Supplementary information

Extreme pH-tolerant FeOOH@NiAl-LDH nanohybrid adsorbents: Ultra-stable dye adsorption driven by multiple synergistic mechanisms and potent antibacterial performance

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Text S1 Materials

Nickel nitrate hexahydrate (Ni(NO₃)₃·6H₂O), Ferric chloride hexahydrate (FeCl₃·6H₂O), aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O), urea, ammonium fluoride (NH₄F), N,N-dimethylformamide (DMF), sodium hydroxide (NaOH), hydrochloric acid (HCl), Congo red (CR) dyes were provided by Chengdu Kelong Chemical Co., Ltd., China. The terephthalic acid (TPA) was provided by Shanghai Aladdin Biochemical Technology Co., Ltd., China. The deionized water was made in the laboratory. All reactants were analytical purity and used as received.

Text S2 Characterization and measurements

X-ray diffraction (XRD) patterns were obtained by using Bruker D8 Advance Xray diffractometer (Bruker, German) with Cu K α radiation (40 kV, 300 mA, λ = 0.1542 nm) to confirm the crystal structure. Data were collected in a scan range from $2\theta = 5$ to 70° with a step size of 0.05°. The grain size of the adsorbent was calculated using Scherrer equation $(D = K\lambda/\beta cos\theta)$, where K is the Scherrer constant (0.89), D is the crystal grain size (nm), λ is the X-ray wavelength (0.154056 nm) for Cu K α , β is the angle of diffraction peak and θ is the full width at half maximum (FWHM) of the peak (003). Fourier-transform infrared (FTIR) spectra were recorded in the range from 4000 to 400 cm⁻¹ by FTIR spectrometer (Nicolet-6700, USA). The morphology images were observed via the scanning electron microscope (SEM, JSM 7800F, Japan) and transmission electron microscope (TEM, FEI Tecnai G2 F20, USA). The chemical composition of samples was tested by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA). The specific surface area and pore size were calculated by the Brunauer-Emmett-Teller (BET) method from the nitrogen adsorption curve (ASAP2460, USA), with a degassing temperature of 130 °C and a degassing time of 10 h.

Text S3 Adsorption property

The adsorption experiments were completed in a narrow-necked reagent bottle (250 mL) containing 100 mL of 200 mg/L Congo red (CR) solution. Then 20 mg of adsorbents were added into the narrow-necked reagent bottle, and protected from light shaking at 150 rpm for 3 h in a constant temperature shaker. The adsorption experiments were carried out at natural pH, except for the effect of pH on the experimental conditions and kept at room temperature. The absorbance of CR in the collected solution was measured by UV-vis spectrophotometer (UV-2550, Japan) at 500 nm wavelength, and the residual concentration of CR was calculated by the Lambert-Beer law. The UV-Vis standard curve for the CR solution is shown in Figure S1. The adsorption capacity (q_e) and removal rate (R%) for CR was calculated according to the following formulas:

$$q_e = \frac{\left(C_0 - C_e\right) \times V}{M} \tag{1}$$

$$R\% = \frac{C_0 - C_e}{C_0} \times 100\%$$
(2)

where C_0 (mg/L) denotes the initial concentration of CR; C_e (mg/L) is the concentration of CR equilibrium; V (L) is the volume of CR; M (g) is the mass of the used adsorbent.

The above experimental conditions are the original standard conditions. The effects of different variable conditions on the adsorption capacity were investigated by the controlled variable method, and the specific conditions were as follows:

- Different adsorbent dosage: 0.1–0.5 g/L;
- > Initial dye concentration: 50-250 mg/L;
- ➤ Contact time: 0-180 min;
- Temperature: 298.15/308.15/318.15 K;

▶ pH: 2–12.

Text S4 Adsorption kinetic studies

The relationship between adsorption capacity and the contact time of an adsorbent can be described by adsorption kinetics, which is an indispensable analytical method in the adsorption process. The common models are pseudo-first-order kinetics, pseudo-second-order kinetics, and Intra-particle diffusion. Additionally, the Elovich equation is satisfied in chemical adsorption processes and is suitable for systems with heterogeneous adsorbing surfaces. It can be applied to the chemical adsorption process and applied to classifications with heterogeneous adsorption surfaces. The linear equations for each of the three kinetic models are as follows:

Pseudo-first-order:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

$$q_t = k_{di}t^{\frac{1}{2}} + C \tag{5}$$

Intra-particle diffusion:

Elovich:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{6}$$

where q_t (mg/g) and q_e (mg/g) are the adsorption quantities at time *t* and equilibrium, correspondingly; k_1 (1/min), k_2 (mg/g/min) and k_{di} ((mg·min^{-0.5})/g) are the rate constants of the pseudo-first-order, pseudo-second-order, Intra-particle diffusion respectively; α (mg/g/min) is the initial adsorption rate and β (g/mg) denotes activation energy constant of surface coverage.

Text S5 Adsorption isotherm studies

The isothermal adsorption curve is when two phases in certain temperature conditions, surface adsorption to reach an equilibrium state, the adsorbent, and the concentration of adsorbate in the aqueous solution change law. Langmuir isothermal adsorption model and Freundlich isothermal adsorption model are the most commonly used two major adsorption models. On this basis, the Langmuir isothermal model assumes that the number of adsorption sites on the surface of the adsorbent is evenly distributed there is no other external force between the adsorbents; each adsorption site has the same adsorption capacity as the adsorbate, and the adsorption process belongs to the monolayer adsorption; because the adsorption site on the adsorbent is limited, there is a maximum value of the adsorption capacity of the adsorbent, Qm, under the model; based on the ideal surface and monolayer adsorption, the Langmuir isotherm model applies to physisorption and chemisorption. Differently, the Freundlich isothermal adsorption model assumes that the adsorption occurs on an uneven surface; it can describe the adsorption not only on a monolayer but also on a multilayer; moreover, the Freundlich isothermal adsorption model is an empirical model without a corresponding saturated adsorption capacity. However, the Freundlich isothermal adsorption model is not only also applicable to physical and chemical adsorption, but also has wider applicability than the Langmuir isothermal adsorption model. In addition, the Temkin model is suitable for describing the inhomogeneity of the adsorbent surface and the variation of the adsorption energy with the adsorbed amount, which can more accurately reflect the inhomogeneity of the adsorbent surface. The isothermal adsorption equations models are as follows:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_{max}} + \frac{C_e}{q_{max}}$$
(7)

Langmuir:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{8}$$

Freundlich:

Temkin:

$$q_e = B \ln A_T + B \ln C_e, B = \frac{RT}{B_T}$$
(9)

where q_e is the adsorption quantity at equilibrium; q_{max} (mg/g) denotes the adsorption quantity at maximum corresponding to the Langmuir isotherm model; C_e is the adsorbate concentration at equilibrium; k_L (L/mg) and k_F ((mg/g)/(mg/L)^{1/n}) are the constants of the Langmuir and Freundlich models, correspondingly; 1/n is the adsorption intensity factor. When 1/n>2, the adsorption process is difficult to carry out, and when $0.1 \le 1/n \le 0.5$, the adsorption process is easy to carry out; B (J/mol) is the Temkin isotherm energy constant, R is universal gas constant, T (K) is temperature at which the experiment is carried out, A_T (L/g) is binding constant at equilibrium.

In addition, the Langmuir isothermal adsorption model also has a dimensionless constant (R_L) of the same significance as 1/n in the Freundlich model. The value of the R_L can be calculated as follows:

$$R_L = \frac{1}{1 + K_L C_0} \tag{10}$$

 R_L =0, indicating that the adsorption process is irreversible; 0< R_L <1, indicating that the adsorption process is easy; R_L =1, indicating that the adsorption process is linear; and R_L >1, indicating that the adsorption process is not easy to occur.

Text S6 Adsorption thermodynamics

Adsorption thermodynamics is another important parameter to explore and understand the nature of the adsorption process. To further analyze the intrinsic mechanism of FeOOH@NiAl-LDH adsorption CR, the spontaneous and thermodynamic behavior of the adsorption process is analyzed by using thermodynamic parameters such as the Gibbs free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS). The calculation equations are as follows:

$$ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$
(11)

$$k_d = \frac{q_e}{C_e} \tag{12}$$

$$\Delta G^o = \Delta H^o - T \Delta S^o \tag{13}$$

where C_e and q_e denote the equilibrium CR concentrations in solution and on the adsorbent, respectively; ΔS^o (kJ/mol), ΔH^o (kJ/mol), and ΔG^o (J/K·mol) are standard entropy change, the heat of the adsorption, and Gibbs free energy of adsorption, respectively; R is the ideal gas constant (8.314 J/mol/K) and T (K) denotes the

absolute temperature in Kelvin (K); k_d is adsorption equilibrium constant; $ln(\frac{\gamma_e}{C_e})$ is plotted against C_e at different concentrations and then extrapolated to obtain $ln k_d$ when C_e is zero.

Text S7 Antibacterial activity and observation

Agar plate method: *E. coil* and *S. aureus* were incubated and activated in LB broth medium for 24 h in 37 °C thermostatic shaker with 150 rpm. Then, 50 μ L of the bacterial suspensions (1×10⁵ CFU/mL) were treated with the sample groups for 4h in 37 °C with 150 rpm. About 100 μ L bacterial suspensions (1×10⁴ CFU/mL) were coated in LB plate and cultivated in 37 °C for 24 h. The optical photographs of bacterial colonies were recorded by a digital camera, and the bacterial viability was analyzed by ImageJ software. The corresponding antibacterial rate was calculated as the following equation:

$$R(\%) = \frac{\frac{N_C - N_M}{N_C} \times 100\%}{(14)}$$

Antibacterial rate:

where N_C is the bacterial colony numbers of the control group without treatment,

and N_M is the bacterial colony numbers of the other groups.

Bacterial Morphology Observation: SEM was used to observe the morphologies and structures of bacteria. Specifically, sterilized samples were placed into a 48-well plate and 100 μ L bacterial suspension (1×10⁵ CFU/mL) was injected into the plate. The suspension was cultured with samples for 3 h to ensure the bacteria fully adhered to the surfaces of the materials. Then, the samples were fixed with 4 % (v/v) polyformaldehyde (CH₂O)_n glutaraldehyde for 2 h after removing the excess bacterial suspension. Subsequently, the samples were dehydrated by ethanol with a gradient mass ratio (30 %, 50 %, 70 %, 80 %, 90 %, and 100 %) for 10 min and sprayed with gold for SEM observation.

Text S8 Cell viability

RAW 264.7 cells were cultured with or without different concentrations FeOOH@LDH-30. After 24 h, the CCK-8 working solution (CCK-8/culture medium = 1:10) was added and further incubated for 1 h. The OD value at 450 nm was detected by an enzyme-linked immunosorbent assay plate reader.



Figure S1 (a) Molecular structure of CR. (b) UV-Vis standard curve for CR solution.



Figure S2 Structure and morphology of MOF-235: (a) XRD patterns; (b) FTIR spectra; (c) and (d) SEM images.

To confirm the successful preparation of the precursor, structural and morphological analyses are conducted, as plotted in Figure S2. The XRD pattern clearly shows the characteristic peaks of the MOF-235 at $2\theta = 9.39$, 12.57, 16.16, 18.87, 19.32, and 22.01°, corresponding to the (101), (102), (200), (202), (204), and (3-11), respectively, which are in good agreement with the previous literature [1, 2].

Additionally, the experimental results can match well with the XRD data simulated from the standard MOF-235 crystal structure, and there are no other redundant impurity peaks [3]. Further structural and group analysis of MOF-235 through FTIR (Figure S2b). The broad absorption peak at 3460 cm⁻¹ is attributed to -OH stretching vibrations of surface adsorbed water. The strong peaks at 1597, 1393, 750, and 550 cm⁻¹ correspond to C-O, O-C-O, C-H, and Fe-O vibrations [1, 4]. Meanwhile, the SEM in Figures S2c and d show that MOF-235 is a standard dodecahedron of uniform size and smoothness. In conclusion, the prepared MOF-235 is free of impurity crystal phase with good crystal structure and regular morphology.



Figure S3 Linear plot of Elovich model for CR dye adsorption.



Figure S4 Linear plot of Temkin isotherm for CR dye adsorption onto (a) NiAl-LDH and (b) FeOOH@LDH-30.



Figure S5 (a) N_2 adsorption-desorption isotherms and (b) the pore size distribution of FeOOH@LDH-30 after dsorption.



Figure S6 Removal efficiency of CR by FeOOH@LDH-30 at different concentrations of KCl.



Figure S7 (a) Schematic diagram of cytotoxicity assay; (b-f) Micrographs of cells treated with different concentrations of FeOOH@LDH-30; (g) RAW264.7 cells were treated with FeOOH@LDH-30 for 24 h, the cell viability was then detected by the CCK8 reagent.

Table S1 BET data of NiAl-LDH and FeOOH@LDH-30 before and after adsorption

Samples		$S_{\rm BET} ({\rm m^{2}/g})$	Pore volume (cm ³ /g)	Average pore size (nm)
Before adsorption	NiAl-LDH	49.568	0.289	21.952
	FeOOH@LDH-30	117.115	0.607	20.446
After adsorption	FeOOH@LDH-30	104.671	0.454	18.524

Table S2 Comparison of the adsorption performance between FeOOH@LDH-30 and other previously reported

Samples	$q_{max} \left(mg/g \right)$	t (min)	m (g/L)	pН	References

CE/CSA-1	380.2	360	0.25	8	[5]
alk-MXene/ZIF	539.7	300	0.4	2	[6]
ZnFe-LDHs/FeOOH	867	600	0.1	5	[7]
AlOOH/CoFe ₂ O ₄	565	120	0.3	6.29	[8]
KBC	584.17	360	0.2	9	[9]
cellulose/Ti ₃ C ₂ Tx	1103.7	90	0.4	3-10	[10]
IQMCM	630.2	720	0.15	5	[11]
MXene@Fe ₃ O ₄ @CS	620.2	300	0.2	6	[12]
AmCs@ZIF-8	1156	180	0.3	3-9	[13]
FeOOH@LDH-30	1297	180	0.2	2-12	This work

Table S3 Fitting parameters of the Intra-particle diffusion and Elovich model

	Elovich			Intra-particle diffusion					
Samples	α	β	R^2	k_{d1}	C_1	R2	k_{d2}	C_2	R2
	(ing/g/iiiii)	(g/mg)		(ing inin)/g	(ing/g)	1	(ing inin)/g	(ing/g)	Z
NiAl-LDH	3.63×10^{2}	0.0098	0.97	28.78	240.8	0.98	8.36	431.2	0.98
FeOOH@LDH-10	4.55×10 ³	0.0097	0.96	29.34	503.0	0.99	7.82	707.0	0.93
FeOOH@LDH-30	8.96×10 ⁴	0.0115	0.94	16.60	803.5	0.97	3.54	931.2	0.72
FeOOH@LDH-50	4.35×10 ⁴	0.0114	0.95	17.09	732.9	0.99	3.54	862.7	0.99

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