

## Electronic Supplementary Information

Highly efficient removal of uranium from highly acidic media  
achieved on a phosphine oxide and amino functionalized  
superparamagnetic composite polymer adsorbent

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### **Synthesis of Fe<sub>3</sub>O<sub>4</sub> hollow microspheres prepared by solvothermal method**

Water-dispersible monodisperse hollow Fe<sub>3</sub>O<sub>4</sub> microspheres were synthesized using a hydrothermal method. In a typical experiment, 5 mmol FeCl<sub>3</sub> · 6H<sub>2</sub>O, 10 mmol sodium citrate were dissolved in 80 ml distilled water to form yellow transparent solution. Then 1 g urea was added in above solution, followed by the addition of 0.6 g PAAS. After 30 min vigorously magnetic stirring, the viscous transparent mixture was transferred to a 100 ml Teflon-lined stainless-steel autoclave and maintained at 200 °C for 12 h. The product was collected with a magnet and washed with distilled water and ethanol for several times. Finally, the sample was dried in a vacuum oven at 45 °C for 12 h.

### **Detailed experiments of activated Fe<sub>3</sub>O<sub>4</sub> hollow microspheres by KH570**

Amounts of 0.3 g of hollow Fe<sub>3</sub>O<sub>4</sub> microspheres, 128.0 ml of ethanol and 4.0 ml of KH570 were dissolved in 36.0 ml of distilled water in a 250 ml three-neck flask, and then 4.0 ml of NH<sub>3</sub> · H<sub>2</sub>O was added. The obtained mixture was incubated at 40 °C with moderate shaking at 190 rpm for 12 h. Then, the product was separated using a magnet, washed several times with ethanol and deionized water and dried by lyophilization.

### **Synthesis of magnetic adsorbents bearing carboxyl groups by DPP method**

In a typical run, an amount of 0.15 g of the surface-activated hollow  $\text{Fe}_3\text{O}_4$  microspheres was immersed in 80.0 ml of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 2.0 g ml of ethyleneglycol dimethacrylate (EGDMA) and 2.0 g of acrylic acid (AA) were added to the mixture. Thereafter, the mixture was heated to 90 °C with a ramping rate of 1 °C per minute for 2 h with a mechanical stirring rate of 200 rpm. Then, the obtained hollow  $\text{Fe}_3\text{O}_4/\text{P}$  (EGDMA-AA) microspheres were separated using an external magnet, washed several times with ethanol and deionized water and dried by lyophilization.

### **Synthesis of magnetic adsorbents bearing epoxy groups by DPP method**

In a typical run, an amount of 0.15 g of the surface-activated hollow  $\text{Fe}_3\text{O}_4$  microspheres was immersed in 80.0 ml of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 2.0 g ml of EGDMA and 2.0 g of glycidyl methacrylate (GMA) were added to the mixture. Thereafter, the mixture was heated to 90 °C with a ramping rate of 1 °C per minute for 2 h with a mechanical stirring rate of 200 rpm. Then, the obtained hollow  $\text{Fe}_3\text{O}_4/\text{P}$  (EGDMA-GMA) microspheres were separated using an external magnet, washed several times with ethanol and deionized water and dried by lyophilization.

### **Synthesis of magnetic adsorbents bearing hydroxyl group by DPP method**

In a typical run, an amount of 0.15 g of the surface-activated hollow  $\text{Fe}_3\text{O}_4$  microspheres was immersed in 80.0 ml of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 2.0 g ml of EGDMA and 2.0 g of hydroxyethyl methacrylate (HEMA) were added to the mixture. Thereafter, the mixture was heated to 90 °C with a ramping rate of 1 °C per minute for 2 h with a mechanical stirring rate of 200 rpm. Then, the obtained hollow  $\text{Fe}_3\text{O}_4/\text{P}$  (EGDMA-HEMA) microspheres were separated using an external magnet, washed several times with ethanol and deionized water and dried by lyophilization.

### **Synthesis of magnetic adsorbents bearing ester group by DPP method**

In a typical run, an amount of 0.15 g of the surface-activated hollow  $\text{Fe}_3\text{O}_4$  microspheres was immersed in 80.0 ml of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 2.0 g ml of EGDMA and 2.0 g of methyl methacrylate (MMA) were added to the mixture. Thereafter, the mixture was heated to 90 °C with a ramping rate of 1 °C per minute for 2 h with a mechanical stirring rate of 200 rpm. Then, the obtained hollow  $\text{Fe}_3\text{O}_4/\text{P}$  (EGDMA-MMA) microspheres were separated using an external magnet, washed several times with ethanol and deionized water and dried by lyophilization.

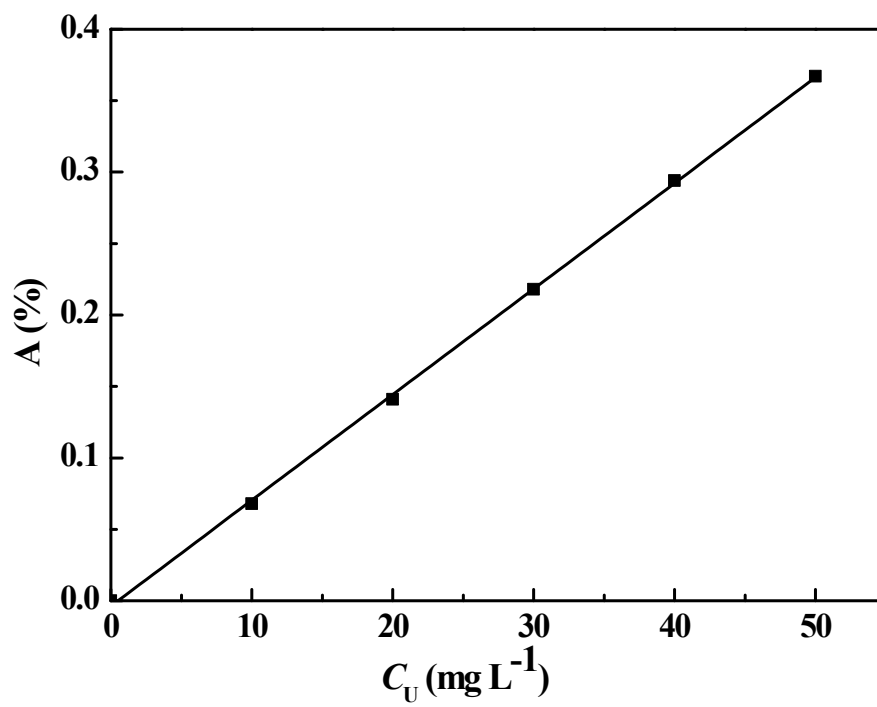
### **Fe<sub>3</sub>O<sub>4</sub>/P (DMAA-DMP) developed by soap free emulsion polymerization**

Diallylamine (DMAA) (2.0 g) and di (methacryloxyethyl) phosphate (DMP) (2.0 g), methyl methacrylate (MMA) (3 g) and acrylic acid (AA) (0.25 g) constituted the oil phase. Next water (75mL) was added to the oil phase was added and homogenized at room temperature with an ultrasound mixer for 10 min. The mixture was then charged in a four-necked flask equipped with a stirrer, a condenser. When the mixture was heated to 54°C, 2.5 g of Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (10%, w/w in water) that had been homogenized at room temperature with an ultrasound mixer for 10 min were added. Subsequently, while the mixture was heated to 70°C, KPS (0.15 g) which had been dissolved in 10 mL water was added. The mixture was maintained at 80°C for 12 h. The reaction mixture was cooled to room temperature and the resulting microspheres were washed with deionized water to remove the excess stabilizer and other impurities. Finally, the separated product was dried in a vacuum oven at 40°C for 12 h to give yellow magnetic composite microspheres (abbreviated as Fe<sub>3</sub>O<sub>4</sub>/P (DMAA-DMP)).

### **P (DMAA-DMP) developed by suspension polymerization**

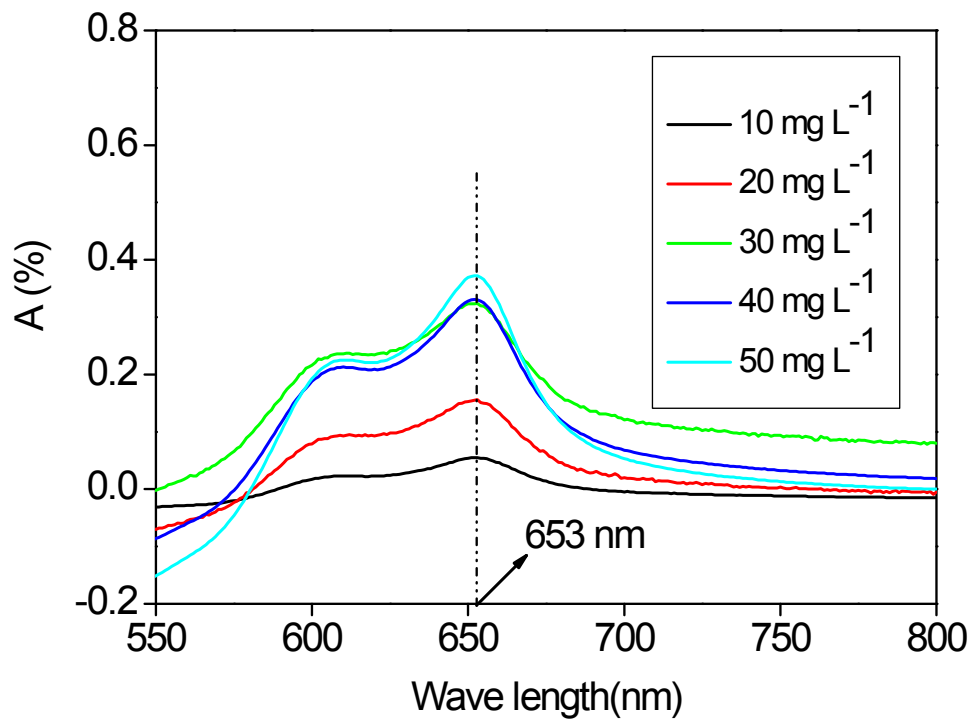
The composition of the aqueous phase was water (250 mL) and poly (vinyl alcohol) (1.5 g). The organic phase was DMAA (2.0 g), DMP (2.0 g), toluene (3.0 mL), and AIBN (0.05 g). Polymerizations were run at 80 °C for 6 h. The resin beads were collected by filtration, washed with water and methanol, and then extracted overnight in a Soxhlet using either methylal. Finally, the beads P (DMAA-DMP) were washed with methanol and diethyl ether before drying in a vacuum oven.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{Eqn (S1)}$$

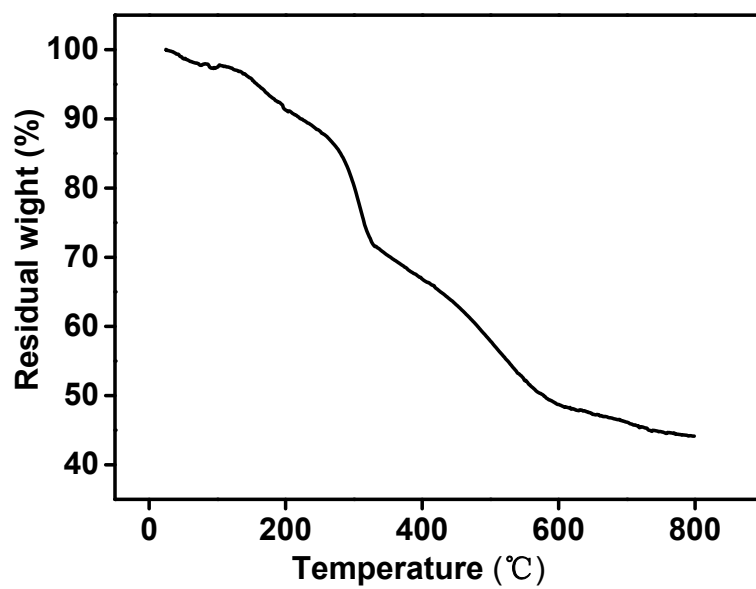


**Fig. S1** The calibration curve

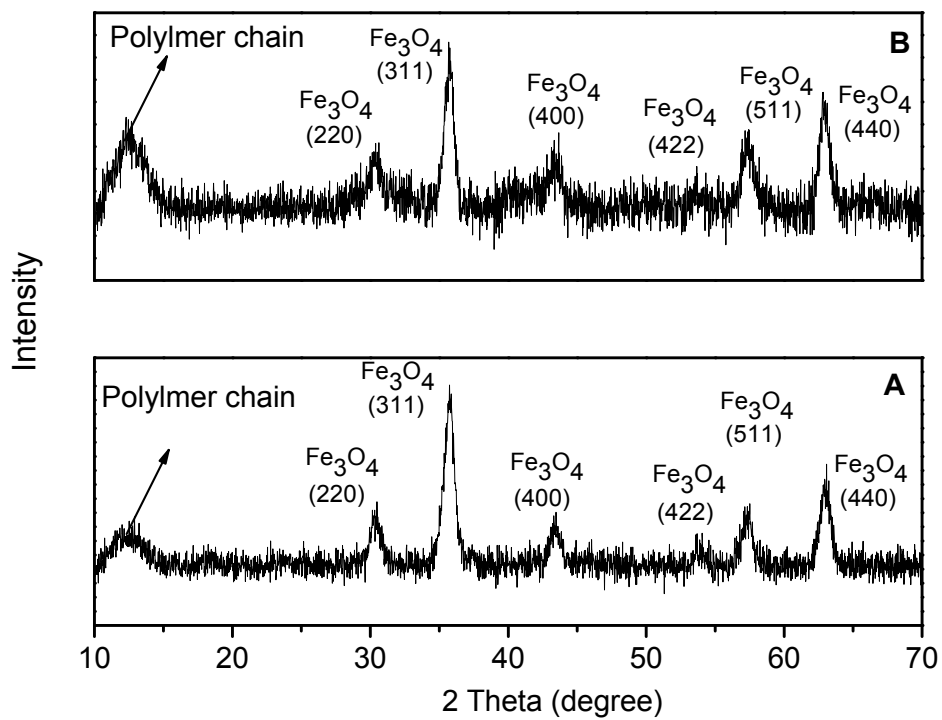




**Fig. S2** UV-Vis spectra for standard solutions



**Fig. S3** Thermogravimetric curve for Fe<sub>3</sub>O<sub>4</sub>/P (DMAA-DMP)



**Fig. S4** XRD pattern of Fe<sub>3</sub>O<sub>4</sub>/P (DMAA-DMP) before (A) and after (B) immersed in the HNO<sub>3</sub> solution at pH value of 0.5 for 24 h

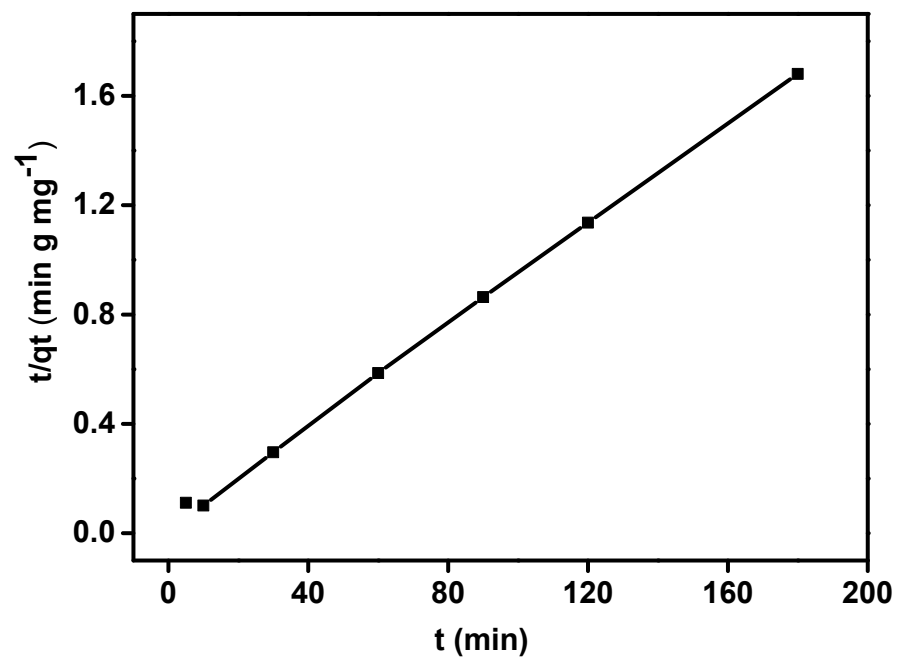
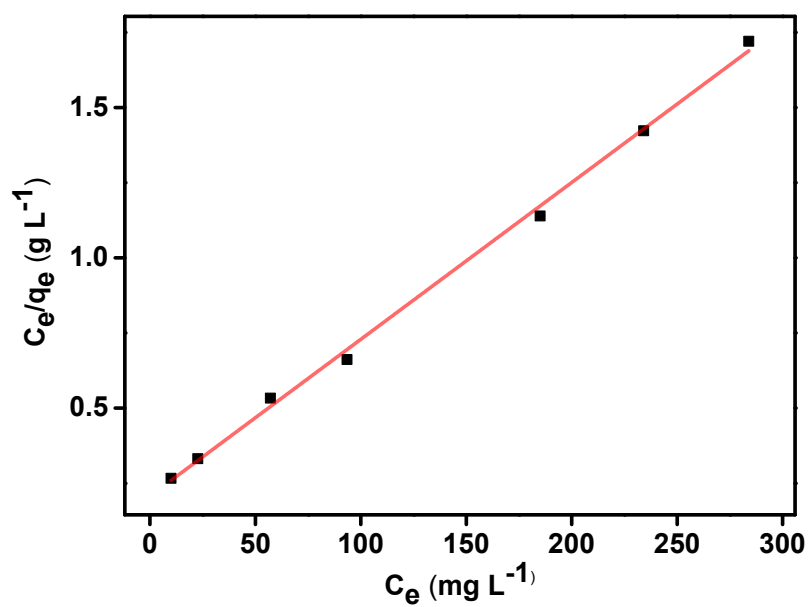
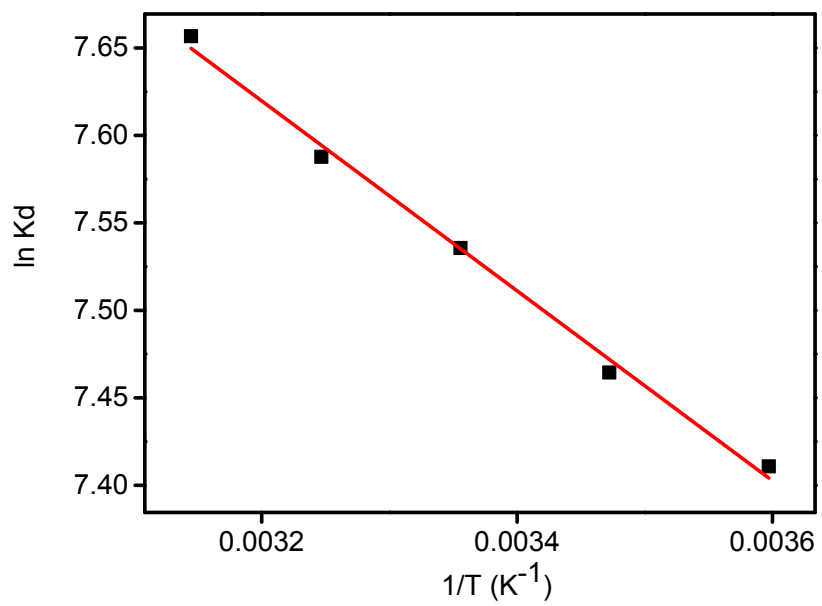


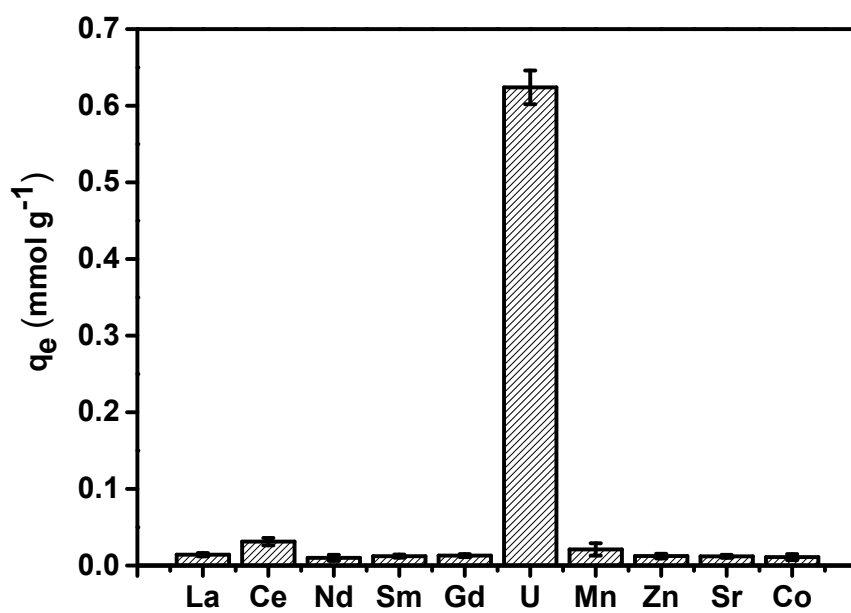
Fig. S5 Pseudo-second-order plot



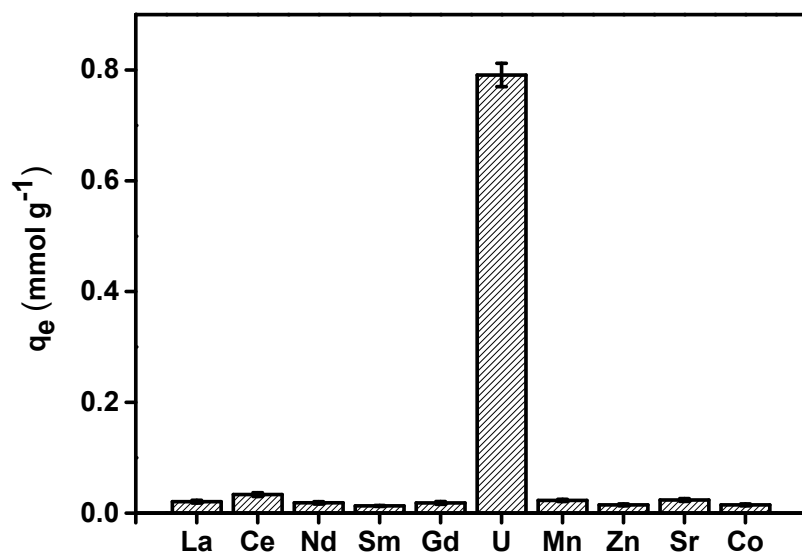
**Fig. S6** Langmuir model fitted the absorption isotherms of U (VI) on  $Fe_3O_4/P(DMAA-DMP)$



**Fig. S7** Thermodynamic fitting plot

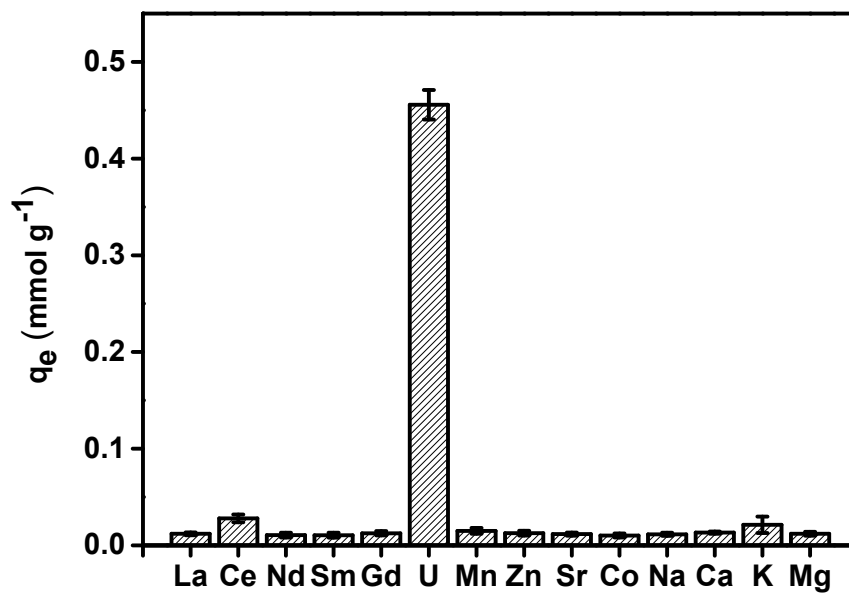


**Fig. S8** Impact of competitive ions on the adsorption capacity for uranium ( $C_0 = 0.5$   $\text{mmol L}^{-1}$  for all cations,  $\text{pH} = 1.5$ ,  $T = 298$  K,  $t = 180$  min, and  $m/V = 0.4$   $\text{g L}^{-1}$ )

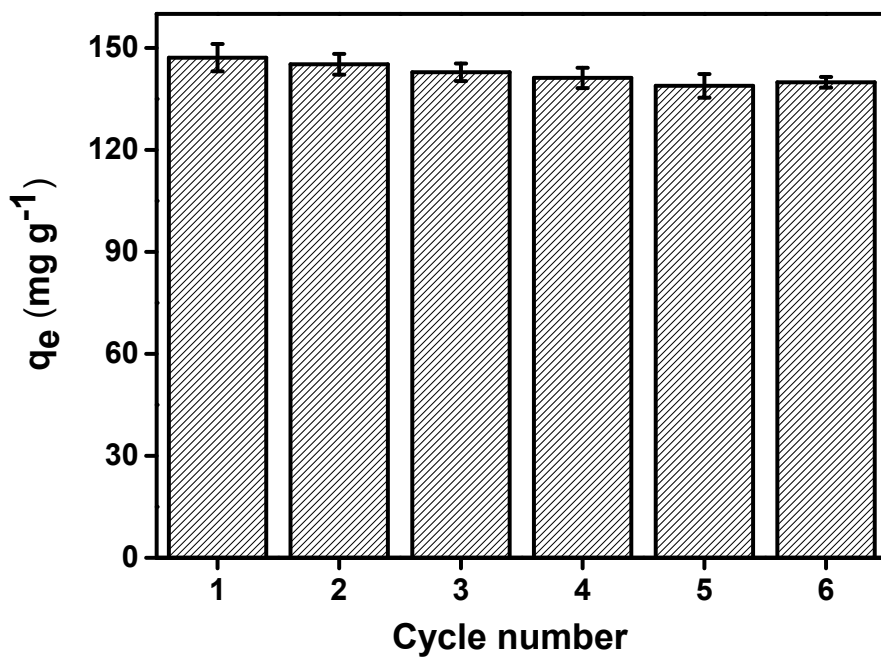


**Fig. S9** Impact of competitive ions on the adsorption capacity for uranium ( $C_0 = 0.5$   $\text{mmol L}^{-1}$  for all cations,  $\text{pH} = 2.5$ ,  $T = 298$  K,  $t = 180$  min, and  $m/V = 0.4$   $\text{g L}^{-1}$ )

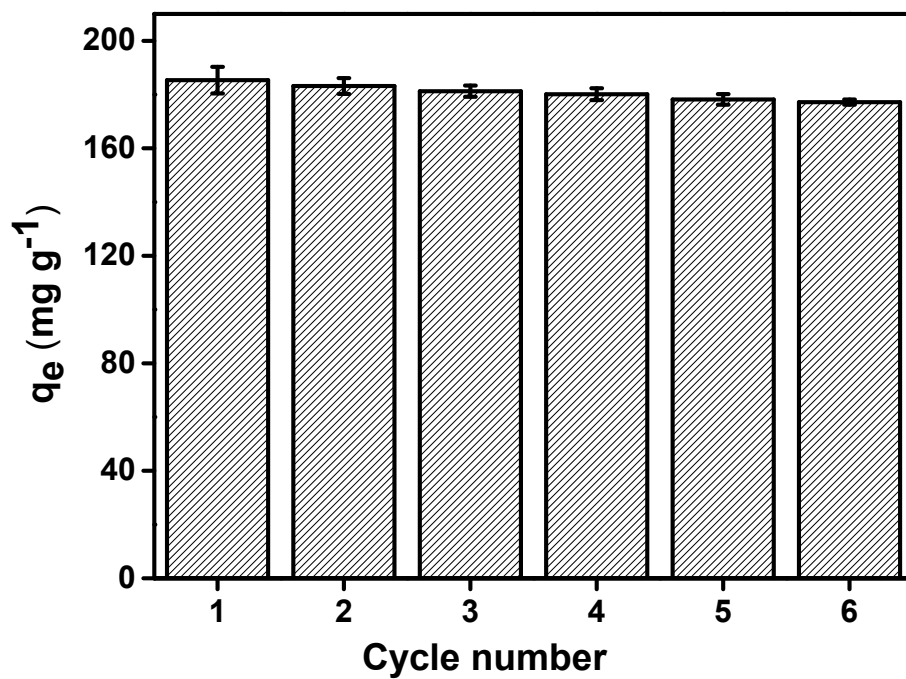




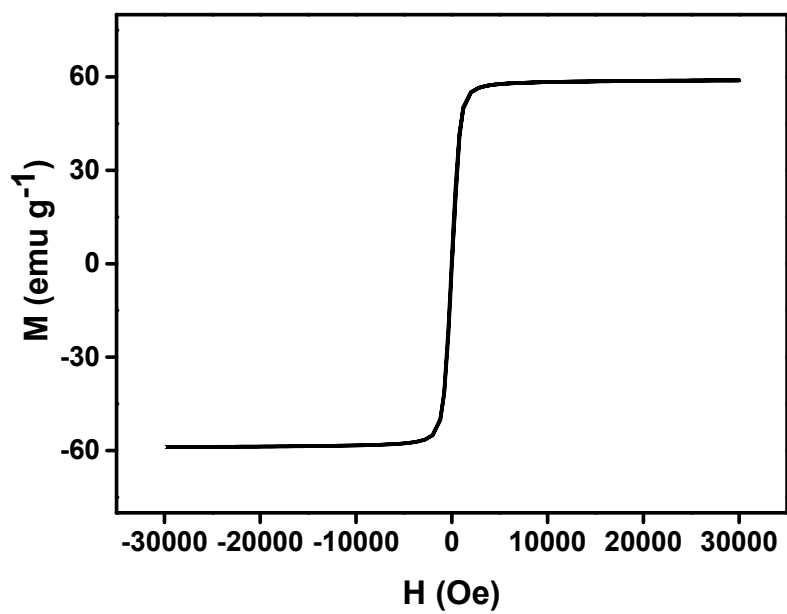
**Fig. S10** Impact of competitive ions on the adsorption capacity for uranium ( $C_0 = 0.5$  mmol L<sup>-1</sup> for all cations, pH = 0.5, T = 298 K, t = 180 min, and m/V = 0.4 g L<sup>-1</sup>)



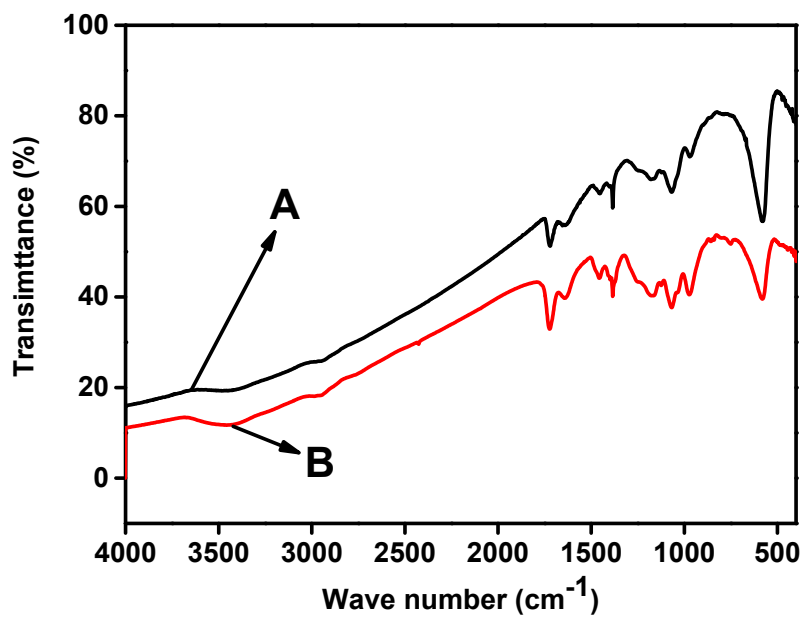
**Fig. S11** Recycling of  $\text{Fe}_3\text{O}_4/\text{P}$  (DMAA-DMP) in the removal of U (VI) ( $T = 298 \text{ K}$ ,  $\text{pH} = 1.5$ ,  $t = 180 \text{ min}$ ,  $m/V = 0.4 \text{ g L}^{-1}$ ,  $C_0 = 100 \text{ mg L}^{-1}$ )



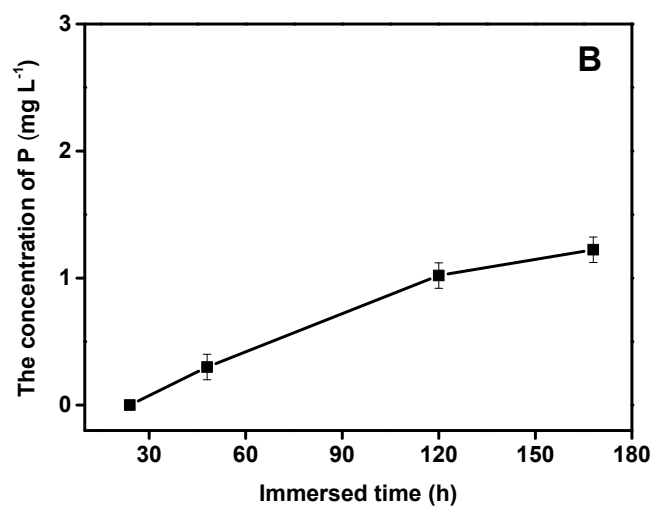
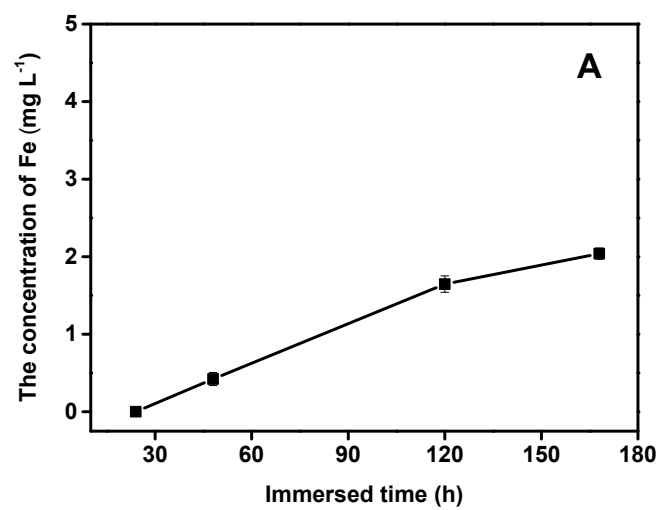
**Fig. S12** Recycling of  $\text{Fe}_3\text{O}_4/\text{P}$  (DMAA-DMP) in the removal of U (VI) ( $T = 298 \text{ K}$ ,  $\text{pH} = 2.5$ ,  $t = 180 \text{ min}$ ,  $m/V = 0.4 \text{ g L}^{-1}$ ,  $C_0 = 100 \text{ mg L}^{-1}$ )



**Fig. S13** The magnetization curve measured at room temperature for  $\text{Fe}_3\text{O}_4/\text{P}$  (DMAA-DMP) after immersed in the  $\text{HNO}_3$  solution at pH value of 0.5 for 24 h



**Fig. S14** (A) Fe<sub>3</sub>O<sub>4</sub>/P (DMAA-DMP) before (A) and after (B) immersed in HNO<sub>3</sub> solution at pH value of 0.5 for 24 h



**Fig. S15** Effect of immersed time on the leaching of Fe (A) and P (B) from the magnetic adsorbent Fe<sub>3</sub>O<sub>4</sub>/P (DMAA-DMP) at pH value of 0.5

**Table. S1**

Kinetic parameters for uranium adsorption on Fe<sub>3</sub>O<sub>4</sub>/P (DMAA-DMP) at pH value of 0.5

Kinetic model	Parameter	Value
Pseudo-first-order	$k_1$ (1 min <sup>-1</sup> )	0.02321
	$q_{e. cal}$ (mg g <sup>-1</sup> )	21.07
	R <sup>2</sup>	0.6345
Pseudo-second-order	$k_2$ [g (mg <sup>-1</sup> min <sup>-1</sup> )]	0.0024
	$q_{e. cal}$ (mg g <sup>-1</sup> )	109.2
	R <sup>2</sup>	0.9989
Intraparticle diffusion	$K_{int}$ [mg (g <sup>-1</sup> min <sup>-1/2</sup> )]	3.50
	$c$ (mg g <sup>-1</sup> )	68.29
	R <sup>2</sup>	0.3217

**Table. S2**

Adsorption isotherms parameters for uranium on Fe<sub>3</sub>O<sub>4</sub>/P (DMAA-DMP) at pH value of 0.5

Adsorbent	Model	Parameter	Value
Fe <sub>3</sub> O <sub>4</sub> /P (DMAA-DMP)	Langmuir	$b$ (L mg <sup>-1</sup> )	0.023
		$q_{max}$ (mg g <sup>-1</sup> )	196.4
		R <sup>2</sup>	0.9975
	Freundlich	$K_F$ (mg g <sup>-1</sup> )	16.22
		$n_F$	2.286
		R <sup>2</sup>	0.9325

**Table. S3**

Thermodynamic parameters of thorium adsorption on Fe<sub>3</sub>O<sub>4</sub>/P (DMAA-DMP) at pH value of 0.5

$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/mol/K)	$\Delta G^\circ$ (KJ/mol)				
		278 K	288 K	298 K	308 K	318 K
4.514	77.79	-17.11	-17.89	-18.67	-19.45	-20.22

**Table. S4**

Comparison of adsorption of uranium on the magnetic adsorbent Fe<sub>3</sub>O<sub>4</sub>/P(DMAA-DMP) before and after immersed in highly acidic media at pH value of 0.5 for 24 h<sup>a</sup>

Adsorbents	q <sub>e</sub> (mg g <sup>-1</sup> )
Fe <sub>3</sub> O <sub>4</sub> /P(DMAA-DMP) <sup>b</sup>	107.1
Fe <sub>3</sub> O <sub>4</sub> /P(DMAA-DMP) <sup>c</sup>	103.2

<sup>a</sup> Sorption condition (C<sub>0</sub>=100 mg L<sup>-1</sup>, pH=0.5, T=298 K, t=180 min, and m/V=0.4 g L<sup>-1</sup>).

<sup>b</sup> The fresh magnetic adsorbent before immersed in highly acidic media at pH value of 0.5 for 24 h.

<sup>c</sup> The magnetic adsorbent after immersed in highly acidic media at pH value of 0.5 for 24 h.



**Table. S5**

Comparison of adsorption of uranium on various magnetic adsorbents in highly acidic media <sup>a</sup>

Adsorbents	$q_{\max}$ (mg g <sup>-1</sup> ) for U (VI)	pH
Fe <sub>3</sub> O <sub>4</sub>	0	0.5
Activated Fe <sub>3</sub> O <sub>4</sub> with KH570	0	0.5
Fe <sub>3</sub> O <sub>4</sub> /P(DMAA-DMP)	196.4	0.5

<sup>a</sup> Sorption condition ( $C_0=100$  mg L<sup>-1</sup> for U (VI),  $T=298$  K,  $t=180$  min, and  $m/V=0.4$  g L<sup>-1</sup>).

**Table.S6**

Comparison of BET specific surface areas of Fe<sub>3</sub>O<sub>4</sub>/P (DMAA-DMP) with Fe<sub>3</sub>O<sub>4</sub> and activated Fe<sub>3</sub>O<sub>4</sub> with KH570 prepared in this work.

Adsorbents	BET specific surface areas (m <sup>2</sup> g <sup>-1</sup> )
Fe <sub>3</sub> O <sub>4</sub>	50.1
Activated Fe <sub>3</sub> O <sub>4</sub> with KH570	45.2
Fe <sub>3</sub> O <sub>4</sub> /P (DMAA-DMP)	26.7

**Table. S7**

Comparison of adsorption capacity for uranium on various magnetic adsorbents in highly acidic media <sup>a</sup>

Adsorbents	$q_{\max}$ (mg g <sup>-1</sup> ) for U (VI)	pH
Fe <sub>3</sub> O <sub>4</sub> /P(DMAA-DMP)	196.4	0.5
Fe <sub>3</sub> O <sub>4</sub> /P(EGDMA-AA)	0	0.5
Fe <sub>3</sub> O <sub>4</sub> /P(EGDMA-GMA)	0	0.5
Fe <sub>3</sub> O <sub>4</sub> /P(EGDMA-HEMA)	0	0.5
Fe <sub>3</sub> O <sub>4</sub> /P(EGDMA-MMA)	0	0.5

<sup>a</sup> Sorption condition ( $C_0=100$  mg L<sup>-1</sup> for U (VI), T=298 K, t=180 min, and m/V=0.4 g L<sup>-1</sup>).

**Table. S8**

Comparison of adsorption capacity of Fe<sub>3</sub>O<sub>4</sub>/P (DMAA-DMP) prepared by DPP method with Fe<sub>3</sub>O<sub>4</sub>/P (DMAA-DMP) developed by soap free emulsion polymerization and P (DMAA-DMP) prepared by suspension polymerization in highly acidic media <sup>a</sup>

Adsorbents	Polymerization method	q <sub>e</sub> (mg g <sup>-1</sup> )
Fe <sub>3</sub> O <sub>4</sub> /P (DMAA-DMP)	DPP	107.1
Fe <sub>3</sub> O <sub>4</sub> /P (DMAA-DMP)	Soap free emulsion polymerization	0
P (DMAA-DMP)	Suspension polymerization	0

<sup>a</sup> C<sub>0</sub> = 100 mg L<sup>-1</sup>, T = 298 K, t = 180 min, pH=0.5, m/V = 0.4 g L<sup>-1</sup>