In situ carbothermal reduction synthesis of Fe nanocrystals embedded into N-doped carbon nanospheres for highly efficient U(VI) adsorption and reduction

Kairuo Zhu\textsuperscript{a,b}, Changlun Chen\textsuperscript{a,b,d,⁎}, Mingwanchen Xu\textsuperscript{a}, Ke Chen\textsuperscript{a}, Xiaoli Tan\textsuperscript{a}, M. Wakeel\textsuperscript{c}, Njoud S. Alharbi\textsuperscript{d}

\textsuperscript{a} Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, Hefei 230031, PR China
\textsuperscript{b} Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Soochow University, Suzhou 215123, PR China
\textsuperscript{c} Department of Environment Sciences, Bahauddin Zakariya University, Multan, Pakistan
\textsuperscript{d} Department of Biological Sciences, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

**GRAPHICAL ABSTRACT**

U(VI) adsorption and reduction by Fe nanocrystals embedded into N-doped carbon nanospheres.

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**ABSTRACT**

In this work, magnetic porous nitrogen doped carbon structures containing well-dispersed active Fe nanocrystals (Fe/N-C) are fabricated conveniently via Fe\textsuperscript{3+}-mediated polymerization of dopamine as precursor combined with in situ post carbonization process, thus allowing the entire encapsulation of active Fe nanocrystals in the interior. The obtained functional hybrid materials at 700 °C (Fe/N-C-700) show spherical structure, high proportion of metallic Fe nanocrystals, ultrahigh surface area, and easy magnetic separation property, affording excellent U(VI) removal capability (232.54 mg·g\textsuperscript{−1}), surpassing the Fe/N-C samples pyrolyzed at different temperatures and nano zero-valent iron. During the adsorption process, effects of water chemistries (i.e., reaction time, pH, carbonates concentration and temperature) on U(VI) adsorption on Fe/N-C-700 are full explored, and the well-dispersed Fe nanocrystals play important role in reducing into U(IV). Meanwhile, nitrogen dopant could make function well in the electrostatic interaction and partial reduction of U(VI). The present study demonstrates that Fe/N-C-700 nanospheres derived from Fe-PDA have potential application for the preconcentration and immobilization of U(VI).
1. Introduction

Uranium, one of the primary nuclear materials as well as a highly poisonous component in nuclear waste, exceedingly threatens natural water resource and human health worldwide [1–4]. Hence, it is an extremely indispensable task to find effective treatments in reducing uranium contamination. Currently, considerable efforts have been made for developing novel functional materials which are capable of integrating chemical reduction and adsorption process for U(VI) uptake from water [5–8]. Among of which, nano zero-valent iron (NZVI) attracts much more attention due to its large surface area, high surface energy and reaction activity. However, unmodified NZVI particles suffer poor air stability and easy agglomeration due to their intrinsically high surface energy [9–11]. To overcome these limitations, loading metallic nanoparticles on natural and synthetic supports is a powerful method to improve their reaction performance [12–18]. Following this, it is encouraging and important to study the hybrid materials for better control of the NZVI particle aggregation and further optimize their reactivity and stability.

Nowadays, porous carbon materials have been widely used as the support substrates for metallic nanoparticles due to their high adsorption capacity, chemical stability and low cost [19–21]. In particular, embedding active metallic nanoparticles into porous carbon materials (M-C) can efficaciously avoid the conglomeration and augment the stability of thermodynamics [22–25]. Compared to the post-growth of active metallic nanoparticles on pre-synthesized porous carbon, high temperature thermal treatment is a more straightforward route to convert metal and carbon-based compounds/composites into M-C hybrid materials [26–29]. Along with the carbonization of organic/polymeric segments at high temperature, the metallic species will be converted into active metallic particles by synchronous carbothermic reduction and firmly attached into porous carbon substrates simultaneously. Such process provides a robust and scalable approach for the mass production of metal-carbon hybrid materials.

Dopamine, a synthetic mimic of an essential component of mussel adhesive proteins as well as, can easily self-polymerize at room temperature to form polydopamine (PDA), and it is also an outstanding carbon source which can yield thin carbon coatings [24,30–32]. In addition, dopamine possesses reduction ability and contains chelating -OH groups which can "capture" metal ions (i.e., Fe, Ni, Co) during one-pot synthesis of transition metal ion-PDA complexes [33]. Making better use of the distinct reactivity and thermal stability, metal ion-PDA complexes can serve as desirable precursors to embed metallic nanoparticles into N-doped carbon nanostructures (M/N-C) through direct pyrolysis. More recently, Fe/N-C hybrid materials have attracted enhanced attention in the contaminant remediation, in which well-dispersed active Fe nanoparticles exhibit excellent oxygen reduction reaction catalytic activity and nitrogen dopant can endure Fe/N-C abundant function groups on the surface [22,23,26,34,35]. Meanwhile, Fe/N-C hybrid materials possess highly porous structure with manageable chemical properties and conveniently magnetic separation [36,37].

Motivated by these, it can be expected to synthesize Fe/N-C hybrid materials derived from Fe-PDA complexes to achieve concurrent reduction and adsorptive removal of U(VI). Herein, we report a rational and scalable synthetic method to prepare magnetic porous Fe/N-C hybrid materials via simply introducing Fe^{3+} ions into tri aqeous solutions of self-polymerizable dopamine as precursor, followed by in situ activation-graphitization process (Fig. 1). Under one-pot oxidative polymerization process, highly uniform-sized Fe-PDA nanoparticles are firstly synthesized. Then, the obtained Fe-PDA nanoparticles experience heat-treatment under an Ar atmosphere to convert Fe-PDA complexes into Fe/N-C hybrid materials. The epoxy and hydroxyl groups in the Fe-PDA complexes explosively decompose to release a large amount of H_{2}O, CO, and CO_{2} gases during the heat-treatment process, which leads to the production of abundant voids due to the volume shrinking at high temperature [22]. In addition, the existence of stable carbon matrix could efficiently avoid Fe nanocrystals aggregation and afford high specific surface area [29]. The local structure and chemical functions of Fe/N-C hybrid materials can be optimized by changing the pyrolysis temperature [34], as well the U(VI) removal efficiency of Fe/N-C composites could be affected. Notably, novel composites comprising similar compositions but different morphologies manifest substantially distinct catalytic activities [38]. In this study, the engineered Fe/N-C hybrid nanospheres obtained at 700 °C are found to show the impressive U(VI) removal capacity. The physical and chemical characterization of the synthesized Fe/N-C-700 (for Fe/N-C-T, in which T represents the heat-treatment temperature) is conducted systematically. The adsorption behavior of Fe/N-C-700 is further investigated under different water chemistry conditions (e.g., contact time, pH, carbonates concentration, and temperature). And the adsorption and reduction mechanisms are discussed in detail. Fe/N-C-700 clearly manifests great expectation for U(VI) removal by concurrent adsorption and reduction.

2. Experimental section

2.1. Chemicals

All common chemicals were purchased from Sigma-Aldrich and used without further purification. U(VI) stock solution containing 240 mgL^{-1} was prepared by dissolving an appropriate amount of UO_{2}(NO_{3})_{2}·6H_{2}O in Milli-Q water.

2.2. Preparation of Fe/N-C

Fe-PDA nanospheres were prepared according to the previous reports [39]. Typically, 1.0 g of dopamine was dissolved in 1000 mL of Milli-Q water. Then, 1.76 mmol of FeCl_{3}·6H_{2}O was added. After 10 min, 10 mmol of Tris was added to adjust the pH and the reaction mixture was stirred for 30 h. The obtained Fe(III)-PDA complexes were separated from the solutions by centrifugation, washed with Milli-Q water, and then freeze-dried for 24 h. Finally, to get Fe/N-C hybrid materials, the obtained Fe(III)-PDA complexes were calcined at 650, 700, 800 and 900 °C for 2 h under an argon atmosphere, with the 5 °Cmin^{-1} temperature ramp rate. For comparison, NZVI particles were synthesized according the former reports [40]. N-doped carbon spheres derived from PDA spheres without adding FeCl_{3}·6H_{2}O, were prepared through the same calcination process with Fe/N-C-700. (See in Supporting content)

2.3. Batch adsorption experiments

The whole experiments were carried out in 10 mL polyethylene tubes by batch technique. In brief, the suspension of adsorbent and background electrolyte solution (0.001 molL^{-1} Na_{2}CO_{3}) were pre-equilibrated for 24 h, and then U(VI) stock solution were added to obtain the desired concentrations. The desired pH was adjusted by adding negligible volumes of 0.1–0.01 molL^{-1} HCl or NaOH. The effect of carbonate ions was investigated with different concentration of Na_{2}CO_{3} at pH 6.0. The above suspensions were oscillated for the appropriate time and then centrifuged at 9000 rpm for 20 min. The concentration of residual U(VI) was determined with an Arsenazo-III spectrophotometer method at 650 nm [41].

Characterization methods, data analysis model and are presented in the Supporting content.

3. Results and discussion

3.1. Characterization of Fe/N-C

The phase and composition of all the derived Fe/N-C composites were investigated by means of X-ray powder diffraction, which
confirmed the formation of Fe/N-C after annealing the Fe-PDA at high temperatures (Fig. 2A). For Fe/N-C-700, Fe/N-C-800 and Fe/N-C-900, the diffraction peaks of Fe/N-C samples at 44.8° and 65.2° correspond to the (1 1 0) and (2 0 0) facets of α-Fe, indicating the existence of a great quantity of metallic Fe (PDF NO. 87-0722, Fig. 2B). More remarkable, the peaks at 37.8°, 42.9°, 45.9° and 49.1° could be well indexed to the characteristic diffraction of Fe₃C (PDF NO. 85-1317). Meanwhile, the peak strength of Fe₃C species enhances with the increasing carbonization temperature, which can be attribute to the increasing of Fe₃C composition. For Fe/N-C-650, the diffraction peaks at 30.1°, 35.4°, 43.1°, 57.0° and 62.5° correspond to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) planes of Fe₂O₃ (PDF NO. 79-0419), respectively. Furthermore, the diffraction peaks at 30.1°, 35.4°, 57.0° and 62.5° present in the XRD pattern of Fe/N-C-700, demonstrating that there is a small quantity of Fe₂O₃ existing in the Fe/N-C-700. It’s noteworthy that there is no metallic Fe and Fe₃C species existing in the XRD patterns of the as-prepared Fe-PDA (Fig. S2) and Fe/N-C-650, meaning that carbothermic reduction occurs when T > 650 °C. During a pyrolysis process, fused ring structures of Fe-PDA complexes become graphitized, the Fe³⁺ chelated with -OH groups is first transformed into Fe₂O₃, and then reduced to Fe₃O₄ [33,42,43]. With increasing the pyrolysis temperature, Fe₃O₄ can be further reduced to metallic Fe and the formation of Fe₃C phase is due to the regional dissolution of carbon atoms into the Fe crystal lattice. In addition, the sharp XRD peak at 26.0° of Fe/N-C-900 demonstrates that the graphitization degree of Fe/N-C is enhanced with increasing carbonization temperature [44]. Based on the XRD patterns, Fe/N-C-700 owns the maximum proportion of metallic Fe, so we chose 700 °C as the optimal heat-treatment temperature, and selected the Fe/N-C-700 sample for more detailed studies.

The morphology and structural evolution from Fe-PDA to Fe/N-C-700 were well manifested by SEM and TEM. From Fig. 3A, the Fe-PDA displays well-defined nanospheres with a rough surface and an average diameter of about 144 nm (Fig. S3A). From Fig. 3B, the Fe-PDA nanospheres are in situ converted into Fe/N-C-700, obviously observed that the particle sizes reduce and the average size of the spheres is approximately 96 nm (Fig. S3B). Furthermore, many macroporous concaves arise inside the sphere skeletal structure, which can be ascribed to the collapse of polymer carbon skeleton. It is noteworthy that the pyrolysis temperature can greatly

![Fig. 1. Illustration of the fabrication process for Fe/N-C-700 and the possible microstructures of the N-doped carbon in Fe/N-C-700.](image)

![Fig. 2. (A) XRD patterns of all the Fe/N-C samples; (B) XRD standard patterns of Fe₃C, metallic Fe, and Fe₂O₃.](image)
affect the surface nanostructure of Fe/N-C samples. For Fe/N-C-650, the spherical profile keeps perfect, however, for Fe/N-C-800, the spherical profile starts disappear, and only a mass of nanoparticles maintain in Fe/N-C-900 (Fig. S4). In Fig. 3C, highly dispersive small Fe3O4/Fe/Fe3C nanoparticles (5–20 nm) are entirely encapsulated within the carbon matrix, benefiting the synthesis of metallic Fe (the redox reaction between carbon and Fe3O4). In addition, atomic lattice fringes with a distance of 0.21 nm, manifesting a highly crystalline structure, corresponding to the (1 1 0) plane of metallic Fe are clearly observed (Fig. 3D). Elemental mapping of the Fe/N-C-700 displays the distribution of the three elements within the spherical structures (Fig. 3E). One can see that Fe element is only existed in the carbon sphere, demonstrating that the Fe3O4/Fe/Fe3C nanoparticles are uniformly embedded into the carbon sphere.

The feature structure of Fe/N-C-700 nanospheres was confirmed by FTIR (Fig. 4A). Two bands at ~1405 and 1440 cm$^{-1}$ are observed, ascribing to the stretching vibration of the C-N ($v_{C-N}$) and the C==C ($v_{C=C}$) groups, respectively [36]. The characteristic peak of Fe-O ($v_{Fe-O}$) is observed at 500–600 cm$^{-1}$ and the band at 3451, 1633 cm$^{-1}$ is associated with -OH stretching vibration ($v_{OH}$), bending vibration ($\beta_{OH}$) of absorbed water molecule, respectively.

The Raman spectrum was used to analyze the carbon quality in Fe/N-C-700 nanospheres. As displayed in Fig. 4B, two strong peaks are found at 1352 and 1600 cm$^{-1}$, corresponding to the disordered D band and graphitic G band of carbon, respectively. The intensity ratio $I_D/I_G$ is calculated to be 0.96, indicating a high graphitization degree. Furthermore, the Raman spectra of all of the Fe/N-C samples were also studied (Fig. S5), the values of $I_D/I_G$ gradually increase with increasing heat treatment temperature from 650 to 800 °C, however, it reduces for Fe/N-C-900. It’s noteworthy that there are the obvious peak series

![Image](image_url)
between 200 and 600 cm\(^{-1}\) in Fe/N-C-900, which is commonly ascribed to stretching modes between iron and carbon atoms \[22\]. Therefore, the change trend of \(I_D/I_G\) values can be illustrated by the increased graphitization degree of carbon along with the elevated pyrolysis temperature and the catalytic effect of metallic Fe \[25\].

The magnetization curve of the Fe/N-C-700 in Fig. 4C indicates that Fe/N-C-700 exhibits a ferromagnetic behavior and the saturated magnetization value is \(\sim 65.5\) emu·g\(^{-1}\). The magnetization is inherited from the Fe/Fe\(_3\)C/Fe\(_3\)O\(_4\) phases. This great magnetic feature guarantees effective separation of Fe/N-C-700 in practical applications.

TGA and DTG were conducted to evaluate the content of Fe/N-C-700 in air (Fig. 4D). The observed TGA curve of Fe/N-C-700 represents two steps of weight loss. The first weight loss stage (< 150 °C) is attributable to absorbed water elimination. Of note, one slight weight increases from 150 to 330 °C due to the transformation of Fe (Fe3O4 or Fe3C) to \(\alpha\)-Fe\(_2\)O\(_3\) \[45\]. Furthermore, the second weight loss step (< 525 °C) is attributes to the combustion of N-doped carbon matrix. Weight loss is determined to be stabilized after 600 °C, indicating the complete combustion of N-doped carbon matrix and oxidation of iron compounds into \(\alpha\)-Fe\(_2\)O\(_3\). The DTG result displays an endothermic peak at 440 °C, indicative of the existence of the graphitic carbon \[29\]. The final content of \(\alpha\)-Fe\(_2\)O\(_3\) is \(\sim 32.44\) wt%. Therefore, the elemental Fe proportion is computed to be \(\sim 22.71\) wt% (Eqs. (S1)).

The nitrogen adsorption-desorption isotherm of Fe/N-C-700 is shown in Fig. 4E. The Fe/N-C-700 exhibits a protuberant hysteresis loop in the relative pressure range from 0.4 to 0.9, manifesting that the
coexistence of microporosity and mesoporosity [29]. The adsorption amount increased dramatically at a relative pressure close to 1.0, because of the filling of space in Fe/N-C-700 [44]. In view of the nitrogen quantity adsorbed at different relative pressures, the surface area of Fe/N-C-700 is calculated to be 343.02 m²·g⁻¹, and the average pore diameter is 40.87 Å. The surface areas are 74.91 m²·g⁻¹ for Fe/N-C-650 and 280.13 m²·g⁻¹ for Fe/N-C-800. The surface area of Fe/N-C-900 is the largest among the obtained Fe/N-C samples, and achieve 419.89 m²·g⁻¹ (Fig. S6). Of course it's really the same result for the total pore volume. Because of the approximate spherical profile and the incorporation of the high proportion of metallic Fe in the interior, the surface area for Fe/N-C-700 is not maximum but suitable for adsorption. The porous property and the high surface area of the Fe/N-C-700 nanospheres can provide more active adsorption sites and they are conducive to the fast transport of U(VI) in interconnected pore structure systems, thus enhancing the adsorption capacity.

3.2. U(VI) removal capacity by Fe/N-C samples

For comparison, all of Fe/N-C samples were employed to adsorb U(VI). Fig. 5A shows the amount of U(VI) adsorbed onto Fe/N-C increases successively with the rise of original U(VI) concentrations, suggesting more U(VI) ions transported from the aqueous solution to the Fe/N-C. The adsorption data were fitted using the Langmuir, Freundlich and D-R models (Fig. S7) and the relative parameters calculated from three models are listed in Table S1. From the correlation coefficients (R²), the adsorption data better fit the Langmuir model, suggesting that the binding energy on the whole surface of Fe/N-C is homogeneous, and chemisorption is related to the adsorption process [46]. The maximum removal capacity of 232.54 mg·g⁻¹ on Fe/N-C-700 is much higher than those of Fe/N-C-650 (78.63 mg·g⁻¹), Fe/N-C-800 (210.17 mg·g⁻¹), Fe/N-C-900 (153.55 mg·g⁻¹), and NZVI (95.27 mg·g⁻¹) (Fig. 5B). The Fe/N-C-700 has optimal comprehensive conditions containing spherical structure, high surface area, the porous property, as well as high proportion of metallic Fe nanocrystals in the N-doped carbon matrix. All above of factors lead to the promotion of the electrochemical corrosion of metallic Fe, which generates electrons for the synergistic reduction and adsorptive removal of U(VI). The maximum U(VI) adsorption capacity onto Fe/N-C-700 was compared with other various adsorbents under various conditions and presented in Table S2. One can find that the U(VI) adsorption capacity onto Fe/N-C-700 is far higher than that of others, further demonstrating the excellent U(VI) adsorption potential of Fe/N-C-700.

3.3. Removal kinetics

The removal rate is commonly considered as a crucial criterion to evaluate the potential applications of the adsorbent. Thus, the effect of contact time for the adsorption of U(VI) onto Fe/N-C-700 was investigated at an initial U(VI) concentration of 20 mg·L⁻¹. Fig. 6A shows that the adsorption capacity quickly increases at the first contact time of 15 min, afterwards, increases at a slower rate and finally achieves adsorption equilibrium after 20 min. The adsorption kinetic curve was simulated by the pseudo-first-order and pseudo-second-order kinetic models (Eqs. (S8) and (S9)). The related kinetic parameters and the correlation coefficients (R²) were determined by line regression (Fig. 6B and C) and are listed in Table 1. The plots of the pseudo-second-order kinetic model show quite good linearity with R² values of 0.998 (pseudo-first-order: 0.910), which confirms that pseudo-second-order model fit well the adsorption kinetic curve, suggesting a chemical adsorption process [47]. Furthermore, an intraparticle diffusion model (Eq. (S10)) was also employed to study U(VI) removal kinetics. From Fig. 6D, the fitting curves display a piecewise line with two different slopes, indicating that the whole adsorption process involves two steps with different limiting processes. The first rapid section indicates U(VI) diffusion to the external surface of Fe/N-C-700 and occupation of the active sites of Fe/N-C-700, followed with slow diffusions into pores in the second stage. Meanwhile, no stage passes through the origin, manifesting that the rate controlling steps do not only include intraparticle diffusion, and other reactions (i.e., chemical redox) may be involved [48].

3.4. Effect of solution pH and carbonate ions

Solution pH is a vital variable influencing the adsorption capacity. U(VI) removal efficiency on Fe/N-C-700 in 0.001 mol/L Na₂CO₃ solution was examined from pH 2 to 10 and displayed in Fig. 7A. The U(VI) removal capacity increases markedly with the rise of solution pH from 2.0 to 6.0, whereas reduces at pH > 7.0. It is noteworthy that pH is demonstrated to affect the surface properties of adsorbents and relative distribution of U(VI) species [49]. Surface charge values of Fe/N-C-700 were measured and displayed in Fig. 7B, the point of zero charge value of Fe/N-C-700 is 4.6, which is much lower than 6.8 (magnetic porous carbon) [50], and 6.3 (granular activated carbon) [51], 5.6 (N-doped Fe/Fe₃C@C-800) [22]. The low pHpzc is caused by nitrogen dopants

![Figure 5](image-url)

**Fig. 5.** (A) Adsorption isotherms of U(VI) removal onto Fe/N-C pyrolyzed at different temperatures (T = 283 K, pH = 6.0, m/V = 0.14 g·L⁻¹, and t = 300 min); (B) the corresponding adsorption capacities for U(VI) removal onto different samples.
from polydopamine thermolysis. Therefore, Fe/N-C-700 exhibits a negatively charged surface at pH > 4.6. As displayed in Fig. 7C, U(VI) mainly exists as positively charged species (i.e., UO₂²⁺, UO₂OH⁺, (UO₂)₂(OH)²⁺ and (UO₂)₃(OH)⁵⁺) at pH < 6.0 and negatively charged species (i.e., UO₂(CO₃)²⁻ and UO₂(CO₃)⁴⁻) at pH > 7.0. Consequently, the increased adsorption amount of U(VI) on Fe/N-C-700 at pH 2.0–6.0 could be attributed to the strong surface complexation between positive charged radionuclide species and negatively charged surface of the Fe/N-C-700. At pH > 4.6, the negative surface charge of Fe/N-C-700 distinctly manifests the formation of U(VI)-carbonate species, which are stable in aqueous phase and are difficult to interact with Fe/N-C-700 [52]. From Fig. 7D, U(VI) removal reduces as CO₃²⁻ concentration increasing from 0.001 to 0.020 mol·L⁻¹. It can be ascribed to more stable U(VI)-carbonate species existing in the Fe/N-C-700/U(VI) system with increasing CO₃²⁻ concentration [53].

3.5. Thermodynamic studies

The solution temperature plays a significant role in reaction rate and removal efficiency, the adsorption isotherms of U(VI) at 283, 298, and 313 K onto Fe/N-C-700 are displayed in Fig. 8A. In addition, to better investigate the adsorption mechanism and quantify the adsorption data, the three equilibrium models were also employed to quantitatively analyze the adsorption process and displayed in Fig. S7. Through comparing the correlation coefficients, it's clearly find that the Langmuir model with a higher correlation coefficient (R²) fitted better to the thermodynamic isotherm data than the other two adsorption models (shown in Table S1). The calculated Qₘ of the Langmuir model exhibits the evident uptrend with the increasing of temperature, which indicates that higher temperature promotes the removal of U(VI) by the Fe/N-C-700.

Traditional thermodynamic parameters (ΔH⁰, ΔS⁰, and ΔG⁰) for U (VI) adsorption onto Fe/N-C-700 were calculated from the van’t Hoff isothermal equation (Eqs. (S11) and (S12)) and presented in Fig. 8B and Table 2. The positive value of ΔH⁰ proves the endothermic process. The negative ΔG⁰ value and the positive ΔS⁰ value reveals that the process is spontaneous with high affinity, which indicates that more active sites interact with U(VI) species and more water molecules participate in the reaction with the increasing of adsorption temperature [54].

Table 1

<table>
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<th>Model</th>
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<td>0.101</td>
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<td>pseudo-second-order</td>
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<td></td>
<td>k₃''(mg·g⁻¹·min⁻¹/²)</td>
<td>e''</td>
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<tr>
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3.6. Reusability

The investigation of the adsorbent reusability is a critical process to consider its enhancement of the economic value. Therefore, the reusability of Fe/N-C-700 was studied. Typically, after each run, the recycled adsorbent was immersed in 0.2 mol·L\(^{-1}\) Na\(_2\)CO\(_3\) solution and shaken for 12 h, then centrifuged and washed by Milli-Q water repeatedly several times for the adsorbent regeneration. The collected solid was then freeze-dried at -60 °C for 24 h. Fig. 8C displays the reuse performance of the Fe/N-C-700 in the U(VI) removal during six recycles.

![Image](Fig. 8A) Adsorption isotherms of the U(VI) removal onto Fe/N-C-700 at 283, 298 and 313 K (m/V = 0.14 g·L\(^{-1}\), pH = 6.0, and t = 60 min); (B) plot of \(\Delta G^\circ\) versus T; (C) recycle property of Fe/N-C-700. The inset is a digital photograph of the magnetic separation after six recycling tests.

<table>
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<th>T (K)</th>
<th>(\Delta G^\circ) (kJ·mol(^{-1}))</th>
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<th>(\Delta H^\circ) (kJ·mol(^{-1}))</th>
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<td>313</td>
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Table 2: Thermodynamic parameters for U(VI) removal onto Fe/N-C-700.
recycling tests. Although, a slight decline in the U(VI) removal is observed after each cycle, the reduction is less than 15% after six recycling tests, displaying the good reusability of Fe/N-C-700. The inset digital image of Fig. 8C shows the magnetic separation property of Fe/N-C-700 after six recycling tests, indicating its convenient separation or efficient enrichment in practical application.

3.7. Adsorption and reduction mechanism

The interaction mechanism of U(VI) on Fe/N-C-700 was demonstrated by EDS, FTIR and XPS technique. In Fig. S8A, the element of U was detected in the EDS image of the U(VI)-loaded Fe/N-C-700, manifesting that U(VI) is successfully adsorbed on the Fe/N-C-700. Moreover, the FTIR spectra of U(VI)-loaded Fe/N-C-700 exhibits a sharp peak at $\sim 1383$ cm$^{-1}$ (Fig. S8B), which is probably due to the adsorbed NO$_3^-$ on samples that originated from the metal nitrates (i.e., UO$_2$(NO$_3$)$_2$·6H$_2$O) [55,56]. The band at $\sim 896$ cm$^{-1}$ is observed, attributing to the antisymmetric vibration of the [O=U=O]$^{2+}$ group [57]. The total scans of XPS spectra for pure and U(VI)-loaded Fe/N-C-700 were shown in Fig. 9A. The presence of characteristic peak of U 4f after U(VI) loaded demonstrates the high adsorption ability of Fe/N-C-700. The U 4f peak was conducted to determine the relative proportion of U(VI) and U(IV) in U(VI)-loaded Fe/N-C-700 sample, as shown in Fig. 9B. The U(IV) peaks are located at 382.0 and 392.7 eV, meanwhile, the U(VI) peaks found at 384.2 and 393.4 eV, are assigned to the adsorbed uranyl onto Fe/N-C-700. Since the binding energy of U(VI) is higher than that of U(IV), a shift or broadening of the U 4f peaks to lower energies is indicative of the reduction of U(VI) to a lower oxidation state [58].

A detailed Fe 2p XPS analysis of the pure and U(VI)-loaded Fe/N-C-700 was shown in Fig. 9C, two pairs of peaks for Fe 2p$_{1/2}$ (726.1 and 724.1 eV) and Fe 2p$_{3/2}$ (712.4 and 710.8 eV) confirm the existence of metallic Fe or Fe$_3$C [41]. After U(VI) loaded, the appearance of Fe 2p$_{3/2}$ at 711.0 and 713.2 eV is ascribed to Fe(III) species such as Fe$_2$O$_3$ and FeOOH [22]. The existence of Fe(III) indicates that Fe(II) is involve in reducing U(VI) [35]. The redox reaction between metallic Fe and U(VI) takes place under equations.

$$\text{UO}_2^{2+} + \text{Fe} \rightarrow \text{UO}_2 + \text{Fe}^{2+}$$

$$\text{UO}_2^{2+} + 2\text{Fe}^{2+} \rightarrow \text{UO}_2 + 2\text{Fe}^{3+}$$

$$3\text{UO}_2^{2+} + 2\text{Fe} \rightarrow 3\text{UO}_2 + 2\text{Fe}^{3+}$$

Furthermore, heterogeneous atoms generally play a crucial role to remove metal ions [59]. Therefore, to investigate the impact of particular nitrogen functionalities for the removal of U(VI) is valuable. Fig. 9D displayed the N 1s XPS spectra of the pure and the U(VI)-loaded Fe/N-C-700. N 1s peak could be deconvoluted into three peaks (pyridinic N at 398.70 eV, graphitic N at 400.97 eV and oxidized N at 403.33 eV) and the peak strength obviously decreases after U(VI)
loaded, indicating that nitrogen functionalities could act as active sites on the adsorbent surface via the coordination of U(VI) ions [22,59]. To further investigate the reduction mechanisms, the XPS spectra of the pure N-C and U(VI)-loaded N-C were recorded in Fig. S9. From Fig. S9A and S9B, the existence of U(VI) verified that the adsorbed U(VI) was partially reduced to insoluble U(IV), meaning that reduction also existed in the N-C-U(VI) system. The nitrogen-containing functional groups of the N-C, Fe/N-C-700 before and after U(VI) loaded were compared in Table S3, it can be observed that after U(VI) loaded, the molar ratio of pyridinic N are greatly reduced, while that of graphitic N enhanced, meaning that the redox reaction occurred between U(VI) ions and the nitrogen functionalities of N-C, Fe/N-C-700. So, the negative charge of nitrogen functionalities is very beneficial for the adsorption and reduction of cationic U(VI), showing a positive impact of nitrogen heteroatoms on the U(VI) uptake.

The possible interaction mechanism could be clarified by two key approaches: adsorption as well as redox reaction. First, the cationic U(VI) was sorbed on the negatively charged active sites of Fe/N-C-700 via electrostatic interaction. Then, the surface sorbed U(VI) were reduced to U(IV) by the metallic Fe, and then the U(IV) were further acquired by Fe/N-C-700. Moreover, nitrogen dopant also plays a key role in the adsorption and redox processes, on the one hand, it improves the negative charge density, leading to an increase in remarkably electrostatic driving forces between the cationic U(VI) and the Fe/N-C-700. On the other hand, it can provide many basic sites promoting a reductive environment for U(VI) ions.

4. Conclusions

Fe nanocrystals embedded into N-doped carbon composites were successfully synthesized by one-pot Fe3+ -mediated polymerization of dopamine, followed by in situ activation-graphitization of the resultant Fe-PDA complexes. The prepared Fe/N-C-700 showed distinct advantages: the spherical structure, ultrahigh surface area and easy magnetic separation from solution. The macroscopic adsorption experiments displayed the U(VI) adsorption kinetics and isotherms and efficient enrichment of radionuclides on graphene-supported oxidation-polymerized, Environ. Sci. Technol. 47 (2013) 9904–9910.


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