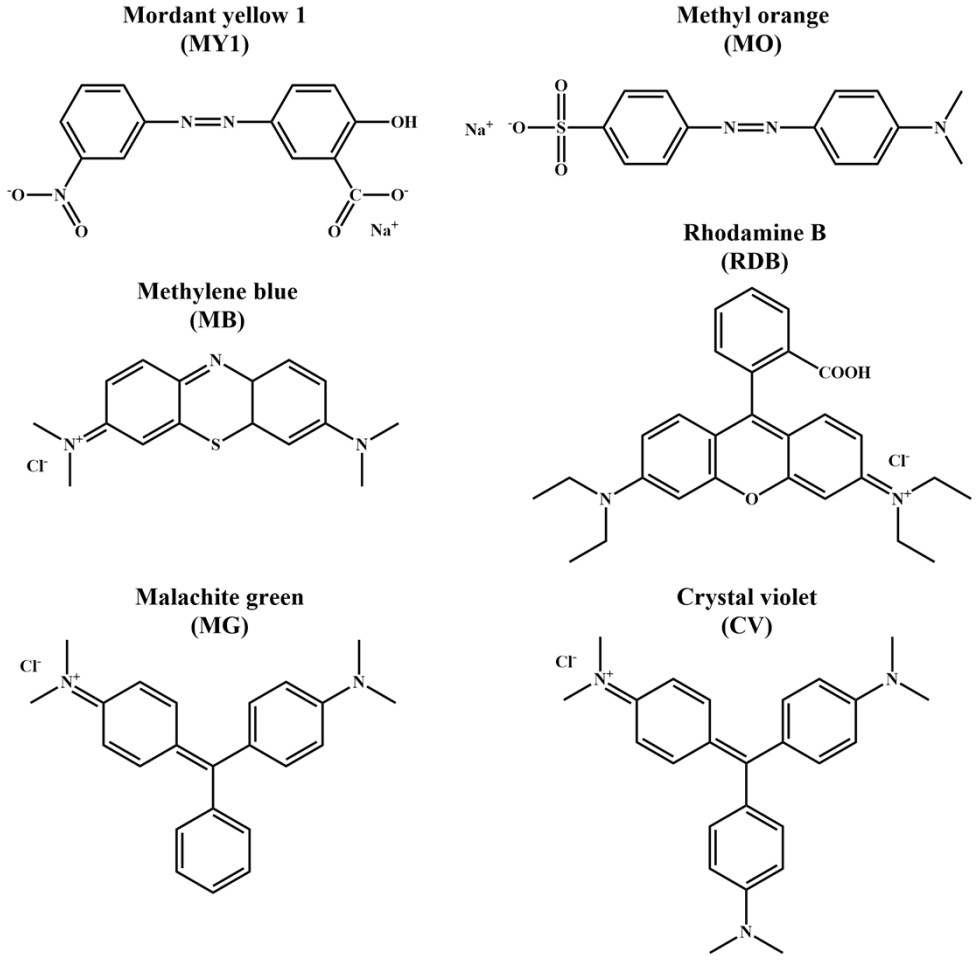

Fig. S4. Summary of the chemical structure formulae of the organic dyes used

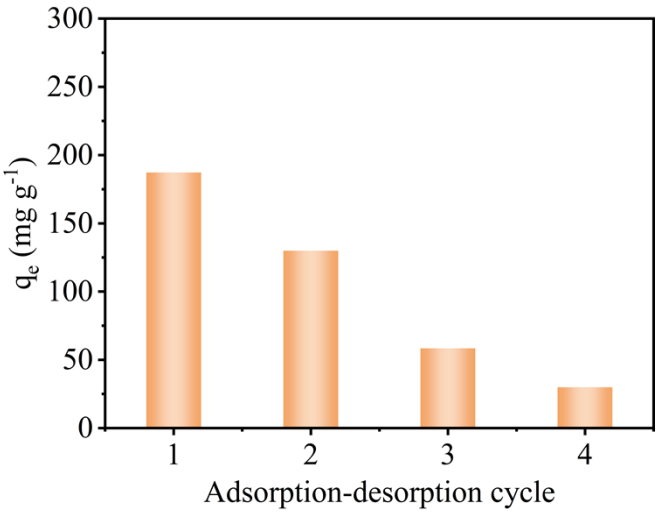

Fig. S5. Recyclability of Fe_3O_4@ZIF-8-PSS for the CV adsorption.

Table S1. Surface area and pore characteristics parameters

Sample	S_{BET} (m/g)	Pore volume (cm^3/g)	DFT porous size (nm)
Fe_3O_4	68.3	0.112	0.43
Fe_3O_4@ZIF-8-PSS	226	0.179	0.43, 0.45-0.77

Table S2. Thermodynamic parameters of by Fe_3O_4@ZIF-8-PSS.

T (K)	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (KJ/(mol K))
298	-15.8		
308	-18.1	51.07	0.224
318	-20.4		

Table S3 Comparison of the CV adsorption capacities for different adsorbents

Adsorbents	Adsorption capacities (mg g^{-1})	Reference
MWCNTs/$Mn_{0.8}Zn_{0.2}Fe_3O_4$	5.23	[3]

HKUST-1	59.5	[4]
Chitosan-graphite oxide modified polyurethane	64.935	[5]
NH_2-MIL-125(Ti)	129.87	[6]
Activated-carbon-HKUST-1	133.3	[4]
Zero-valent iron	172.4	[7]
Cd-MOF	221	[8]
Fe_3O_4@ZIF-8-PSS	382	This work

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