Fe_3O_4@ZIF-8: A Magnetic Nanocomposite for Highly Efficient UO_2^{2+} Adsorption and Selective UO_2^{2+}/Ln^{3+} Separation

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Experimental details

1. *Chemicals and reagents*

All chemicals were purchased commercially and used without further purification. All testing solutions were prepared with Milli-Q water. $UO_2(NO_3)_2$•$6H_2O$ (ACS grade) was purchased from Merck, Germany. A standard stock solution of U(VI) was prepared by dissolving the appropriate amounts of $UO_2(NO_3)_2$•$6H_2O$ in deionized water.

2. *Instruments*

Powder X-ray diffraction (PXRD) was performed on a Rigaku/max 2550 diffractometer with Cu K_α radiation Field-emission ($\lambda = 1.5418$ Å, continuous, 40 kV, 15 mA, increment = 0.02°). Scanning Electron Microscope (SEM) images were conducted on a Hitachi S-4800. TEM (Transmission Electron Microscope) images were taken on a FEI Tecnai G2 F20 with an accelerating voltage of 200 KV. UV−Vis spectroscopic studies were collected on a UV-4000 spectrophotometer. Inductively coupled plasma (ICP) analyses were conducted on a Perkin-Elmer Optima 3300DV spectrometer.

3. *Synthesis of Fe_3O_4 nanoparticles*

Fe_3O_4 nanoparticles were synthesized according to previous report by a chemical coprecipitation method. In a general preparation, 1.622 g (6 mmol) of iron (III) chloride hexahydrate and 1.39 g (5 mmol) ferrous sulfate heptahydrate were dissolved in 40 mL deionized water and kept stirring at 90 °C for a few minutes. 5 mL ammonia solution ($NH_3 \cdot H_2O$, 28%) were added into the mixture slowly to precipitate. After continuously stirring for 10 min, 4.4 g (15 mmol) trisodium citrate dihydrate were added, and kept stirring at this temperature for 30 min. After cooling down, the as-synthesized Fe_3O_4 nanoparticles were separated by a magnet and washed with water and ethanol several times. The solid materials were re-dispersed in 100 mL H_2O for subsequent use.

4. *Synthesis of Fe_3O_4@ZIF-8 nanocomposite*

0.246 g (3 mmol) 2-methylimidazole was added into 25mg Fe_3O_4 nanoparticles and stirred for 5min at 30℃. 0.148 g (0.5 mmol) of zinc nitrate hexahydrate was added into the mixture and stirred another 30 min before separated. The separated sample was washed with methanol more than three times and dried in vacuum at 60 °C.

5. *Adsorption experiments*

All adsorption experiments were carried out by a batch method at ambient temperature in air. In general procedure, 4 mg Fe_3O_4@ZIF-8 nanocomposite was added into 10 mL solution of UO_2^{2+} or the solution with many completing metal ions in a beaker. The mixture was stirred for a certain time at ambient temperature, and then the solid sorbent was quickly removed by a magnet within two minutes. 1 mL aforementioned supernatant was measured and transferred into a glass container with 2 mL aqueous solution of arsenazo-III (0.05%) in it, and the concentration of UO_2^{2+} was diluted to one over twenty-five of the original solution using deionized water determined by UV–Visible spectrometry with arsenazo-III as the chromogenic agent at wavelength of 651 nm. For the selectivity experiment, the concentration of ions was conducted by inductively coupled plasma optical emission spectrometer.

5.1 The standard curve

The absorbance of arsenazo-III with different concentration of UO_2^{2+} were measured at wavelength of 651 nm which attributed to the U-arsenazo III complex. The standard curve was obtained by the absorbance as a function of U concentration, and a linear equation with high correlation coefficient (R^2=0.99) was fitted as shown in Fig. S2.

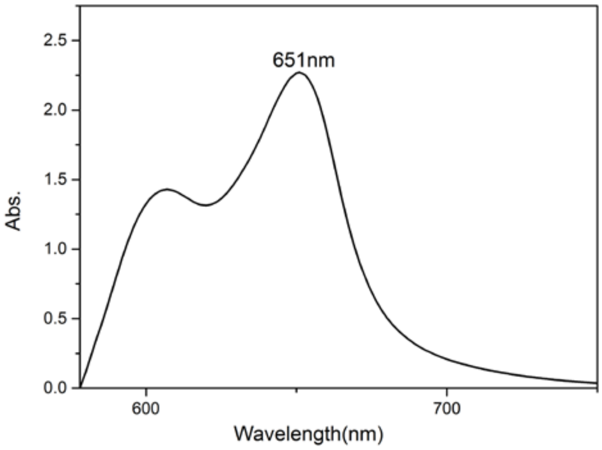

Fig. S1 UV–Visible spectrometry of arsenazo-III as the chromogenic agent with U.

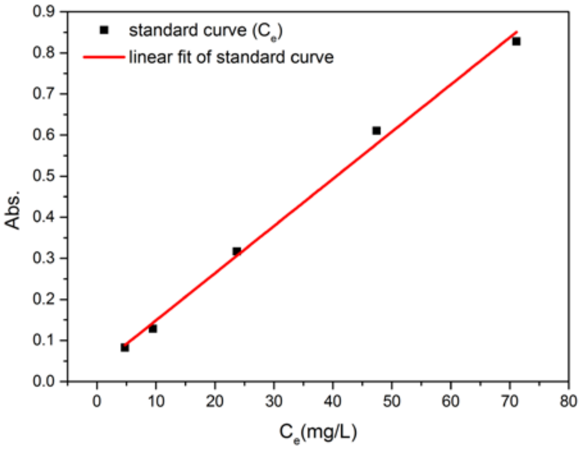

Fig. S2 The standard curve of the concentration of U.

5.2 UO_2^{2+} *adsorption at different pH conditions*

The adsorption capacity of U, q_e(mg/g), was calculated by the following equation:

$$q_e = \frac{(c_0 - c_e) \times V}{m}$$

where c_0 and c_e are the initial and equilibrium concentration of U (mg/L), respectively. V and m represents the volume of the solution (mL) and the weight of the sorbent Fe_3O_4@ZIF-8. Solution pH is an important factor for U absorption, and the U species in the aqueous solution convert the free UO_2^{2-} to the multi-nuclear hydroxide complexes such as $(UO_2^{2+})_3(OH)^{5+}$ with the increasing of pH. The adsorption capacity of U onto the adsorbent at different pH is shown in Table S1.

Table S1 UO_2^{2+} adsorption on Fe_3O_4@ZIF-8 nanocomposite at different pH conditions.

pH	2	3	4	5	6
Abs	0.4915	0.077	0.0823	0.1829	0.2087
q_e	18.89416	109.1598	108.0057	86.098	80.47953

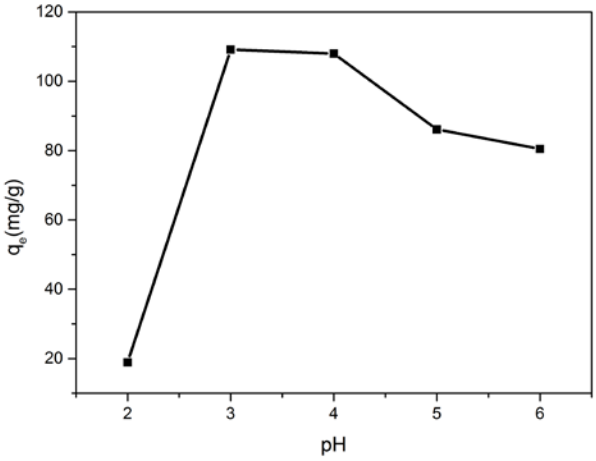

Fig. S3 The UO_2^{2+} adsorption capacity at different pH.

5.3 Adsorption kinetic

The adsorption kinetic were studied using experiments with different contacting time at initial U concentration of 250 mg/L at pH=3. Pseudo-second-order kinetic model is described as the following function:

$$\frac{t}{q_t} = \frac{1}{k_s + q_e^2} + \frac{1}{q_e} t$$

where q_e represents the amount of U on the adsorbent under equilibrium, and K_s is pseudo-second-order adsorption rate constant. Figure S3 shows that the t/q_t as a function of t fit very well with a line at high correlation coefficient of 0.99, indicating that the adsorption procedure according with pseudo-second-order adsorption.

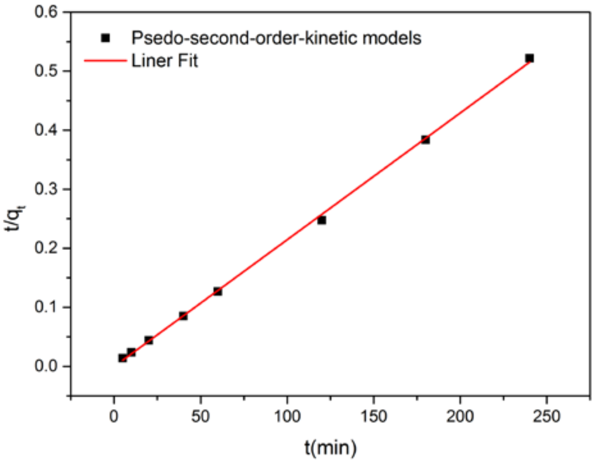

Fig. S4 Pseudo-second-order kinetic model of UO_2^{2+} adsorption on adsorbent.

5.4 Adsorption isothermal

The Langmiur isotherm model was fitted to the experiment data to study the adsorption model. The Langmiur isotherm model indicates that the adsorption procedure carries out on a homogeneous surface through the monolayer adsorption. The equation of the Langmiur isotherm model is represented as following:

$$\frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m}$$

where q_m is the maximum adsorption when the adsorption reaches equilibrium, and k_L is a constant characterized by the affinity of the adsorbate with the adsorbent. The value of c_e/q_e as the function of c_e were plotted and fitted with a linear equation from which the q_m and k_L could be calculated according to the slope and intercept.

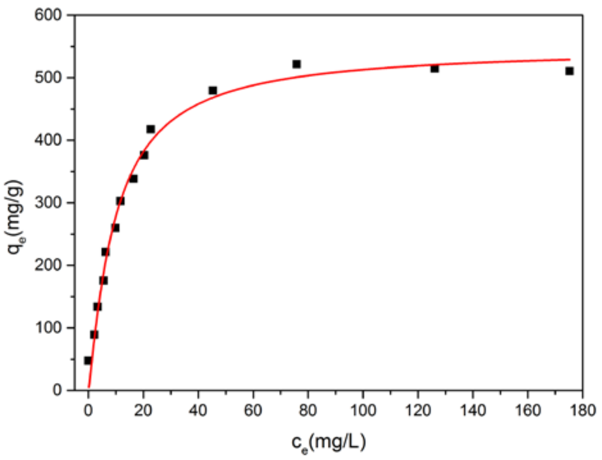

Fig. S5 Adsorption isothermal of UO_2^{2+} on the Fe_3O_4@ZIF-8

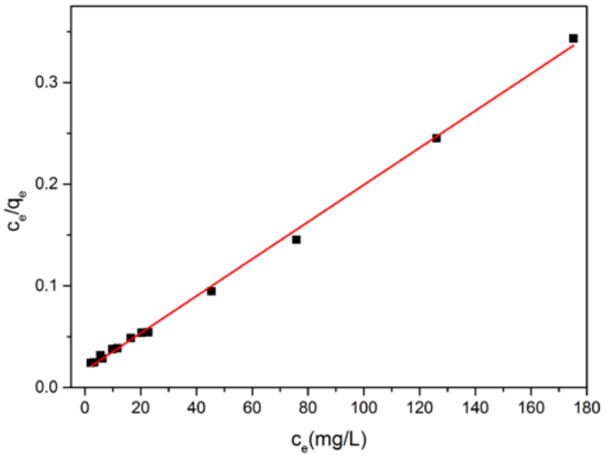

Fig. S6 Linearized plot of Langmuir isothermal model for UO_2^{2+} adsorption.

Table S2 The UO_2^{2+} adsorption capacity of different samples.

sample	Abs	q_e (mg/g)
Fe_3O_4	1.9751	169.8613
ZIF-8	0.3227	529.7045
Fe_3O_4@ZIF-8	0.5549	479.3872

5.5 Selectivity text

The selectivity text of UO_2^{2+} adsorption from aqueous solution containing lanthanide ions was carried out at pH=3. The initial concentration of all metal ions is 1mmol/L, and the residual concentration in the supernatant of metal ions was determined inductively coupled plasma mass spectrometry (ICP-MS).

The selectivity coefficient ($S_{U/M}$) for U relative to competing ions is defined as:

$$S_{U/M} = \frac{K_d^U}{K_d^M}$$

$$K_{\mathrm{d}} = \frac{(c_0 - c_e) \times \mathrm{V}}{c_e \times \mathrm{m}}$$

where K_d^U and K_d^M are the distribution ratio of U and competing ions in adsorbent and solution, respectively.

Table S3 The selectivity coefficients of U for lanthanide ions on the adsorbent.

sample	La	Nd	Eu	Dy	Er
q_e(mg/g)	25.8	42.5	12.5	43.2	28.3
K_d	173.6	294.6	74.4	299.2	134.9
$S_{U/M}$	56.6	33.4	132.2	32.9	72.9

5.6 Desorption experiments

1 mol/L Na_2CO_3 as the elution solution was used to desorption experiment. After the adsorption equilibrium was obtained, the solid sample was separated by a magnet in a few minutes, and the supernate of the sample was taken out with equal volume of Na_2CO_3 solution instead. The desorption samples were stirred for 3 hours to get equilibrium and separated by a magnet. The UO_2^{2+} concentration in the supernate of the desorption samples were determined by UV–Visible spectrometry. The desorption quantity of U was calculated from the difference of U content before and after desorption in the supernatant. Desorption efficiency is described as amount of U desorption to adsorption ratio.

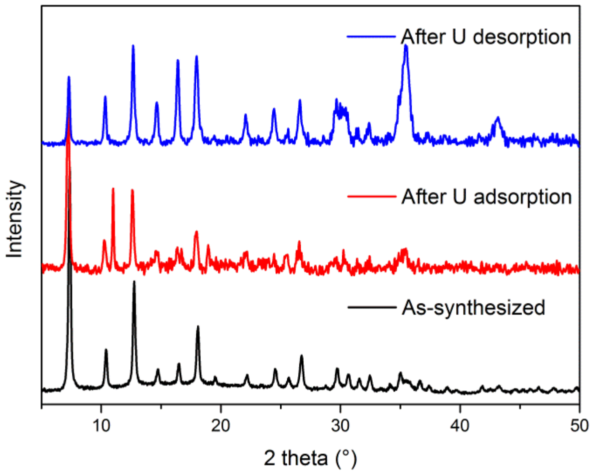

Fig. S7 The PXRD patterns of Fe_3O_4@ZIF-8 after U adsorption and desorption.