Electronic Supplementary Material

Recyclable hydrolyzed polymers of intrinsic microporosity-1/Fe_3O_4 magnetic composites as adsorbents for selective cationic dye adsorption

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Characterization

The PIM/Fe_3O_4 composite adsorbent were characterized by various techniques. The nuclear magnetic resonance (NMR) spectra were determined by AVIII HD 600 spectrometer. The Fourier transform infrared (FTIR) spectra were analyzed in a Thermo Nicolet IR200 (Thermo Nicolet Corporation, USA) with the scanning wave number of 500-3500 cm-1. The water contact angle (WCA) of PIM-1 membrane and HPIM-1 membrane were acquired in an OCA20 (Dataphysics, Germany). The X-ray diffraction (XRD) patterns were analyzed on a Shimadzu XRD-6100 (0.5° s^{-1}, 10-80°). Thermogravimetric analysis (TGA) was performed via T7300 NSK LTD apparatus. The material was further characterized using X-ray photoelectron spectroscopy (XPS). To measure the magnetic properties of the products, vibrating a sample magnetometer (VSM) (LakeShore 7404) was used to investigate their ferrimagnetic behaviors. The morphology of HPIM/Fe_3O_4 were characterized by scanning electron microscope (SEM) (JEOL/JSM-6700F) at 5 kV, and the elements distribution were determined by the transmission electron microscopy (TEM) (Philips-FEI/Tecnai G2 F30 S-Twin). The pore properties were measured using a BET surface area analyzer at 77 K after degassing them at 120 ℃ for 6 hours.

Adsorption experiments

The adsorbent was placed in a 50 mL conical flask containing 20 mL of dye solution for batch adsorption experiments. The conical flask was then transferred to a room temperature shaking incubator with a shaking speed of 150 rpm. Various parameters, including analogy experiments (Fe_3O_4, PIM-1, HPIM-1 and HPIM/Fe_3O_4), pH of the solution (4-10), contact time (20-480 min), initial MB concentration (50-500 mg L^{-1}) and temperature (5-45 ℃) were investigated to study their effects on the removal performance of MB.

To evaluate the adsorption performance of HPIM/Fe_3O_4 towards different ionic dyes, two types of anionic dyes (MO and CR) and three types of cationic dyes (Rh-B, MS, and MG) were employed. The HPIM/Fe_3O_4 was added to a 20 mL dye solution with an initial concentration of 10 mg L^{-1}, using 10 mg of the adsorbent for each experiment. Additionally, the selective adsorption of $HPIM/Fe_3O_4$ for mixed dyes was examined using a cationic/anionic mixture (MB/MO) solution. Both processes were conducted for a duration of 5 hours.

The equations provided below are used to calculate the removal efficiency (R, %) and adsorption capacity (qe, mg/g) of the dyes at their respective maximum wavelengths (λ_{max}) [1]:

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

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

where C_0 / $mg \cdot L^{-1}$ represents the initial concentration and C_e / $mg \cdot L^{-1}$ represents the equilibrium concentration of the dyes solution; V / L denotes the volume of the dye solution, and M / g refers to the weight of the adsorbent.

Desorption experiments

To study the reusability of $HPIM/Fe_3O_4$, the adsorption-desorption processes were carried out. The adsorption experiment was carried out by constant temperature incubator shaker and operated at 150 rpm at 25 ℃. The initial MB concentration was 100 mg L^{-1} and the adsorbent dose was 10 mg. 1 mol L^{-1} HCl-ethanol mixed solution (1:1) was used as suitable desorption agent for MB, and the desorption process was conducted for 5 h to achieve complete desorption.

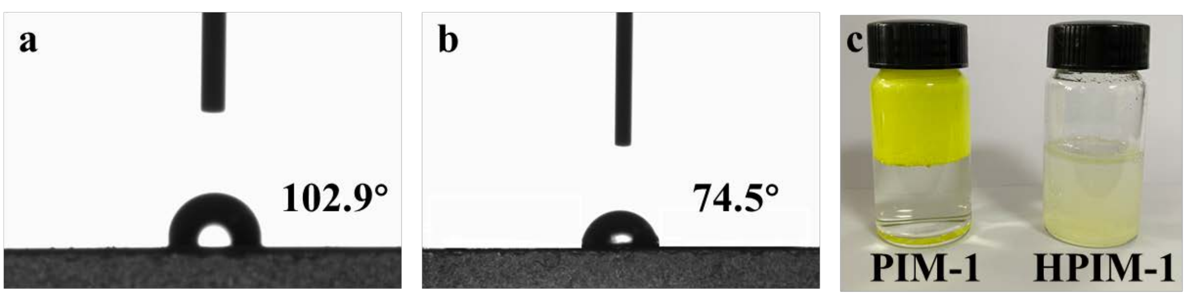

Fig. S1. Water contact angle of (a) PIM-1 membrane and (b) HPIM-1 membrane, (c) Digital photo of the dispersibility of PIM-1 and HPIM-1 in water

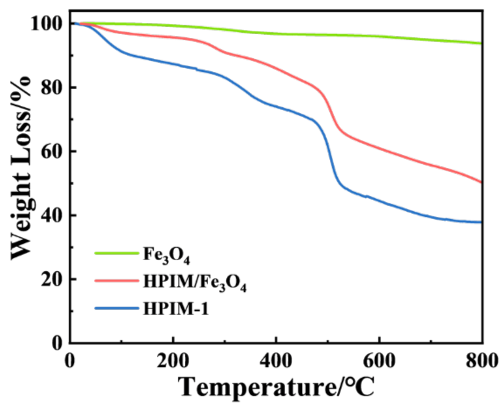

Fig. S2. TGA results of Fe_3O_4, HPIM-1 and HPIM/Fe_3O_4.

Table. S1 XPS survey data (atomic percentage) of the different elements in the materials.

Samples	Elements / At. %		
	C 1s	O 1s	N 1s
PIM-1	27.89	4.35	0.79
HPIM-1	27.89	10.68	1.76

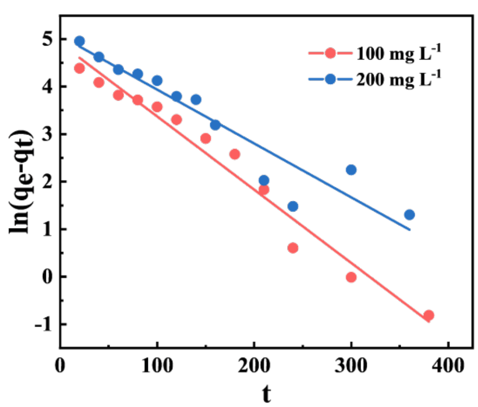

Fig. S3. The pseudo-first-order model fitted curves of MB adsorption on HPIM/Fe_3O_4

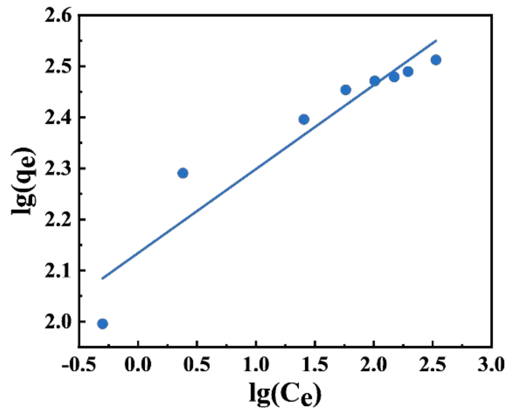

Fig. S4. Freundlich model fitted curves of MB adsorption on HPIM/Fe_3O_4

Table S2. Comparison of the maximum monolayer adsorption of MB onto diverse magnetic biosorbents.

magnetic biosorbent	Q_m / mg g^{-1}	reference
Chitosan/organic rectorite-Fe_3O_4 intercalated composite	24.69	[2]
Magnetic nanocomposites of cellulose	40.5	[3]
Magnetic cellulose/graphene oxide composite	70.03	[4]
Humic acid-coated Fe_3O_4 nanoparticle	93.1	[5]
EDTAD-modified magnetic chitosan	117.53	[6]
Magnetic carbonaceous adsorbent	163.93	[7]
Magnetic chitosan/graphene oxide composite	180.83	[8]
Glutamic acid modified chitosan magnetic composite	182.5	[9]
Carrageenan coated magnetic iron oxide nanoparticle	185.3	[10]
Magnetic peach gum bead	231.5	[11]
Polyvinylpyrrolidone modified magnetic rGO/$CoFe_2O_4$	333.3	[12]
HPIM/Fe_3O_4 composite adsorbent	413.2	This work

The descriptions and equations of sorption thermodynamics:

Thermodynamic parameters, including free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), can be employed to describe the feasibility, spontaneity and nature of adsorbate-adsorbent interactions. The following equations can be employed to calculate these thermodynamic parameters[13]:

$$K_c = \frac{1000K_L(molecularweight\ of\ adsorbate)(adsorbate)^{\circ}}{\gamma} \quad (3)$$

$$\Delta G = -RTlnK_0 \quad (4)$$

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

$$lnK_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

where (adsorbate)° represents the standard concentration of the adsorbate (1 mol L^{-1}) and γ denotes the coefficient of activity. K_c is the non-dimensional thermodynamic equilibrium constant, which can be determined using Eq. (3). R is the universal gas constant, and T (K) represents the absolute temperature.

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