# Highly efficient extraction of uranium from strong HNO$_3$ media achieved on a phosphine oxide functionalized superparamagnetic composite polymer microspheres

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**Synthesis of Fe₃O₄ hollow microspheres prepared by solvothermal method**

Water-dispersible monodisperse hollow $Fe_3O_4$ microspheres were synthesized using a hydrothermal method. In a typical experiment, 5 mmol $FeCl_3 \cdot 6H_2O$, 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.

**Synthesis of Fe₃O₄@SiO₂ microspheres prepared by the hydrolysis of tetraethylorthosilicate (TEOS)**

$Fe_3O_4$ MNPs (1.0 g) was dispersed in a mixture of isopropanol (250 mL) and water (10 mL) by ultrasonic irradiation. After addition of 40 mL of ammonia solution (25 wt %), a mixture of TEOS (3.0 mL) and isopropanol (50 mL) was added dropwise to the reaction solution with mechanical stirring at room temperature. The suspension was mechanically stirred vigorously for 18 h at room temperature. The resulting $Fe_3O_4@SiO_2$ particles were washed by deionized water and ethanol and then collected by an external magnet.

**Detailed experiments of activated Fe₃O₄@SiO₂ microspheres by KH570**

Amounts of 0.3 g of Fe$_3$O$_4$@SiO$_2$ 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$_3$·H$_2$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 $Fe_3O_4@SiO_2$ microspheres was immersed in 80.0 ml of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 1.5 g of trimethylolpropane trimethacrylate (TRIM) and 1.5 g of acrylic acid (AA) were added to the mixture. Thereafter, the mixture was heated to refluxing temperature of acetonitrile for 2 h. Then, the obtained hollow $Fe_3O_4@SiO_2$ /P (TRIM-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 amide groups by DPP method**

In a typical run, an amount of 0.15 g of the surface-activated $Fe_3O_4@SiO_2$ microspheres was immersed in 80.0 ml of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 1.5 g of trimethylolpropane trimethacrylate (TRIM) and 1.5 g of acrylic amide (AM) were added to the mixture. Thereafter, the mixture was heated to refluxing temperature of acetonitrile for 2 h. Then, the obtained hollow $Fe_3O_4@SiO_2$ /P (TRIM-AM) 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 $Fe_3O_4@SiO_2$ microspheres was immersed in 80.0 ml of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 1.5 g of TRIM and 1.5 g of glycidyl methacrylate (GMA) were added to the mixture. Thereafter, the mixture was heated to refluxing temperature of acetonitrile for 2 h. Then, the obtained hollow $Fe_3O_4@SiO_2$/P (TRIM-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 $Fe_3O_4$ microspheres was immersed in 80.0 ml of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 1.5 g of TRIM and 2.0 g of hydroxyethyl methacrylate (HEMA) were added to the mixture. Thereafter, the mixture was heated to refluxing temperature of acetonitrile for 2 h. Then, the obtained hollow $Fe_3O_4$/P (TRIM-HEMA) microspheres were separated using an external magnet, washed several times with ethanol and deionized water and dried by lyophilization.

**The optimization of the synthetic route of the magnetic adsorbent Fe₃O₄@SiO₂/P (TRIM-VPA)**

As described in our work, the magnetic adsorbent $Fe_3O_4@SiO_2$/P (TRIM-VPA) was developed by distillation-precipitation polymerization (DPP). It has been found that the amount of VPA and TRIM had a great influence on the performance of the adsorbent and the amount of AIBN had no obvious effect on the property of the magnetic adsorbent. For example, when the amount of the used TRIM is less, the acid resistance of the magnetic polymer microspheres will become poor, due to TRIM is a crosslinking agent and has three vinyl groups. The function of TRIM is to enhance the strong acid resistance of the magnetic adsorbent further. Thus, when the TRIM was chosen as a monomer, the surface of $Fe_3O_4@SiO_2$ will be coated by a highly crosslinked polymer P (TRIM-VPA) obtained by DPP method, which could result in the $Fe_3O_4@SiO_2$/P (TRIM-VPA) has a good acid resistance further.

Besides, the amount of VPA has an obvious effect on the uranium adsorption capacity of the prepared magnetic adsorbent. For example, when the amount of VPA was 1.0 g, the uranium adsorption capacity of the prepared magnetic adsorbent was much less than that of the magnetic adsorbent when the 1.5 g of VPA was used. The function of VPA is to assure the prepared magnetic adsorbent has the ability to extract uranium from strong $HNO_3$ media, due to phosphine oxide groups have been reported to show a strong affinity towards uranium in strong $HNO_3$ media.
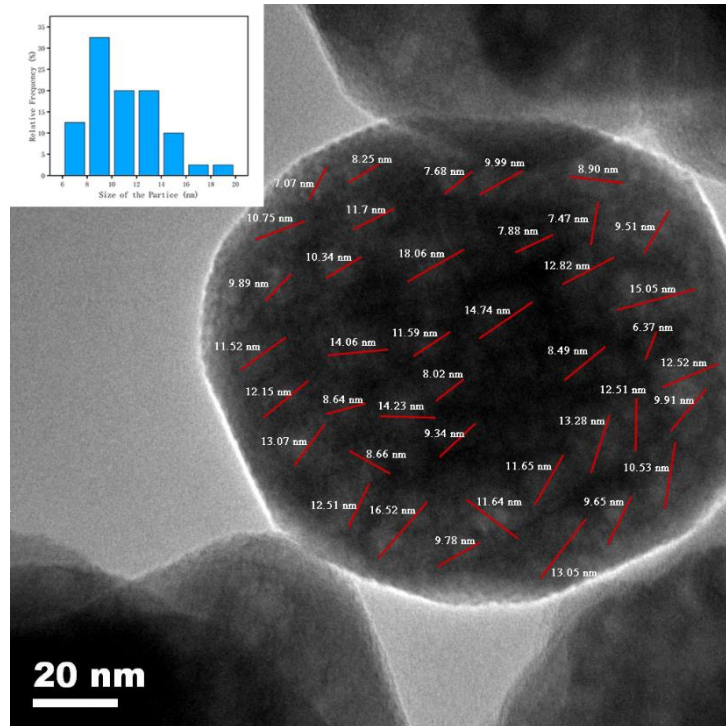
Thus, after optimization, the dosage of TRIM, VPA and AIBN was chosen to be 1.5 g, 1.5 g and 0.08 g respectively. Under this experimental condition, the value of uranium adsorption capacity of the magnetic adsorbent can reach up to the maximum.

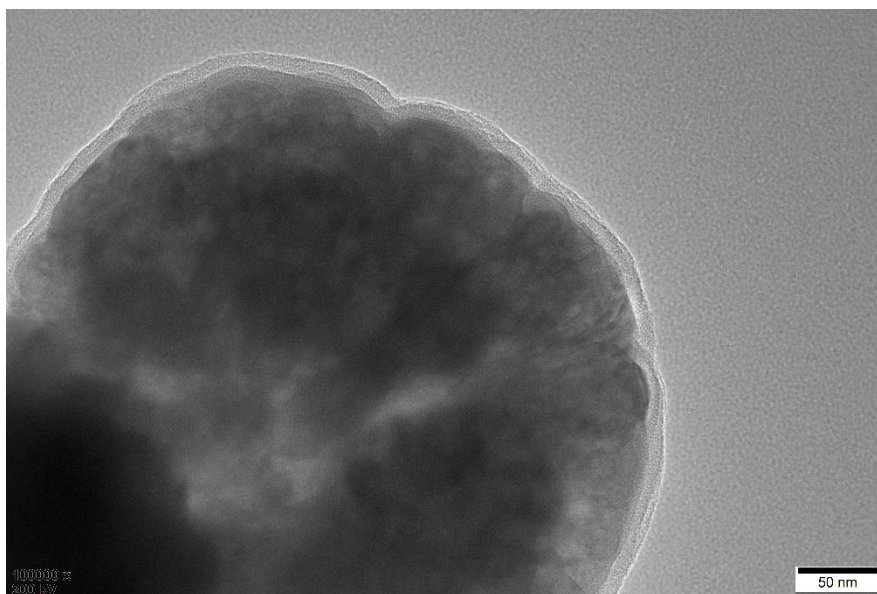$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad\qquad \text{Eqn (S1)}$$
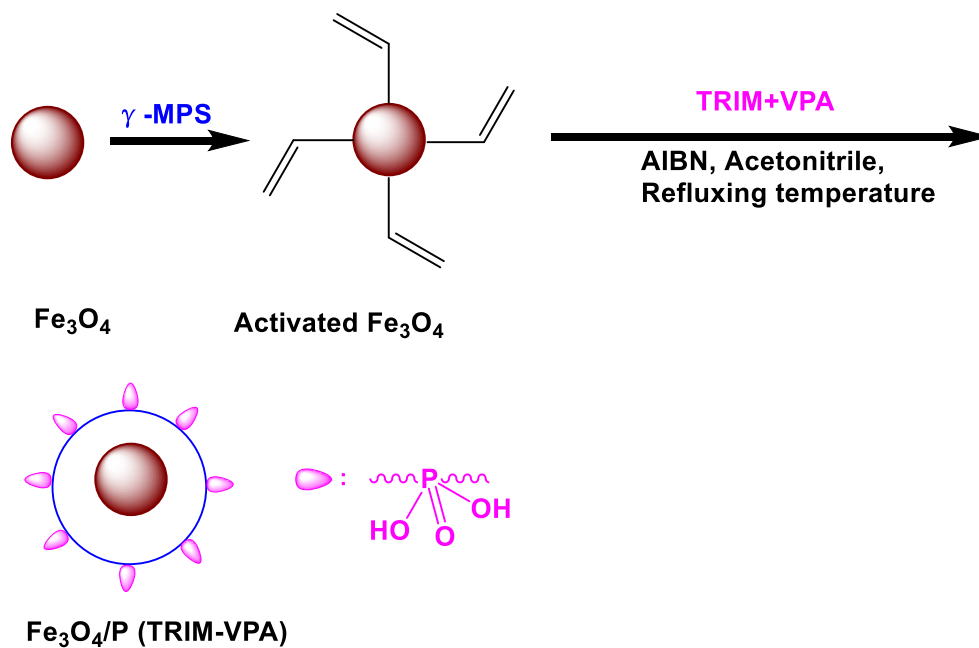
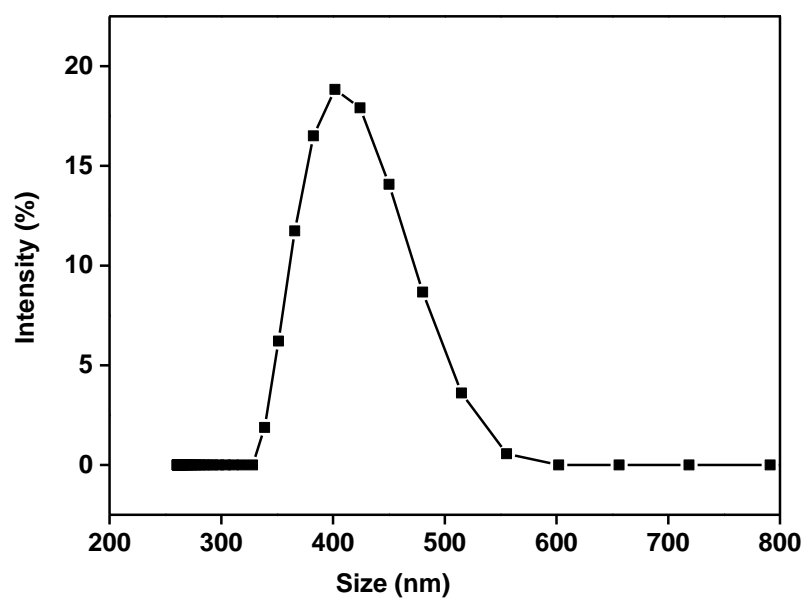**Scheme S1** Proposed synthesis of the magnetic adsorbent Fe₃O₄/P (TRIM-VPA)

**Fig. S1** The high-resolution TEM image of $Fe_3O_4$ (Inset: the $Fe_3O_4$ primary nanoparticle size distribution)

**Fig. S2** The high magnification TEM image of $Fe_3O_4@SiO_2$
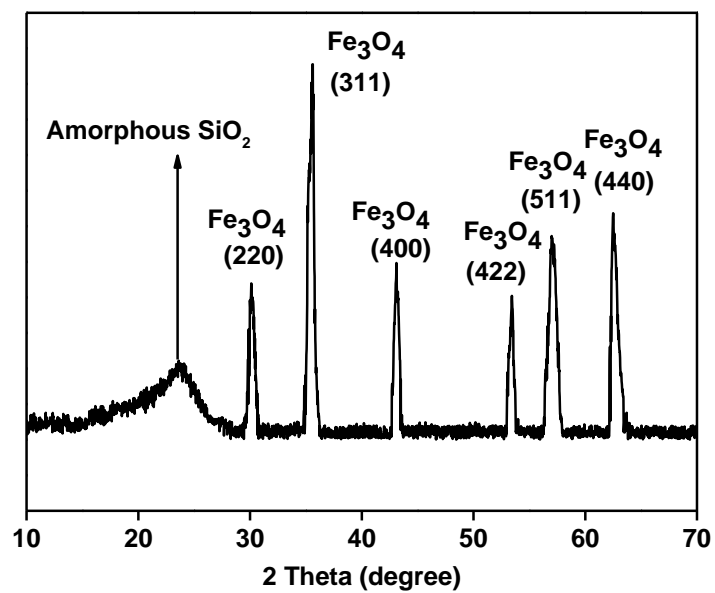
**Fig. S3** Particle size distribution of $Fe_3O_4@SiO_2/P(TRIM-VPA)$

**Fig. S4** XRD pattern of $Fe_3O_4@SiO_2$
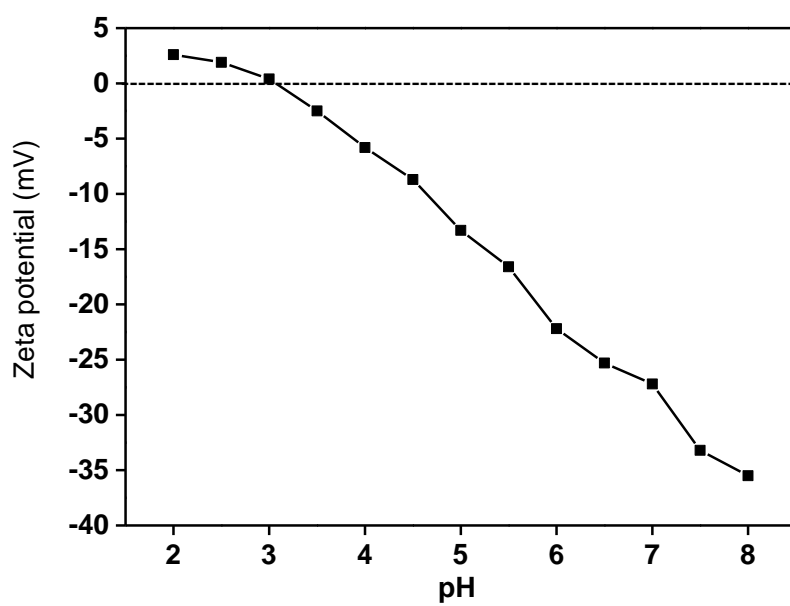
**Fig. S5** Zeta potentials of the magnetic adsorbent $Fe_3O_4@SiO_2/P$ (TRIM-VPA) as a

function of pH
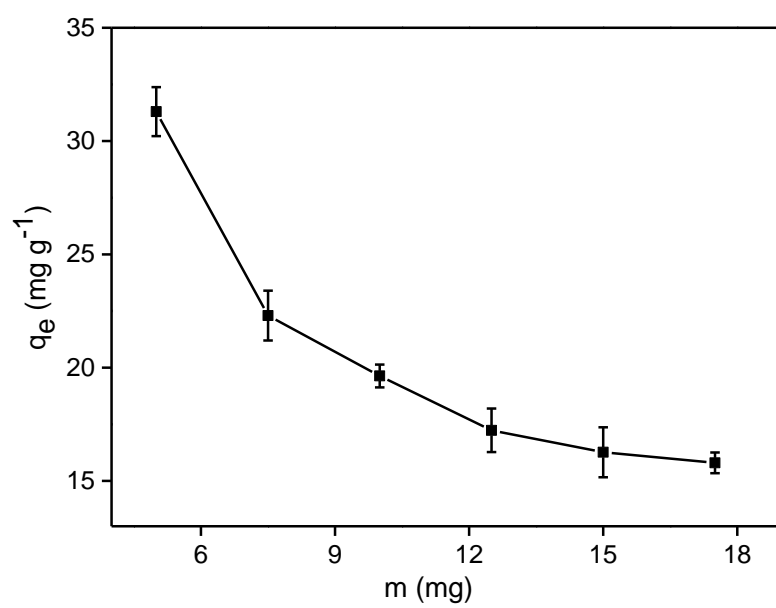
**Fig. S6** Effect of the amount of the magnetic adsorbent on the uranium adsorption capacity ($C_0$ = 100 mg L$^{-1}$, t=30 min, T = 298 K , $c$(H$^+$)=4 mol L$^{-1}$, V = 25 mL)
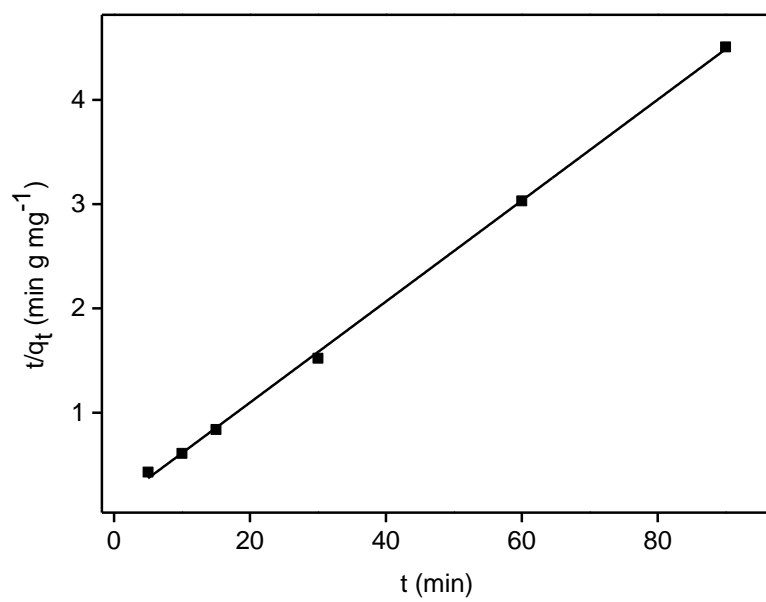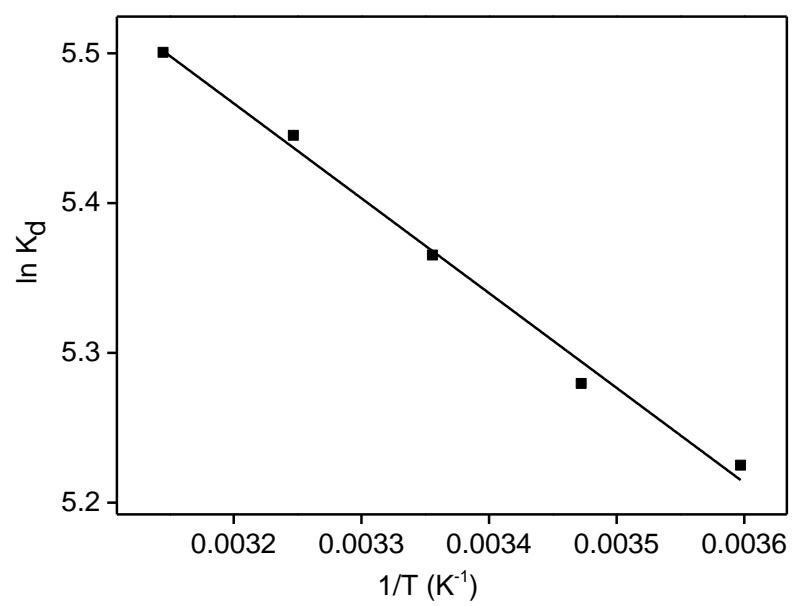
**Fig. S7** The pseudo-second-order plot
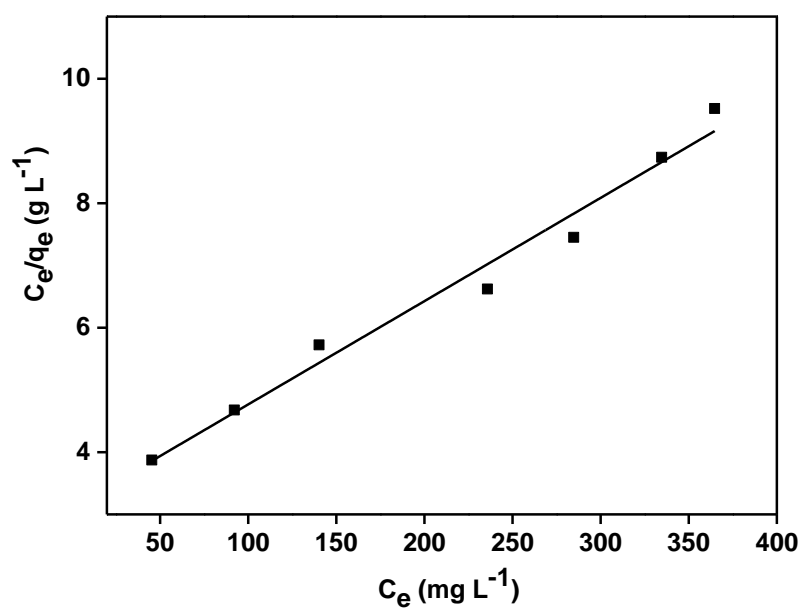
**Fig. S8** The Langmuir model fitted the absorption isotherms of U (VI) on $Fe_3O_4@SiO_2/P$
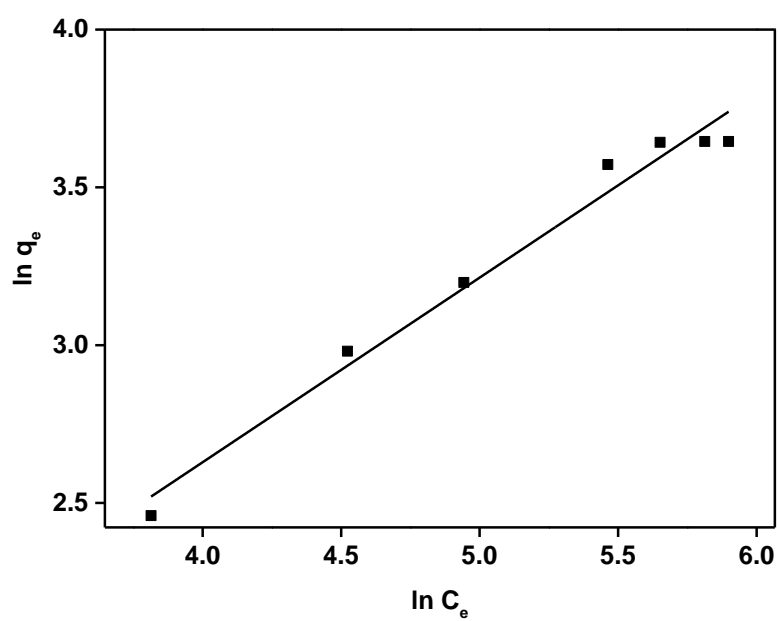
(TRIM-VPA)
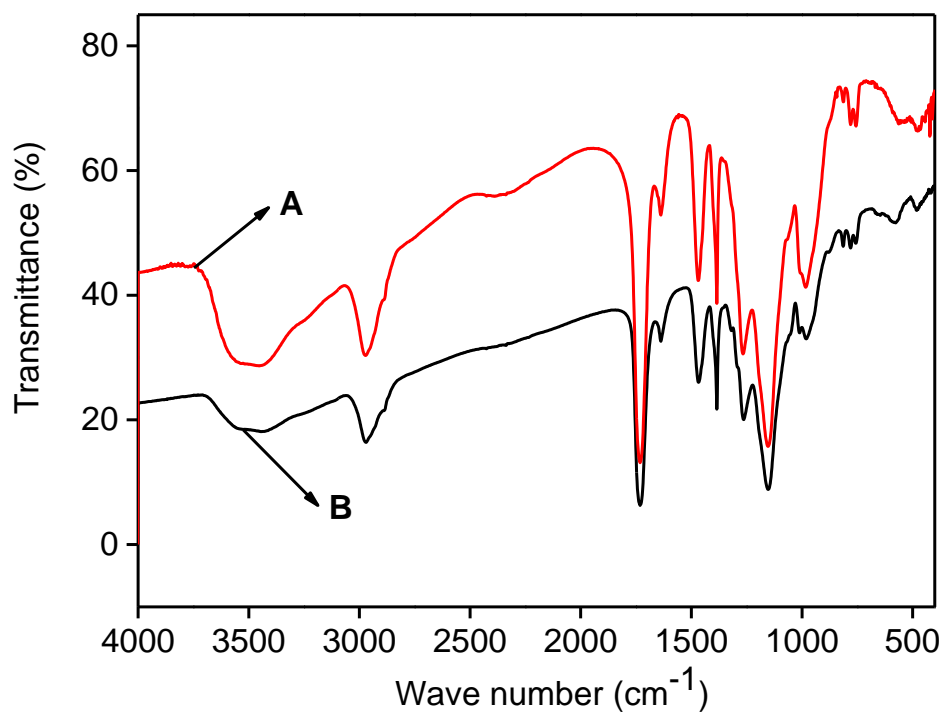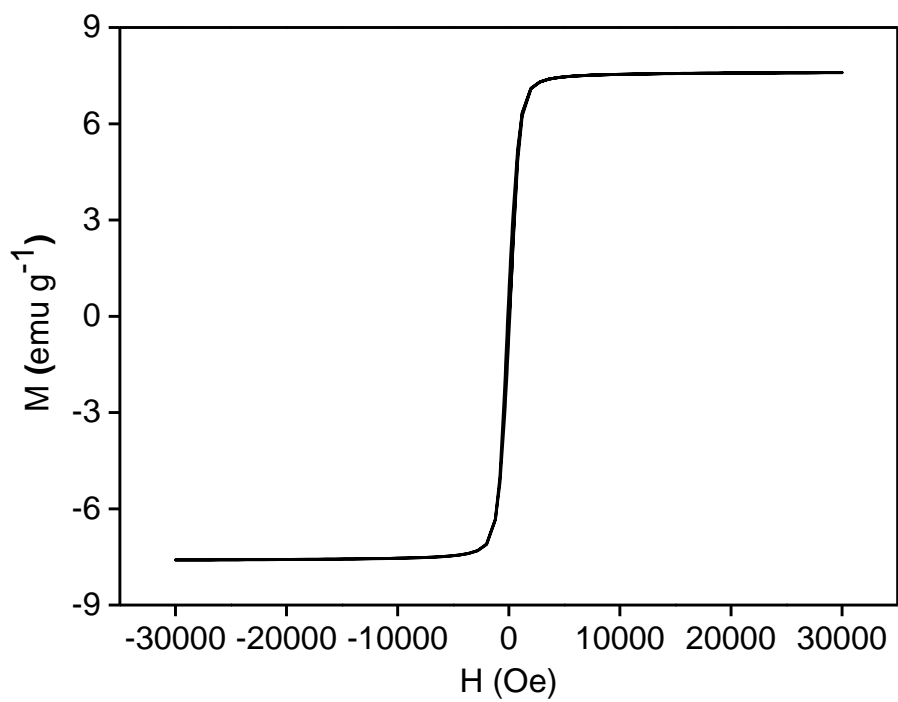
**Fig. S9** The Freundlich model fitted the absorption isotherms of U (VI) on $Fe_3O_4@SiO_2/P$
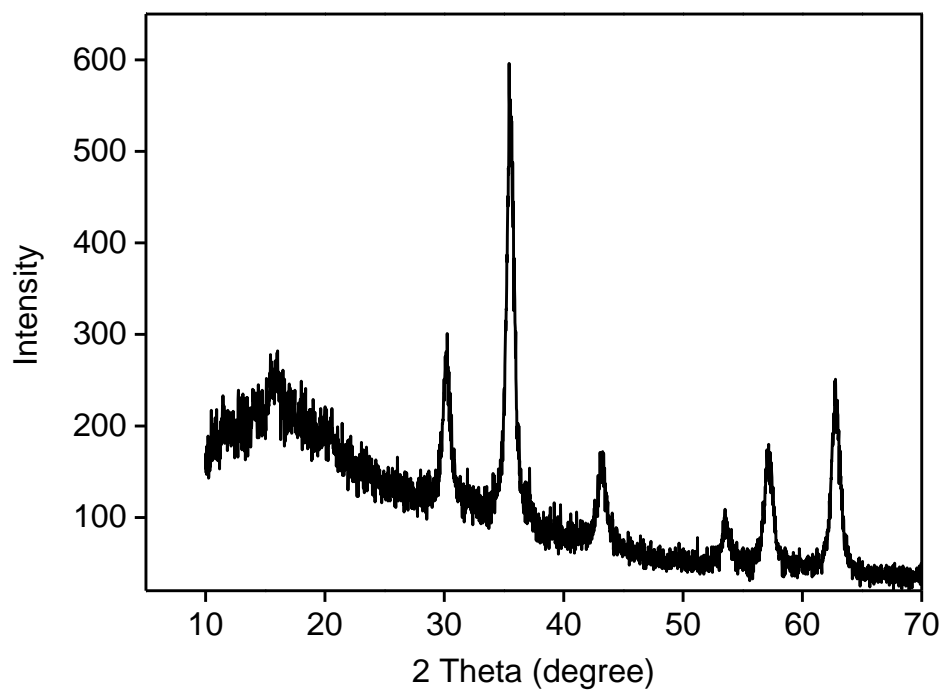
(TRIM-VPA)

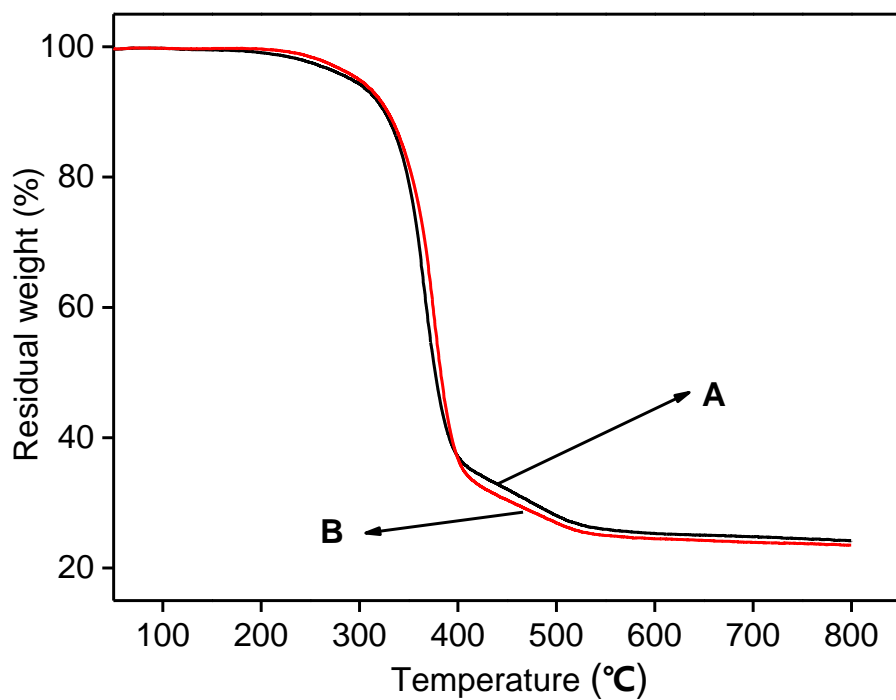**Fig. S10** Thermodynamic fitting plot

**Fig. S11** FT-IR spectra of (A) the fresh magnetic adsorbent and (B) the magnetic adsorbent

after immersed in 4 mol L$^{-1}$ of HNO$_3$ solution for 24 h.

**Fig. S12** The magnetization curve measured at room temperature for $Fe_3O_4@SiO_2/P$ (TRIM-VPA) after immersed in 4 mol $L^{-1}$ of $HNO_3$ solution for 24 h.

**Fig. S13** XRD pattern of $Fe_3O_4@SiO_2/P(TRIM-VPA)$ after immersed in 4 mol $L^{-1}$ of $HNO_3$

solution for 24 h.

**Fig. S14** TG curve of (A) the fresh magnetic adsorbent and (B) the magnetic adsorbent after

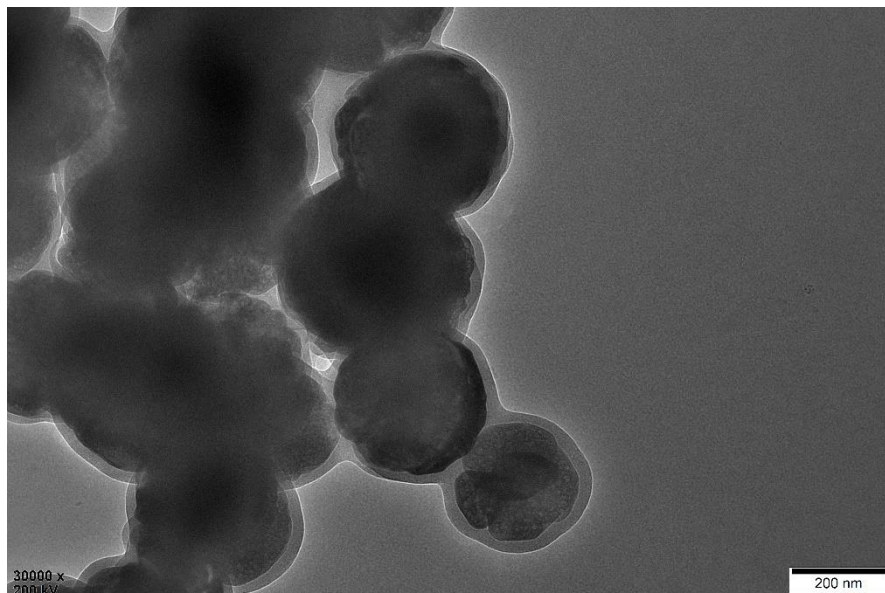immersed in 4 mol L$^{-1}$ of HNO$_3$ solution for 24 h.

**Fig. S15** The TEM image of $Fe_3O_4@SiO_2$ /P (TRIM-VPA) after immersed in 4 mol $L^{-1}$ of

$HNO_3$ for 24 h
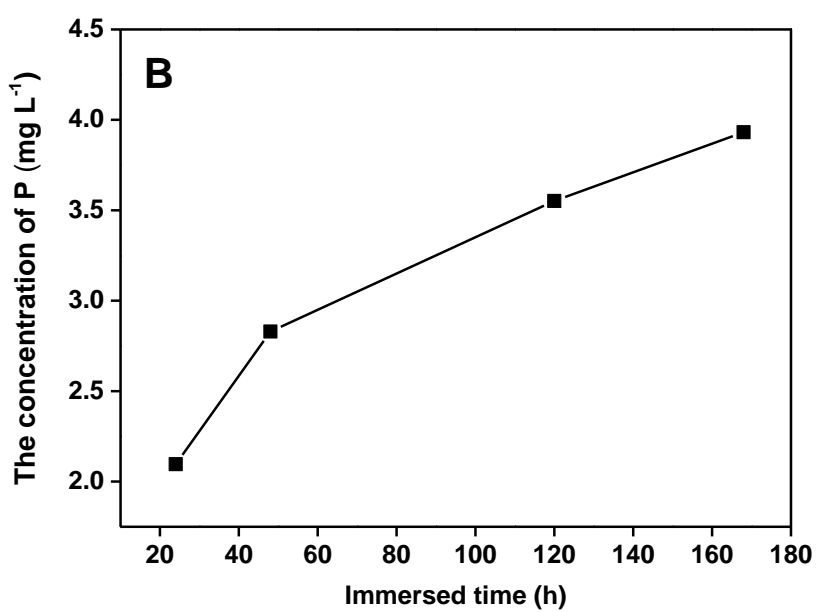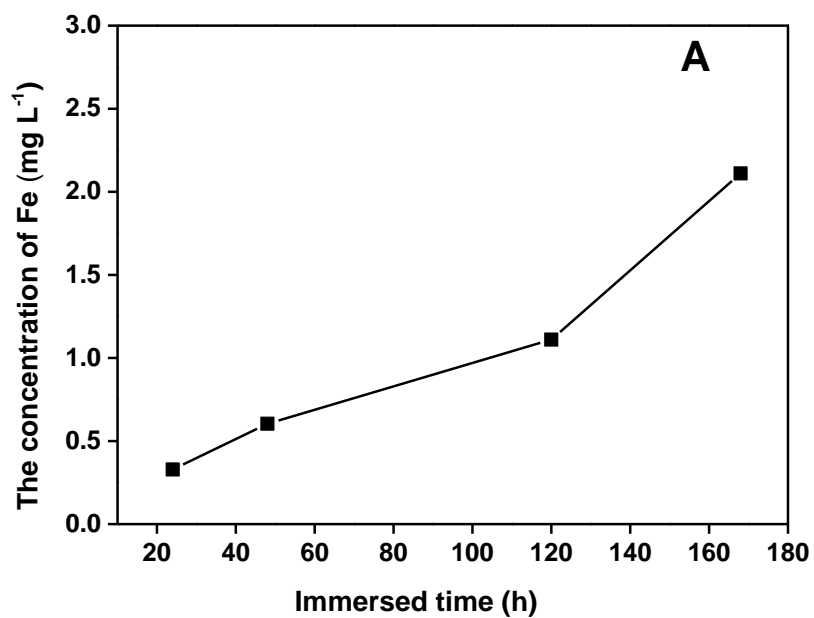
**Fig. S16** Effect of immersed time on the leaching of Fe (A) and P (B) from the magnetic

adsorbent Fe$_3$O$_4$@SiO$_2$/P (TRIM-VPA) in 4 mol L$^{-1}$ of HNO$_3$

**Table. S1**

Kinetic parameters for uranium adsorption on $Fe_3O_4@SiO_2/P$ (TRIM-VPA) in 4 mol $L^{-1}$ of $HNO_3$ solution

| Kinetic model | Parameter | Value |
|---|---|---|
| Pseudo-first-order | $k_1$ (1 $min^{-1}$) | 0.0696 |
| | $q_{e.\ cal}$ (mg $g^{-1}$) | 6.5355 |
| | $R^2$ | 0.7828 |
| Pseudo-second-order | $k_2$ [g (mg$^{-1}$ min$^{-1}$)] | 0.0184 |
| | $q_{e.\ cal}$ (mg $g^{-1}$) | 20.65 |
| | $R^2$ | 0.9993 |
| Intraparticle diffusion | $K_{int}$ [mg (g$^{-1}$ min$^{-1/2}$)] | 1.8228 |
| | c (mg $g^{-1}$) | 6.7199 |
| | $R^2$ | 0.6047 |

**Table. S2**

Adsorption isotherms parameters for uranium on $Fe_3O_4@SiO_2/P$ (TRIM-VPA) in 4 mol $L^{-1}$ of $HNO_3$ solution

| Adsorbent | Model | Parameter | Value |
|---|---|---|---|
| **$Fe_3O_4@SiO_2/P$ (TRIM-VPA)** | Langmuir | b (L mg $^{-1}$) | 0.0053 |
| | | $q_{max}$ (mg $g^{-1}$) | 60.4 |
| | | $R^2$ | 0.9756 |
| | Freundlich | $K_F$ (mg $g^{-1}$) | 1.3357 |
| | | $n_F$ | 1.7097 |
| | | $R^2$ | 0.9742 |

**Table. S3**

Thermodynamic parameters of thorium adsorption on $Fe_3O_4@SiO_2/P$ (TRIM-VPA) in 4 mol $L^{-1}$ of $HNO_3$ solution

| $\triangle H°$ (KJ/mol) | $\triangle S°$ (J/mol/K) | $\triangle G°$ (KJ/mol) | | | | |
|---|---|---|---|---|---|---|
| | | 278 K | 288 K | 298 K | 308 K | 318 K |
| 5.264 | 62.29 | -12.05 | -12.67 | -13.29 | -13.92 | -14.54 |

**Table. S4**

Comparison of uranium adsorption capacity and selectivity on $Fe_3O_4@SiO_2/P$ (TRIM-VPA) before and after soaked in 4 mol $L^{-1}$ of $HNO_3$ solution [a]

| Adsorbents | $q_{max}$ (mg $g^{-1}$) | $S_u$ | $c$ ($H^+$) (mol $L^{-1}$) |
|---|---|---|---|
| $Fe_3O_4@SiO_2/P$ (TRIM-VPA) before soaked in 4 M of $HNO_3$ solution | 60.4 | 61.2 % | 4 |
| $Fe_3O_4@SiO_2/P$ (TRIM-VPA) after soaked in 4 M of $HNO_3$ solution | 58.7 | 60.2 % | 4 |

[a] Sorption condition ($C_0$=100 mg $L^{-1}$ for U (VI), T=298 K, t=30 min, and m/V=0.4 g $L^{-1}$).

**Table. S5**

Comparison of adsorption of uranium on various magnetic adsorbents in strong $HNO_3$ media [a]

| Adsorbents | $q_{max}$ (mg g$^{-1}$) | $c$ (H$^+$) (mol L$^{-1}$) |
|---|---|---|
| $Fe_3O_4$ | 0 | 4 |
| $Fe_3O_4@SiO_2$ | 0 | 4 |
| Activated $Fe_3O_4@SiO_2$ with KH570 | 0 | 4 |
| $Fe_3O_4@SiO_2$/P (TRIM-VPA) | 60.4 | 4 |

[a] Sorption condition ($C_0$=100 mg L$^{-1}$ for U (VI), T=298 K, t=30 min, and m/V=0.4 g L$^{-1}$).

**Table. S6**

Comparison of BET specific surface areas of $Fe_3O_4@SiO_2$/P (TRIM-VPA) with $Fe_3O_4$, $Fe_3O_4@SiO_2$, and activated $Fe_3O_4@SiO_2$ with KH570 prepared in this work.

| Adsorbents | BET specific surface areas (m$^2$ g$^{-1}$) |
|---|---|
| $Fe_3O_4$ | 50.1 |
| $Fe_3O_4@SiO_2$ | 36.2 |
| Activated $Fe_3O_4@SiO_2$ with KH570 | 29.7 |
| $Fe_3O_4@SiO_2$/P (TRIM-VPA) | 23.2 |

**Table. S7**

Comparison of adsorption of uranium on various magnetic adsorbents in strong $HNO_3$ media [a]

| Adsorbents | $q_{max}$ (mg g$^{-1}$) | $c$ (H$^+$) (mol L$^{-1}$) |
|---|---|---|
| $Fe_3O_4$@$SiO_2$/P (TRIM-GMA) | 0 | 4 |
| $Fe_3O_4$@$SiO_2$/P (TRIM-AA) | 0 | 4 |
| $Fe_3O_4$@$SiO_2$/P (TRIM-AM) | 0 | 4 |
| $Fe_3O_4$@$SiO_2$/P (TRIM-HEMA) | 0 | 4 |
| $Fe_3O_4$@$SiO_2$/P (TRIM-VPA) | 60.4 | 4 |

[a] Sorption condition ($C_0$=100 mg L$^{-1}$ for U (VI), T=298 K, t=30 min, and m/V=0.4 g L$^{-1}$).

**Table S8**

The energy parameters of the two systems.

| Ratio of P=O: $UO_2(NO_3)_2$ | $\Delta E_{gas}$ (kcal mol$^{-1}$) |
|---|---|
| 1:1 | -33.0 |
| 2:1 | -64.0 |