RSC Advances

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

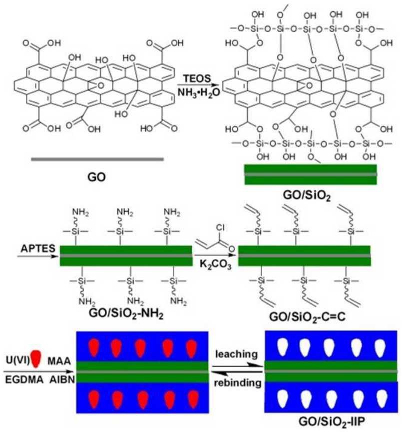
You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/advances

A novel surface ion-imprinted polymer based on graphene oxide was synthesized for the selective adsorption of U(VI).



RSC Advances Accepted Manuscript

Journal Name

ARTICLE

Synthesis and characterization of surface ion-imprinted polymer based on SiO_2-coated graphene oxide for selective adsorption of uranium(VI) †

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Hu Meng,[ab] Zheng Li,*[a] Fuyin Ma,[ab] Xiaoning Wang,[ab] Wei Zhou[a] and Lan Zhang[a]

A novel surface ion-imprinted polymer based on graphene oxide for the selective adsorption of U(VI) has been synthesized. The resultant adsorbent was characterized by FT-IR, SEM, TGA and Raman spectroscopy. The adsorption behaviors of U(VI) onto the imprinted polymer were investigated as functions of pH, contact time, temperature and initial U(VI) concentration by batch experiments. A fast adsorption kinetics was clearly observed and the selectivity study revealed that the U(VI)-imprinted polymer exhibited excellent selectivity and good affinity to U(VI) in the presence of competitive ions. Meanwhile, the prepared imprinted polymer showed good reusability and stability.

1. Introduction

Graphene, which consists of one-atom-thick planar sheets of sp^2-bonded carbon atoms arranged in a honeycomb lattice, has attracted tremendous attention in the field of material science due to its high specific surface area and excellent mechanical, thermal, and electrical properties.[1-4] Graphene oxide (GO), which consists of a single-layer of graphite oxide, contains abundant oxygen functional groups on the basal planes and edges. [5-8] The oxygen-containing groups endow it with excellent aqueous dispersion and make it easy to modify.[7] Therefore, GO is an excellent precursor to the preparation of various GO-based composites.[9] Moreover, the thermal stability and electrical properties of polymers could be greatly improved by the incorporation of GO sheets into the composite materials.[10,11]

Uranium is widespread in the environment. The inhalation of uranium or its compounds results in progressive or irreversible renal injury and in acute cases may lead to kidney failure and death due to its weak radioactivity and chemical toxicity.[12-15] Therefore, the selective removal and recovery of uranium from environmental samples has attracted more and more attention.[15-20] Considering the high specific surface area and abundant oxygen-containing functional groups on both basal planes and edges of GO, GO and its composites may have high sorption capacity for heavy metal ions from aqueous solutions.[21] GO and its various composites have been prepared for adsorption of uranium(VI) and a high adsorption capacity was obtained.[22-27] However, most of them are lack of selectivity.

The ion imprinted polymer (IIP) is a promising sorbent in selective separation and preconcentration of uranium(VI) due to its high selectivity and good affinity for the target ion. Traditional IIP has encountered with various limitations such as incomplete template removal, slow mass transfer and inaccessible binding sites situated deep inside the bulk of the polymer matrix.[29,30] In order to overcome these problems, the surface ion-imprinting technique where the binding sites are situated at the surface or in the proximity of polymer surface is developed, providing the complete removal of templates, low mass-transfer resistance and good accessibility to the target species.[31] GO, with good hydrophilicity, high specific surface area and excellent mechanical properties, should be an excellent candidate as a supporting material for preparing surface IIP composites to obtain rapid adsorption and increase the accessibility of the binding sites. Many surface molecular imprinted polymer (MIP) composites based on GO have been prepared via RAFT polymerization for sensors.[28,29] A rapid response equilibrium towards template molecular was observed. Furthermore, Liu et al. reported a surface ion-imprinted polymer based on GO for removal of Sr(II) from aqueous solution by using RAFT polymerization.[10] However, to the best of our knowledge, a surface IIP composite based on graphene oxide for selective adsorption of uranium(VI) has not been reported.

In this article, a novel ion-imprinted polymer based on graphene oxide was synthesized by surface imprinting technique. Methacrylic acid was used as the hydrophilic functional monomer due to its strong tendency toward U(VI) according to hard-hard interaction concept.[32-35] The characterization of the synthesized polymeric sorbent and the

---

[a] Center for Excellence TMSR Energy System and CAS Key Lab of Nuclear Radiation and Nuclear Energy Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, 201800, P. R. China. Tel.: +86-21-39194693; E-mail: lizheng04@sinap.ac.cn.

[b] University of Chinese Academy of Sciences, Beijing, 100049, P. R. China.

†Electronic Supplementary Information (ESI) available: Kinetic parameters, adsorption thermodynamic linear plot, Langmuir and Freundlich isotherm parameters and FT-IR spectrum of GO/SiO2-IIP after five adsorption-desorption cycles. See DOI: 10.1039/x0xx00000x

RSC Advances Accepted Manuscript

adsorption behaviors of U(VI) onto the imprinted polymer are described and discussed.

2. Experimental

2.1 Chemicals and reagents

Methacrylic acid (MAA), 3-aminopropyltriethoxysilane (APTES), ethylene glycol dimethacrylate (EGDMA) and tetraethyl orthosilicate (TEOS) were purchased from Sigma-Aldrich (USA). Acryloyl chloride was obtained from TCI Co., Ltd. (Japan). 2, 2'-azobisisobutyronitrile (AIBN) and graphite powder were obtained from Sinopharm Group Chemical Regent Co., Ltd. (Shanghai, China). Other chemicals used were of analytical grade. Milli-Q water was used in all experiments.

2.2 Synthesis of vinyl groups functionalized SiO_2-coated GO (GO/SiO_2-C=C)

GO was prepared according to the modified Hummers method.[36] GO/SiO_2 sheets were synthesized by using a sol–gel technique.[29] Typically, 40 mL of GO (0.6 g L^{-1}) aqueous solution was added into 320 mL of ethanol, followed by addition of 16 mL of NH_3•H_2O. After stirring for 20 min, 0.8 mL of TEOS was added into the mixture. Then, the mixture was sonicated for 12 h and kept overnight at room temperature. Finally, the product was centrifuged and washed with ethanol and water three times, respectively. The product was dried in vacuum oven at 60 °C for 24 h to obtain GO/SiO_2 sheets. Then, 0.2 g of GO/SiO_2 and 8 mL of APTES were added into 50 mL anhydrous toluene. The mixture was refluxed for 12 h under nitrogen atmosphere. The product was separated by centrifuge and washed with toluene and ethanol. The resultant amino groups functionalized GO/SiO_2 (GO/SiO_2-NH_2) was further acryloylated for the preparation of vinyl groups functionalized GO/SiO_2 (GO/SiO_2-C=C). Typically, the GO/SiO_2-NH_2 was dispersed in 50 mL anhydrous toluene. Then, 1 ml of acryloyl chloride and 1 g of anhydrous potassium carbonate were added. The mixture was vigorously stirred for 12 h at room temperature under dry nitrogen. The product was separated by centrifuge and washed with toluene, water and ethanol and dried in vacuum oven at room temperature for 24 h.

2.3 Synthesis of U(VI)-imprinted polymer (GO/SiO_2-IIP) and non-imprinted polymer (GO/SiO_2-NIP)

GO/SiO_2-IIP was prepared by thermal polymerization. Typically, 0.5 mmol of $UO_2(NO_3)_2$•$6H_2O$ was slowly added to 25 mL of 2-methoxyethanol containing 1 mmol of methacrylic acid with continuous stirring. After the mixture was stirred for 3 h at room temperature, 0.1 g of GO/SiO_2-C=C in 10 mL of 2-methoxyethanol, 8 mmol of EGDMA, 30 mg of AIBN were added. The above solution was purged with nitrogen for 15 min while cooled in ice bath. Then, the mixture was stirred and heated at 60 °C under nitrogen atmosphere for 24 h. The product was obtained by filtration, washed with acetone and DDW. Finally, U(VI) was leached from the product using 3 M HCl solution repeatedly until no U(VI) in the filtrate was detected. The non-imprinted polymer (GO/SiO_2-NIP) was also prepared using an identical procedure in the absence of U(VI).

2.4 Characterization

The concentration of metal ions was analyzed by ICP-AES (PerkinElmer, USA). FT-IR measurements were performed using the Nicolet iN 10 FT-IR spectrometer (Thermo-Fischer, USA) over a range from 400 to 4000 cm^{-1}. The surface morphology of the polymer particles was examined by scanning electron microscope (LEO 1530VP, USA). Thermo-gravimetric analysis was performed using a thermal analysis instrument (SSC/5200 SII, Seiko, Japan), at nitrogen atmosphere, from room temperature to 800 °C at a heating rate of 10 °C min^{-1}. Raman measurements were carried out using T64000 Raman Spectrometer at a laser excitation wavelength of 514 nm (Jobin Yvon Co., France)

2.5 Batch sorption experiments

Batch experiments were performed to study the adsorption behaviors of GO/SiO_2-IIP towards U(VI). 50 mg of GO/SiO_2-IIP was added to 10 mL of metal ions solution after adjusting to the desired pH value. After the mixture was shaken for a certain amount of time, the solution was centrifuged and the concentration of the metal ion in the solution was determined by ICP-AES. The distribution coefficient D (mL g^{-1}), the adsorption capacity Q (mg g^{-1}), the percentage of metal ion adsorbed on the sorbent %uptake, the selectivity coefficient $S_{U/M}$ and the relative selectivity coefficient k' were calculated as the following equations:

$$\mathrm{D} = \frac{(C_0 - C_e)V}{C_e W} \qquad (1)$$

$$\mathrm{Q} = \frac{(C_0 - C_e)V}{W} \qquad (2)$$

$$\%\mathrm{uptake} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (3)$$

$$S_{U/M} = \frac{D_U}{D_M} \qquad (4)$$

$$k' = \frac{S_{IIP}}{S_{NIP}} \qquad (5)$$

where C_0 and C_e represented the initial and equilibrium concentration the metal ion (mg L^{-1}), respectively, V was the volume of solution (L) and W was the mass of the sorbent (g).

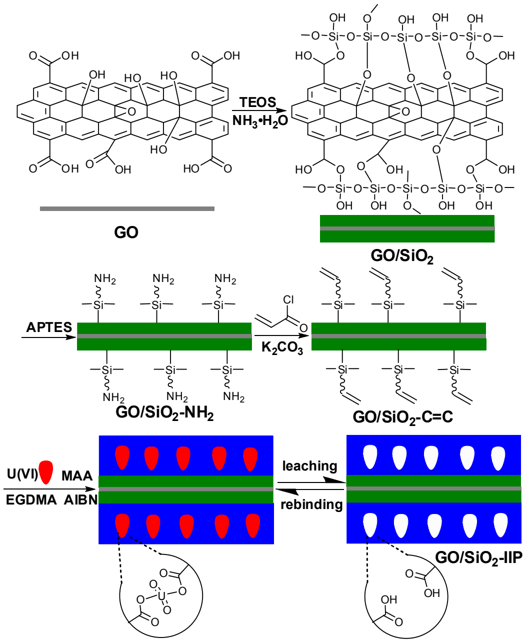
3. Results and discussion

3.1 Preparation of GO/SiO_2-IIP

The novel GO/SiO_2-IIP was prepared via a surface graft polymerization as shown in Scheme 1. In order to improve the surface chemical property of GO, GO was coated with SiO_2 to obtain a homogeneous graft of more vinyl groups. GO/SiO_2 was initially synthesized by the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in the water–alcohol mixture of GO under basic condition. SiO_2 was covalently coated on the surface of GO through the reaction of TEOS with the protic functional groups (e.g. –OH, –COOH) on the surface of GO.[29,37] Amino groups were subsequently introduced onto the surface of GO/SiO_2 by silylated reaction with APTES. The resultant

RSC Advances Accepted Manuscript

GO/SiO_2-NH_2 was further acryloylated with acryloyl chloride for synthesis of GO/SiO_2-C=C. Then, the GO/SiO_2-C=C was added into the polymerization solution containing template ion (U(VI)), functional monomer (MAA), cross linker (EGDMA) and initiator (AIBN). The vinyl groups introduced on the surface of GO/SiO_2 can direct the selective occurrence of imprinting polymerization at the surface.[31,38,39] The U(VI)-imprinted polymer was covalently bound on the surface by the copolymerization of vinyl end groups with functional monomer and cross linker. Finally, U(VI) was leached by HCl solution.



Scheme 1 The preparation route for GO/SiO_2-IIP.

The FT-IR spectra of GO, GO/SiO_2, GO/SiO_2-C=C, GO/SiO_2-IIP, unleached GO/SiO_2-IIP and GO/SiO_2-NIP were shown in Fig. 1A. Compared with GO, GO/SiO_2 showed the characteristic peaks of silica, which indicated that SiO_2 was successfully coated on the surface of GO. The band at 1088 cm^{-1} was attributed to the Si-O-C/Si-O-Si asymmetric vibration, while the typical peak at 1735 cm^{-1} assigned to the carboxylic groups of GO disappeared. This phenomenon suggested that the carboxylic groups were converted to Si-O-C bond.[40,41] Furthermore, the peaks at 798 and 464 cm^{-1} can be ascribed to the Si-O-Si symmetric vibration and bending vibration, respectively.[36] Additionally, the peak at 969 cm^{-1} was assigned to the Si-OH stretching.[37] GO/SiO_2-C=C displayed a characteristic peak at 1563 cm^{-1}, which was assigned to amide group stretching vibration, indicating the vinyl group was successfully introduced onto the GO/SiO_2. GO/SiO_2-IIP displayed three new peaks around 1729, 1254 and 1155 cm^{-1}, which were assigned to C=O stretching vibration of ester groups and carboxylic groups, C-O symmetric and asymmetric stretching vibration of ester groups, respectively,[38] indicating that IIP was successfully grafted onto the surface of GO/SiO_2. In addition, the characteristic peak of U(VI) was observed at 928 cm^{-1} in unleached GO/SiO_2-IIP,[42,43] which disappeared in the spectrum of GO/SiO_2-IIP. The result indicated that the U(VI) ions have been eluted from the ion-imprinted polymer. The spectrum of GO/SiO_2-NIP was similar to that of GO/SiO_2-IIP. All of these peaks confirmed the successful synthesis of GO/SiO_2-IIP.

The surface morphology of GO/SiO_2 and GO/SiO_2-IIP was examined by SEM and TEM. As shown in Fig. 1B, a homogeneous coating layer was clearly observed on the surface of GO as a result of SiO_2 coating. The SEM image of GO/SiO_2 in Fig. 1C displayed a smooth surface and layered structure. Compared with GO/SiO_2, GO/SiO_2-IIP (Fig. 1D) showed a rough and porous surface due to IIP grafted to the surface of GO/SiO_2.

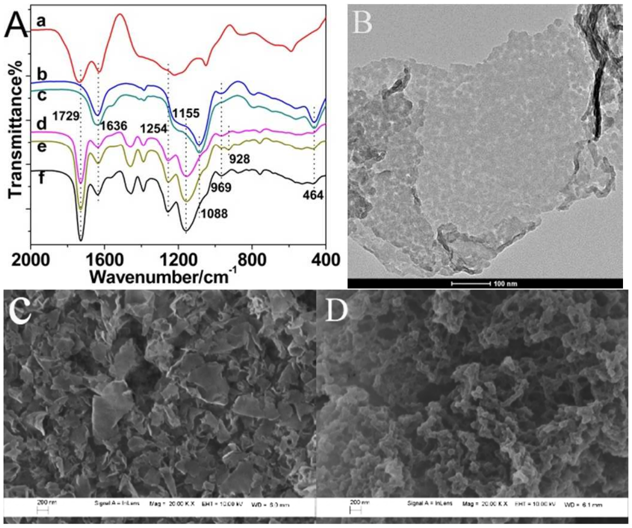


Fig. 1 (A) FT-IR spectra of GO (a), GO/SiO_2 (b), GO/SiO_2-C=C (c), GO/SiO_2-IIP (d), unleached GO/SiO_2-IIP (e) and GO/SiO_2-NIP (f). (B) TEM image of GO/SiO_2. (C) SEM image of GO/SiO_2. (D) SEM image of GO/SiO_2-IIP.

Raman spectroscopy is a powerful tool for characterizing carbonaceous materials due to their high Raman intensity.[44] As shown in Fig. 2A, two prominent peaks were clearly observed at around 1600 and 1350 cm^{-1}, corresponding to the G peak representing sp^2 ordered crystalline graphite-like structures and the D peak resulting from a disordered sp^3 carbon structure, respectively.[45] The intensity ratio (I_D/I_G) is characteristic of the extent of disorder present within in materials.[46] The calculated I_D/I_G ratios of GO, GO/SiO_2, GO/SiO_2-C=C and GO/SiO_2–IIP were 0.959, 0.990, 1.024 and 1.191, respectively, indicating an increase in disorder. Compared with GO, the increased ratio for GO/SiO_2 may be attributed to SiO_2 coating on GO. Similarly, the increase in the I_D/I_G ratio of GO/SiO_2-C=C and GO/SiO_2–IIP might be ascribed to the covalent interaction of GO/SiO_2 with the vinyl groups and IIP, respectively. All these results suggested that GO/SiO_2–IIP was successfully synthesized.

TGA curves of GO, GO/SiO_2, GO/SiO_2-C=C and GO/SiO_2–IIP were displayed in Fig. 2B. The weight loss of GO from room temperature to 100 °C could be attributed to the loss of adsorbed water. Meanwhile, the sharp weight loss of GO

RSC Advances Accepted Manuscript

between 100 °C and 250 °C may be assigned to the removal of oxygenated functional groups from GO. Compared with GO, GO/SiO_2 showed a low weight loss due to SiO_2 coating which was resistant to high temperature, indicating that SiO_2 was successfully coated onto GO. Moreover, TGA curve of GO/SiO_2–C=C showed a higher weight loss than that of GO/SiO_2, which confirmed that vinyl groups were successfully grafted onto the surface of GO/SiO_2. The weight loss of GO/SiO_2–IIP increased rapidly from 220 °C to 450 °C because of the thermal decomposition of the grafted imprinted polymer. Furthermore, a particularly high weight loss of about 94% was clearly observed for GO/SiO_2–IIP, which showed that IIP was successfully grafted on the surface of GO/SiO_2. These results further demonstrated the successful synthesis of GO/SiO_2–IIP.

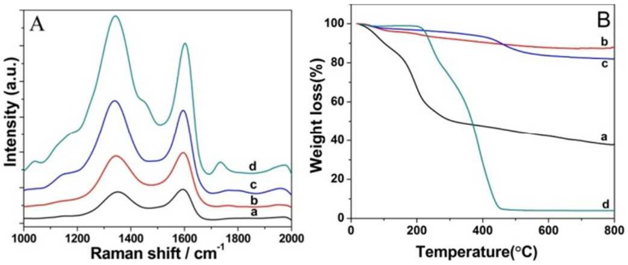


Fig. 2 (A) Raman spectra of GO (a), GO/SiO_2 (b), GO/SiO_2-C=C (c) and GO/SiO_2–IIP (d). (B) TGA curves of GO (a), GO/SiO_2 (b), GO/SiO_2-C=C (c) and GO/SiO_2–IIP (d).

3.2 Adsorption experiments

3.2.1 Effect of pH. It is known that pH is an important parameter affecting the metal ion adsorption. The effect of pH on the U(VI) uptake was studied under pH values ranging from 2 to 5 by batch experiments and the result was presented in Fig. 3. As it can be seen, the percent uptake of U(VI) increased with increasing pH from 2 to 4, and increased slightly in pH from 4 to 5. Therefore, pH 4 was selected for subsequent studies. This result was similar to previous reports.[13.14.19] Generally, uranium concentration was low in real samples. Thus, the performance of GO/SiO_2-IIP on the sorption of U(VI) in low concentration (50 μg L^{-1} and 10 μg L^{-1}) was evaluated at pH 4. The GO/SiO_2-IIP exhibited a high adsorption efficiency (>99%), indicating good affinity towards U(VI).

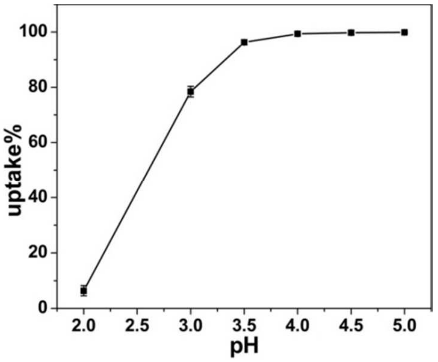


Fig. 3 Effect of pH on the uptake of U(VI) on GO/SiO_2–IIP (C_0 = 5 mg L^{-1}, t = 1h, W = 50mg, V =10 mL and T = 298.15K).

3.2.2 Adsorption kinetics. The effect of contact time on the U(VI) uptake was examined from 0.5 to 40 min and the result was shown in Fig. 4. The adsorption rate was initially fast and more than 99% uptake of U(VI) was achieved within 5 min, indicating that ion-imprinted polymer had a rapid adsorption to U(VI), which might be attributed to the high specific surface area of GO. Compared with U(VI) imprinted polymer reported in previous articles,[13,14] GO/SiO_2–IIP exhibited a much faster adsorption kinetics.

To investigate the kinetic mechanism of adsorption process, the pseudo-first order and pseudo-second order kinetic models were employed to fit the kinetic data. The two models can be expressed as linear form by Eqs. 6 and 7, respectively.[17]

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (6)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (7)$$

Where Q_e (mg g^{-1}) and Q_t (mg g^{-1}) are the amount of U(VI) adsorbed at equilibrium and time t (min), respectively. k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the pseudo-first order and pseudo-second order adsorption rate constant, respectively.

The kinetic parameters of two models are listed in Table S1. It can be observed that the correlation coefficient (R^2) of the pseudo-second order kinetic model(0.9928) is much higher than that of the pseudo-first order kinetic model(0.8928), indicating that the pseudo-second order kinetic model was a more appropriate model for describing the adsorption data. These results suggested that the chemical adsorption step might be the rate-controlling step.[16,17] This result was in accordance with previous reports.[13]

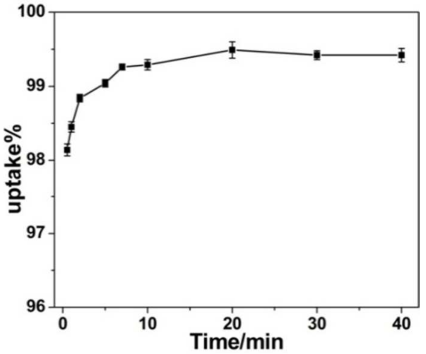


Fig. 4 Effect of contact time on the uptake of U(VI) on GO/SiO_2–IIP (C_0 = 5 mg L^{-1}, pH=4.0, W = 50mg, V =10 mL and T = 298.15K).

3.2.3 Effect of temperature. The effect of temperature on the adsorption of U(VI) was investigated in the temperature range of 15-35 °C and the result revealed that the adsorption amount of U(VI) increased with increasing temperature.

Thermodynamic parameters such as enthalpy change ΔH (kJ mol^{-1}) and entropy change ΔS (J mol^{-1} K^{-1}) were calculated from the linear plot of lnK_d Vs 1/T (Fig. S1) using Eq. 8 and Gibbs free energy change ΔG (kJ mol^{-1}) was calculated from

RSC Advances Accepted Manuscript

Eq. 9.[34] The obtained thermodynamic parameters were summarized in Table 1.

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

Where R is the gas constant (8.314 J mol^{-1} K^{-1}), k_d (L g^{-1}) is the equilibrium constant.

As shown in Table 1, the positive value of ΔH and the negative value of ΔG indicated endothermic and spontaneous nature of adsorption process. The positive value of ΔS showed the increased randomness at the solid-solution interface during the adsorption process.[16] Similar result was previously reported.[33]

Table 1 Thermodynamic parameters for U(VI) adsorption onto GO/SiO_2-IIP

ΔH(kJ mol^{-1})	ΔS(J mol^{-1} K^{-1})	ΔG(kJ mol^{-1})
		298.15K
23.40	89.90	-3.40

3.2.4 Adsorption isotherm. In order to evaluate the adsorption capacity of GO/SiO_2-IIP and GO/SiO_2-NIP towards U(VI), adsorption isotherm experiments were performed by batch experiments in the initial concentration range of 5 to 100 mg L^{-1}. As can be seen in Fig. 5, the amount of U(VI) adsorbed increased with increasing equilibrium concentration of U(VI).

The Langmuir and Freundlich isotherm models were often employed to fit the experimental data, which is important for understanding the adsorption mechanism. The linear form of two models can be expressed by Eqs. 10 and 11, respectively.[47]

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (10)$$

$$\ln Q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (11)$$

Where C_e is the equilibrium concentration of the U(VI) ion (mg L^{-1}), Q_e is the equilibrium adsorption capacity (mg g^{-1}), Q_m is the maximum adsorption capacity (mg g^{-1}), K_L is the Langmuir binding constant related to the energy of adsorption (L mg^{-1}), K_F is Freundlich constant and n is the constant related to adsorption intensity. For Eqs. 10 and 11, linear plots are shown in Fig. 6.

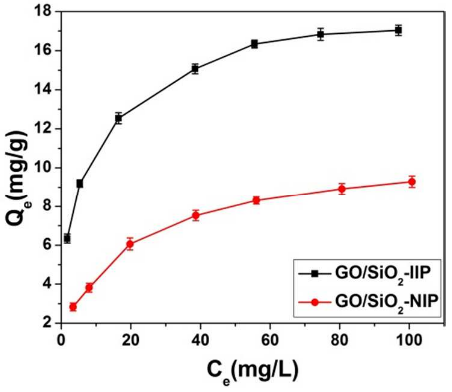


Fig. 5 Adsorption isotherm for the uptake of U(VI) on GO/SiO_2–IIP and GO/SiO_2–NIP (pH=4.0, t = 7min, W = 10mg, V =20 mL and T = 298.15K).

The isotherm parameters of two models were given in Table S2. It was obvious from the correlation coefficient value (R^2) that the Langmuir model fitted the experimental data better than the Freundlich model, which indicated the monolayer adsorption of U(VI) onto the homogeneous surface of GO/SiO_2-IIP.[48] Monier et al.[43] reported similar result. The calculated maximum adsorption capacity of GO/SiO_2-IIP was 17.89 mg g^{-1} which was higher than that reported in previous articles.[14,32]

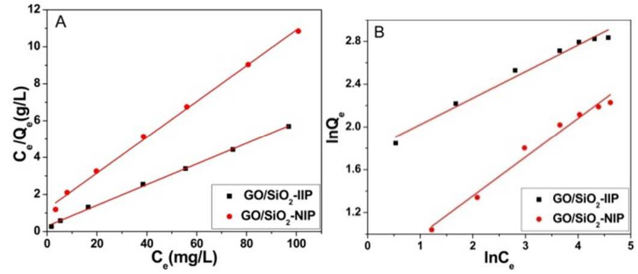


Fig. 6 (A) Langmuir and (B) Freundlich plots for the uptake of U(VI) on GO/SiO_2-IIP and GO/SiO_2-NIP.

3.2.5 Selectivity study. In order to investigate the selectivity of GO/SiO_2-IIP and GO/SiO_2-NIP, selective adsorption of binary mixtures of U(VI)/Cd(II), U(VI)/Ni(II), U(VI)/La(III), U(VI)/Ce(III), U(VI)/Nd(III) and U(VI)/Sm(III) with the same concentration was investigated by using GO/SiO_2-IIP and GO/SiO_2-NIP in a batch mode. These ions were selected as competitive ions due to similar chemical behaviors with U(VI) or being likely to coexist in real samples. The selectivity parameters such as distribution coefficient (D), selectivity coefficient ($S_{U/M}$) and the relative selectivity coefficient (k') were calculated according to Eqs. (1), (4) and (5). The obtained results were listed in Table 2 and the results revealed that GO/SiO_2-IIP was able to selectively adsorb U(VI) in the presence of competitive ions. Furthermore, the relative selectivity coefficient k' was much higher than one. GO/SiO_2-IIP exhibited a higher selectivity towards U(VI) compared with that reported in previous papers.[14,43] These results could be attributed to the creation of the specific recognition sites for U(VI) in the imprinting process.

3.2.6 Reusability study. The reusability of GO/SiO_2-IIP was evaluated by five consecutive adsorption-desorption cycles using 1 M HCl solution as the eluent and the result was shown in Fig. 7. It can be clearly seen from Fig. 7 that the prepared imprinted polymer can be efficiently regenerated and reused without a significant decrease in the percent uptake of U(VI) after 5 cycles. Moreover, the surface morphology and FT-IR spectrum of GO/SiO_2-IIP after five adsorption-desorption cycles were also tested. As shown in Fig. 8 and Fig. S2, no obvious change in the surface morphology and FT-IR spectrum of GO/SiO_2–IIP was observed after 5 cycles. The results

RSC Advances Accepted Manuscript

indicated that GO/SiO_2–IIP has excellent reusability and stability

Table 2 Selective sorption of U(VI) on GO/SiO_2-IIP and GO/SiO_2-NIP

ions	GO/SiO_2-IIP		GO/SiO_2-NIP		
	D(mL g^{-1})	$S_{U/M}$	D(mL g^{-1})	$S_{U/M}$	K’
U(VI)/Cd(II)	1.69×10^4/9.94	1.70×10^3	1.76×10^3/3.96	445	3.82
U(VI)/Ni(II)	1.76×10^4/8.37	2.10×10^3	1.78×10^3/3.82	466	4.5
U(VI)/La(III)	1.73×10^4/30.8	562	1.76×10^3/24.9	70.8	7.94
U(VI)/Ce(III)	1.56×10^4/28.8	542	1.68×10^3/11.3	148	3.66
U(VI)/Nd(III)	1.61×10^4/29.8	539	1.76×10^3/13.2	133	4.05
U(VI)/Sm(III)	1.71×10^4/80.6	212	1.55×10^3/26.6	58.2	3.64

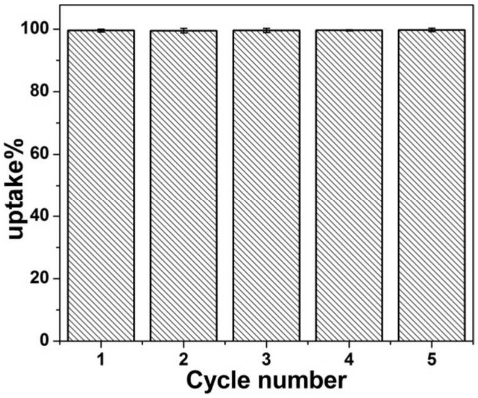


Fig. 7 Reusability of GO/SiO_2–IIP towards U(VI) (C_0 = 5 mg L^{-1}, t=7min, pH=4.0, W = 50mg, V =10 mL, and T = 298.15K).

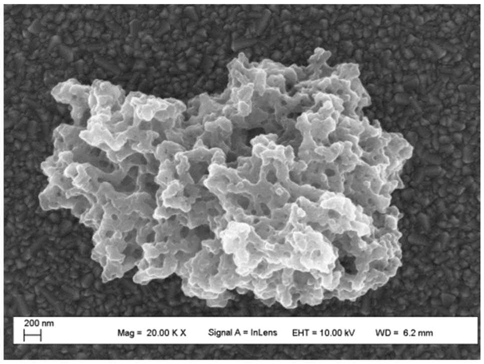


Fig. 8 SEM image of GO/SiO_2–IIP after five adsorption-desorption cycles.

Conclusions

In this work, a novel U(VI)-imprinted polymer based on SiO_2-coated graphene oxide was successfully prepared. The adsorption behaviors of U(VI) on GO/SiO_2–IIP from aqueous solution were evaluated by batch experiments. The results suggested that the adsorption process is pH dependent. The adsorption kinetics followed pseudo-second order kinetic model and a fast adsorption kinetics was observed for GO/SiO_2–IIP, indicating low mass-transfer resistance and good accessibility of binding sites to the target ions. Also, the Langmuir adsorption isotherm was fitted better with the experimental data and the calculated maximum adsorption capacity of GO/SiO_2–IIP and GO/SiO_2–NIP was 17.89 and 10.32 mg g^{-1}, respectively. Moreover, the U(VI)-imprinted polymer exhibited excellent adsorption selectivity and affinity towards U(VI), which showed the potential for treatment of environmental samples and separation of U(VI) from ions with similar property. Meanwhile, GO/SiO_2–IIP could be efficiently regenerated and reused with high adsorption efficiency after five adsorption–desorption cycles, revealing efficient removal of template ions. Hence, the synthesized U(VI)-imprinted polymer is an excellent adsorbent for rapid and selective adsorption of U(VI). The preparation process of GO/SiO_2–IIP in this study is relatively complex and further research is currently in progress to develop a simple and efficient route for preparation of U(VI)-imprinted polymer based on graphene oxide.

Acknowledgements

This work was financially supported by the Strategic Priority Research Program of the Chinese Academy of Science (Grant No. XDA02030000) and National Natural Science Foundation of China (No. 11305244).

RSC Advances Accepted Manuscript

Notes and references

1 H. L. Wang, Q. L. Hao, X. J. Yang, L. D. Lu and X. Wang, ACS Appl. Mater. Interfaces, 2010, **2**, 821.
2 D. Chen, H. B. Feng and J. H. Li, Chem. Rev., 2012, **112**, 6027.
3 G. X. Zhao, J. X. Li, X. M. Ren, C. L. Chen and X. K. Wang, Environ. Sci. Technol., 2011, **45**, 10454.
4 S. J. Park, K. S. Lee, G. Bozoklu, W. W. Cai, S. B. T. Nguyen and R. S. Ruoff, ACS Nano, 2008, **2**, 572.
5 D. D. Shao, G. S. Hou, J. X. Li, T. Wen, X. M. Ren and X. K. Wang, Chem. Eng. J., 2014, **255**, 604.
6 X. D. Zhuang, Y. Chen, G. Liu, P. P. Li, C. X. Zhu, E. T. Kang, K. G. Neoh, B. Zhang, J. H. Zhu and Y. X. Li, Adv. Mater., 2010, **22**, 1731.
7 Z. H. Tang, S. L. Shen, J. Zhuang and X. Wang, Angew. Chem. Int. Ed., 2010, **49**, 4603.
8 Y. X. Xu, W. J. Hong, H. Bai, C. Li and G. Q. Shi, Carbon, 2009, **47**, 3538.
9 S. H. Lee, D. R. Dreyer, J. An, A. Velamakanni, R. D. Piner, S. Park, Y. W. Zhu, S. O. Kim, C. W. Bielawski and R. S. Ruoff, Macromol. Rapid Commun., 2010, **31**, 281.
10 Y. Liu, X. G. Meng, M. Luo, M. J. Meng, L. Ni, J. Qiu, Z. Y. Hu, F. F. Liu, G. X. Zhong, Z. C. Liu, Y. S. Yan, J. Mater. Chem. A, 2015, **3**, 1287.
11 X. M. Yang, Y. F. Tu, L. Li, S. M. Shang and X. M. Tao, ACS Appl. Mater. Interfaces, 2010, **2**, 1707.
12 S. Mishra, J. Dwivedi, A. Kumarc and N. Sankararamakrishnan, RSC Adv., 2015, **5**, 33023.
13 M. C. Liu, C. L. Chen, T. Wen and X. K. Wang, Dalton Trans., 2014, **43**, 7050.
14 N. T. Tavengwa, E. Cukrowska and L. Chimuka, J. Hazard. Mater., 2014, **267**, 221.
15 S. Yusan, N. Yenil, S. Kuzu and M. A. A. Aslani, J. Chem. Eng. Data, 2011, **56**, 2013.
16 P. Ilaiyaraja, A. K. Singha Deb, K. Sivasubramanian, D. Ponraju and B. Venkatraman, J. Hazard. Mater., 2013, **250–251**, 155.
17 M. Y. Zeng, Y. S. Huang, S. W. Zhang, S. X. Qin, J. X. Li and J. Z. Xu, RSC Adv., 2014, **4**, 5021.
18 L. Y. Yuan, Y. L. Liu, W. Q. Shi, Z. j. Li, J. H. Lan, Y. X. Feng, Y. L. Zhao, Y. L. Yuan and Z. F. Chai, J. Mater. Chem., 2012, **22**, 17019.
19 S. Sadeghi and E. AboobakriH, Microchim Acta, 2012, **178**, 89.
20 L. Y. Yuan, Y. L. Liu, W. Q. Shi, Y. L. Lv, J. H. Lan, Y. L. Zhao and Z. F. Chai, Dalton Trans., 2011, **40**, 7446.
21 G. X. Zhao, T. Wen, X. Yang, S. B. Yang, J. L. Liao, J. Hu, D. D. Shao and X. K. Wang, Dalton Trans., 2012, **41**, 6182.
22 Y. G. Zhao, J. X. Li, S. W. Zhang, H. Chena and D. D. Shao, RSC Adv. 2013, **3**, 18952.
23 S. P. Chen, J. X. Hong, H. X. Yang and J. Z. Yang, J. Environ. Radiact., 2013, **126**, 253.
24 R. Hu, D. D. Shao and X. K. Wang, Polym. Chem., 2014, **5**, 6207.
25 Z. J. Li, L Wang, L. Y. Yuan, C. L. Xiao, L. Mei, L. R. Zheng, J. Zhang, J. H. Yang, Y. L. Zhao, Z. T. Zhu, Z. F. Chai and W. Q. Shi, J. Hazard. Mater., 2015, **290**, 26–33.
26 Y. B. Sun, D. D. Shao, C. L. Chen, S. B. Yang and X. K. Wang, Environ. Sci. Technol., 2013, **47**, 9904.
27 Z. J. Li, F. Chen, L. Y. Yuan, Y. L. Liu, Y. L. Zhao, Z. F. Chai and W. Q. Shi, Chem. Eng. J., 2012, **210**, 539.
28 H. M. Qiu, C. N. Luo, M. Sun, F. G. Lu, L. L. Fan, X. J. Li, Carbon, 2012, **50**, 4052.
29 Y. B. Zeng, Y. Zhou, L. Kong, T. S. Zhou and G. Y. Shi, Biosensors and Bioelectronics, 2013, **45**, 25.
30 T. E. Milja, K. P. Prathish and T. P. Rao, J. Hazard. Mater., 2011, **188**, 384.
31 D. M. Gao, Z. P. Zhang, M. H. Wu, C. G. Xie, G. J. Guan and D. P. Wang, J. Am. Chem. Soc., 2007, **129**, 7859.
32 M. Shamsipur, J. Fasihi and K. Ashtari, Anal. Chem., 2007, **79**, 7116.
33 G. D. Saunders, S. P. Foxon, P. H. Walton, M. J. Joyceb and S. N. Port, Chem. Commun., 2000, 273.
34 H. Meng, Q. H. Gao, Z. Li, X. N. Wang, F. Y. Ma, W. Zhou and L. Zhang, J. Mater. Chem. A, 2015, **3**, 13237.
35 R. Say, A. Ersöz and A. Denizli, Sep. Sci. Technol., 2003, **38**, 3431.
36 W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc., 1958, **80**, 1339.
37 L. Kou and C. Gao, Nanoscale, 2011, **3**, 519.
38 X. W. Kan, Y. Zhao, Z. R. Geng, Z. L. Wang and J. J Zhu, J. Phys. Chem. C, 2008, **112**, 4849.
39 Y. L. Wu, M. Yan, Y. S. Yan, X. L. Liu, M. J. Meng, P. Lv, J. M. Pan, P. W. Huo and C. X. Li, Langmuir, 2014, **30**, 14789.
40 K. G. Lee, R. Wi, M. Imran, T. J. Park, J. Lee, S. Y. Lee and D. H. Kim, ACS Nano, 2010, **4**, 3933.
41 W. L. Zhang and H. J. Choi, Langmuir, 2012, **28**, 7055.
42 C. R. Preetha, J. M. Gladis and T. P. Rao, Environ. Sci. Technol., 2006, **40**, 3070.
43 M. Monier and N. H. Elsayed, J. Colloid Interface Sci., 2014, **423**, 113.
44 Y. Liu, L. H. Zhu, Y. Y. Zhang and H. Q. Tang, Sensors and Actuators B, 2012, **171–172**, 1151.
45 G. Eda and M. Chhowalla, Adv. Mater., 2010, **22**, 2392.
46 Y. Li, X. Li, C. K. Dong, J. Y. Qi and X. J. Han, Carbon, 2010, **48**, 3427.
47 Y. M. Ren, P. X. Liu, X. L. Liu, J. Feng, Z. J. Fan and T. Z. Luan, J. Colloid Interface Sci., 2014, **431**, 201.
48 L. Y. Yuan, Z. Q. Bai, R. Zhao, Y. L. Liu, Z. J. Li, S. Q. Chu, L. R. Zheng, J. Zhang, Y. L. Zhao, Z. F. Chai and W. Q. Shi, ACS Appl. Mater. Interfaces, 2014, **6**, 4786.

RSC Advances Accepted Manuscript