Supplementary Materials

Synthesis of magnetic UiO-66-NH_2@EDTA-GO and mechanism study of simultaneous adsorption of heavy metal ions and organic dyes from water

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1 Experiment details

1.1. Reagents and Instruments

Graphite, $KMnO_4$, H_2O_2 (30%), NaOH, $NaNO_3$, $Pb(NO_3)_2$, Methylene blue trihydrate, Ethylenediaminetetraacetic acid (analytical pure) were purchased from Damao Chemical Reagent Factory (Tianjin). Terephthalic acid, $FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$ (analytical pure) were purchased from Macklin Biochemical (Shanghai) Co., Ltd; H_2SO_4 (98%) and HCl (36%) (analytical pure) were purchased from Kemiou Chemical Reagent (Tianjin) Co., Ltd. Zirconium chloride, 2-Aminoterephthalic acid, Methyl orange, N,N-Dimethylformamide, methanol, Acetic acid were obtained from Aladdin Reagent (Shanghai) Co., Ltd. The experimental water was purchased from Wahaha Group (Hangzhou) Co., Ltd.

A NOVA Nano 450 Field Emission Scanning Electron Microscope (SEM) and a JEOL F200 Field Emission Transmission Electron Microscope (TEM) were used to characterize the surface morphology of the sample. The crystal structure and phase purity were characterized Empyrean X-ray diffractometer (XRD) (Cu target, K alpha ray, 40 kV tube voltage, 40 mA tube current, 10°/min scanning rate, and 5-80° scanning range). The surface elemental composition was measured by a Thermo Scientific K-Alpha X-ray Photoelectron Spectroscopy (XPS). The Fourier Transform Infrared Spectroscopy (FT-IR) spectra were recoeded on a Thermo Scientific Nicolet Is10 FT-IR system in the range of 7800-350 cm^{-1}

using standard KBr pellets. The specific surface area and pore diameter distribution of the samples were measured by a Konta Automatic Gas Sorption Analyzer. The concentrations of heavy metal ions were quantitatively analyzed on an AVIO 220 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (wavelength range: 167-900 nm). Quantitative analysis of the concentration of organic dyes in the sample was performed using UV-visible spectrophotometer (T6 New Century, produced by Beijing Puxi General Instrument Co., Ltd.).

1.2. Experimental Procedures

1.2.1. Preparation of UiO-66 and UiO-66-NH_2

Dissolve 0.932 g $ZrCl_4$ and 1.32 g terephthalic acid (BDC) in 50 mL N,N-dimethylformamide (DMF) and stir continuously for 30 min. Then, sonicate the mixture for 30 min and transfer it to a Teflon-lined high-pressure reactor and heat at 120°C for 16 h. Collect the resulting white product by centrifugation and wash it with ethanol, followed by washing with ethanol and deionized water. Dry the sample under vacuum at 50°C to obtain UiO-66. UiO-66-NH_2 is prepared by replacing the organic ligand with 2-aminoterephthalic acid (NH_2-BDC) using the same procedure[1].

1.2.2. Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared by co-precipitation method. $FeCl_2 \cdot 4H_2O$ (0.8 g) and $FeCl_3 \cdot 6H_2O$ (2.3 g) ($n_{Fe(II)} : n_{Fe(III)} = 1:2$) were dissolved in 40 mL of deionized water and sonicated for 5 min. The resulting solution was dripped into a 1 mol·L^{-1} NaOH solution (100 mL) at 70°C, and the reaction continued for 25 min. After the reaction was completed, the precipitated product was recovered using an external magnet. The precipitate was washed three times with deionized water and dried in a 50°C oven for 12 h[2].

1.2.3. Preparation of Fe_3O_4/UiO-66-NH_2

Dissolve 0.2 g Fe_3O_4 in 30 mL DMF and sonicate for 30 min. Then, add 0.2 g $ZrCl_4$ and 0.156 g NH_2-BDC and sonicate for another 30 min. Transfer the mixture to a Teflon-lined high-pressure reactor and hydrothermally react at 120°C for 24 h. After the temperature is lowered to room temperature, wash the sample with ethanol and deionized water and finally vacuum dry it at 50°C to obtain Fe_3O_4/UiO-66-NH_2[3]. The formation of UiO-66-NH_2 is achieved through a coordination reaction with high thermodynamic stability, where $ZrCl_4$ and NH_2-BDC react in DMF to form UiO-66-NH_2 crystals. The composite of Fe_3O_4 nanoparticles is achieved by mixing the Fe_3O_4 magnetic nanoparticles and the precursor of UiO-66-NH_2 in DMF. During the composite process, DMF molecules act as connectors, where the carbonyl (C=O) in DMF molecules can form hydrogen bonds with the hydroxyl (-OH) on the surface of Fe_3O_4 nanoparticles, which can increase the binding force between Fe_3O_4 nanoparticles and UiO-66-NH_2 crystals. Meanwhile, the methyl group (-CH_3) in DMF molecules can undergo electrostatic interaction with the oxide groups on the surface of Fe_3O_4 nanoparticles, resulting in negative charges on the surface of Fe_3O_4 nanoparticles. These negative charges can attract the amino groups ($-NH_2$) with positive charges in UiO-66-NH_2 crystals, leading to encapsulation and self-assembly. In addition, Fe_3O_4 magnetic nanoparticles can also be adsorbed and bound to UiO-66-NH_2 crystals through van der Waals forces and hydrogen bonds.

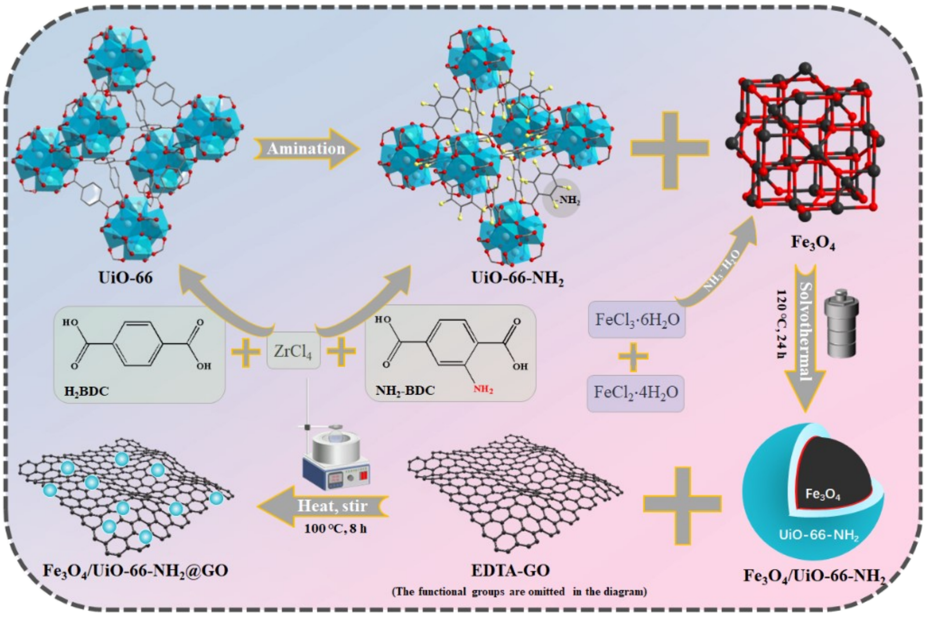
1.2.4. Preparation of Graphene Oxide and EDTA-GO

Improved Hummers method was used to prepare graphene oxide. In an ice-water bath, 3.0 g graphite and 1.5 g $NaNO_3$ were added separately into 69 mL of concentrated H_2SO_4 with mechanical stirring. Then, 9.0 g $KMnO_4$ was slowly added while ensuring that the system temperature was kept below 20°C. The reaction was heated to 35°C and stirred mechanically for 7 h, followed by the slow addition of another 9.0 g $KMnO_4$. The mixture was then stirred mechanically for an additional 14 h. After cooling the system to room temperature, 400 mL H_2O was slowly added, followed by the dropwise addition of 3 mL H_2O_2 (30%) to neutralize any remaining $KMnO_4$. The resulting product was bright yellow, and it was washed to neutrality, vacuum filtered, centrifuged, vacuum dried for 48 h, and ground into a powdery particle. During the washing and drying process, the OH- and H^+ in the interlayer of the graphene oxide were removed in the form of water molecules, resulting in the color of the product changing from bright yellow to dark brown. The resulting product was graphene oxide (GO).

To increase the stability of the composite material, GO was modified with the chelating agent ethylenediaminetetraacetic acid (EDTA). 0.5 g GO was dispersed in 20 mL 10% acetic acid water solution to form a GO dispersion, and 6.0 g EDTA was uniformly dispersed in 100 mL of methanol to obtain an EDTA dispersion. The GO and EDTA dispersions were mixed with mechanical stirring, and the reaction was carried out at room temperature for 24 h. The resulting product (EDTA-GO) was centrifuged, washed with ultrapure water, dried at 50°C in a vacuum drying oven, and ground into a powder for experiments[4]. The carboxyl group in EDTA and the hydroxyl group on the surface of GO underwent esterification reaction, forming EDTA-modified graphene oxide (EDTA-GO) composite material. The carboxyl group on the surface of EDTA-GO can also undergo acylation reaction with the amino group on UiO-66-NH_2, further expanding its application range[5].

1.2.5. Preparation of Fe_3O_4/UiO-66-NH_2@EDTA-GO

Dissolve 0.35 g EDTA-GO in 50 mL DMF, and 0.95 g Fe_3O_4/UiO-66-NH_2 in 100 mL DMF solution, and disperse them separately by ultrasonication for 30 min. After mixing the two solutions, vigorously stir the mixture at 100°C for 8 h. After the product is separated magnetically, wash the sample with ethanol and deionized water. Finally, dry it under vacuum at 50°C to obtain Fe_3O_4/UiO-66-NH_2@EDTA-GO[6]. The amino group (-NH_2) in UiO-66-NH_2 can react with the carboxyl group (-COOH) on the surface of GO to form a carboxamide bond (-CO-NH-); the hydroxyl group (-OH) in UiO-66-NH_2 can react with the carboxyl group (-COOH) on the surface of GO to form an ester bond (-COO-). These chemical bonding reactions can enhance the connection between UiO-66-NH_2 and GO. At the same time, the metal ions in UiO-66 can coordinate with the nitrogen, oxygen, and other functional groups in EDTA to form a metal-ligand coordination bond. In addition, the functional groups (such as hydroxyl and amino groups) in UiO-66-NH_2 can form hydrogen bonds and van der Waals forces with the oxygen-containing groups on the surface of GO. These interaction forces can form strong physical adsorption in the composite material, thereby improving the stability of the composite material. The schematic diagram of the synthetic reaction is shown in scheme S1.



Scheme S1. The schematic diagram of the synthetic reaction for Fe_3O_4/UiO-66-NH_2@EDTA-GO.

1.3. Testing the adsorption performance of adsorbent.

1.3.1. Detection of target contaminants

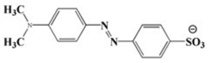
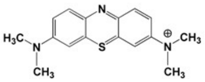
(1) Preparation of Heavy Metal Ion Standard Solution: Weigh 1.598 g of lead nitrate ($Pb(NO_3)_2$) and dissolve it in 1 liter of 1% nitric acid solution. Mix well to obtain a lead ion solution with a concentration of 1000 mg/L. This solution will be used later. ICP-OES uses an inductively coupled plasma to generate a high-temperature plasma. In the plasma, the elements in the sample are excited and emit light at specific wavelengths, which are detected by a detector and converted into signals. By analyzing these signals, the concentration of the elements in the sample can be determined. After the adsorption experiment, the mixed solution was separated by 10000 rpm high-speed centrifuge for 5 min, and the supernatant was taken through 0.22 μm filter membrane, and the concentration of heavy metal ions in it was determined by ICP-OES.

(2) Preparation of Standard Curve for Organic Dye: A spectrophotometer can measure the absorbance of a sample at a specific wavelength, which is usually the maximum absorption wavelength of the substance. According to Lambert-Beer law, the absorbance is proportional to the concentration of the solution. Therefore, as long as the absorbance value of the solution at its maximum absorption wavelength is measured while keeping the thickness of the absorption layer constant, the concentration of the solute in the solution can be calculated using the molar absorbance of the substance used. The specific steps are as follows: Prepare solutions of

methyl orange and methyl blue with a concentration of 1000 mg/L in volumetric flasks as reserve solutions, and store them in the dark. Use a pipette to transfer 10 mL of the reserve solution to a 100 mL volumetric flask, and accurately transfer 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 mL of the above solution to a 25 mL volumetric flask, respectively, and dilute to the mark with water. Since the pH values of the methyl orange solutions are close to neutral, the absorbance can be directly measured at its maximum absorption wavelength λ_{max} = 464 nm. The absorbance of methyl blue is measured at its maximum wavelength λ_{max} = 664 nm. Plot the standard curve using the concentration C as the abscissa and the absorbance Abs as the ordinate, and fit the curve to obtain the standard curves of methyl orange and methyl blue, respectively. The structures of methyl orange and methyl blue are shown in Table S1, and the results are shown in Fig. S1. At a certain time interval, a certain amount of sample is first extracted from the liquid to be measured, and then 1 mL of filtrate is transferred into a stopper colorimetric tube, and an appropriate amount of deionized water is added to dilute it to 10 mL. After shaking well, an appropriate amount of diluted sample is taken in a 10.0mm quartz colorimetric dish for determination. According to the standard curve of methyl orange and methylene blue, the concentration of these two pollutants in the solution is calculated.

Table S1 Properties of organic dye investigated in this work.

Dyes	Molecular structure	Molecular weight	Size[a]	λ_{max}[b]

		(g/mol)	(nm^3)	(nm)
Methyl orange (MO)		327.33	1.54×0.48×0.28	464
Methylene blue (MB)		319.85	1.38×0.64×0.21	664

[a] The ionicity size of MO (anionic) and MB (cationic) (nm^3)[7].

[b] Maximum absorption wavelength (nm).

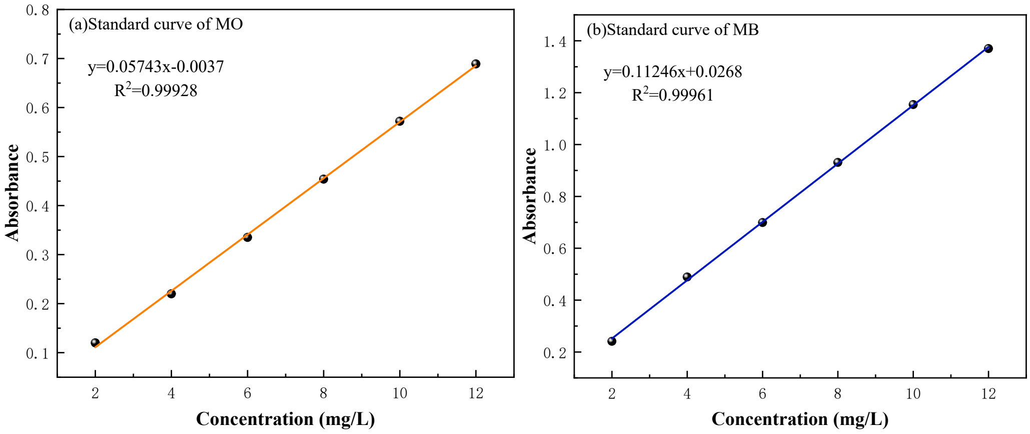


Fig. S1. The standard curves of methyl orange solution (a) and methylene blue solution (b).

1.3.2. Adsorption procedure

(1) The influence of pH on adsorption performance: Adjust the pH of the solution to a range of 2.0 ~ 8.0 by using a 0.1 M HCl or 0.1 M NaOH solution, then add 15 mg of the adsorbent Fe_3O_4/UiO-66-NH_2@EDTA-GO into a 50 mL adsorption tube containing 15 mL of initial concentration of 100 mg/L ion solution or organic dye solution, and oscillate adsorb for 180 min at 293 K. (The mixed solution was separated by a 10000 rpm high-speed centrifuge for 5 min). Subsequently, magnetic separation was performed to observe the change of the concentration of the target adsorbent after Fe3O4/UiO-66-NH2@EDTA-GO adsorption.

(2) The influence of adsorption time on adsorption performance and kinetic study: Add 15 mg of the adsorbent Fe_3O_4/UiO-66-NH_2@EDTA-GO into a 50 mL adsorption tube containing 15 mL of initial concentration of 100

mg/L ion solution or organic dye solution, and control the oscillation temperature at 293 K. Adsorb at the optimum pH condition for different times (10, 20, 30, 40, 50, 60, 90, 120, 150, 180 min), then repeat the steps in (1) and measure the change of the target adsorption concentration after adsorption.

(3) The influence of adsorbent dosage on adsorption performance: Add adsorbent Fe_3O_4/UiO-66-NH_2@EDTA-GO with different dosages (1.0, 1.5, 2.0, 2.5, 3.0 mg/mL) into a 50 mL adsorption tube containing 15 mL of initial concentration of 100 mg/L ion solution or organic dye solution, and control the oscillation temperature at 293 K. After adsorption for a certain time under the optimum pH condition, repeat the steps in (1) and measure the change of the target adsorption concentration after adsorption.

(4) The influence of temperature on adsorption performance and adsorption isotherm model study: Add 15 mg of the adsorbent Fe_3O_4/UiO-66-NH_2@EDTA-GO into a 50 mL adsorption tube containing 15 mL of ion solution or organic dye solution with different initial concentrations (50, 100, 200, 300, 400, 600 mg/L), and adsorb at different temperatures (293, 303, 313 K) under the optimum pH condition for a certain time. Repeat the steps in (1) and measure the change of the target adsorption concentration after adsorption. The sample was tested three times and the average was taken as the experimental result. The adsorption capacity of Fe_3O_4/UiO-66-NH_2@EDTA-GO (Q_e, mg/g) was calculated by Eq. (1), and

the adsorption removal rate was calculated by Eq. (2).

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

$$Removal\ (\%) = \frac{100(C_0 - C_e)}{C_0} \tag{2}$$

Where, Q_e represents the adsorption equilibrium capacity (mg/g); C_0 represents the initial concentration of the adsorbate (mg/L); C_e represents the equilibrium concentration of the adsorbate (mg/L); V represents the volume of the treated sample (L); M represents the mass of sample (g).

1.3.3. Experimental for adsorption of binary composite pollutants.

Table S2 Experimental design used for the binary system of Pb(II) and organic dyes.

Experimental Design for Heavy Metal Ions-Organic Dye Adsorption		**Factor A**: Pb(II) Initial Concentration (mg/L)				
		0	**50**	**100**	**200**	**300**
Factor B: MO, MB Initial Concentration (mg/L)	**0**	N/A	q_e[50,0]	q_e[100, 0]	q_e[200, 0]	q_e[300,0]
	50	q_e[0,50]	q_e[50,50]	q_e[100,50]	q_e[200,50]	q_e[300,50]
	100	q_e[0,100]	q_e[50,100]	q_e[100,100]	q_e[200,100]	q_e[300,100]
	200	q_e[0,200]	q_e [50,200]	q_e[100,200]	q_e[200,200]	q_e[300,200]
	300	q_e[0,300]	q_e [50,300]	q_e[100,300]	q_e[200,300]	q_e[300,300]

1.4. Determination of the pH point zero charges (PZC)

The specific steps are as follows: add 30 mg of adsorbent to a 10 mL NaCl solution (0.01 mol/L) with an initial pH value of 2 ~ 8, and then oscillate the adsorbent on a rotary shaker at room temperature for 48 h to allow the adsorbent to fully contact the solution. Then, measure the pH value of the solution using a pH meter and perform two measurements. The difference between the two results is ± 0.1 pH unit, and the total measurement error estimate of acidity and alkalinity is not greater than ±

3%. The pH drift curve is plotted based on the pH values and the amount of pH changes in different solutions.

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