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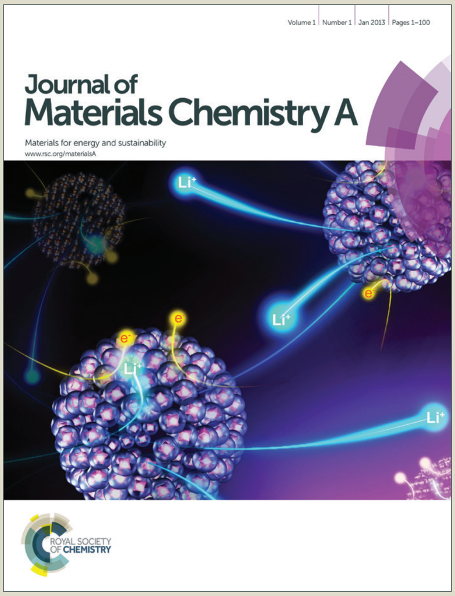

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Introduction of Amino Groups into Acid-resistant MOFs for Enhanced U(VI) Sorption

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Supporting Information (SI): Detailed description of U(VI) sorption experiments and Extended X-ray absorption fine structure (EXAFS) measurements; The U(VI) sorption data fitting by Kinetics models and Isotherm models; Comparison of FTIR spectra and XRD patterns of the sorbents before and after U(VI) sorption; SEM images of the sorbents after U(VI) sorption; Selectivity test for MIL-101-ED as well as compositions of the coexistent ions solution in the test.

Abstract

Metal–organic frameworks (MOFs) have recently been receiving increasing attentions in various scientific fields including nuclear industry due to their unique properties. In this work, the acid-resistant chromium-based MOFs, MIL-101, and its amino derivatives were prepared for exploring the potential usage in separation, removal and/or recovery of radionuclides from aqueous solutions. The synthesized MIL-101-NH_2, MIL-101-ED (ED=Ethanediamine), and MIL-101-DETA (DETA= Diethylenetriamine) were characterized by X-ray diffraction spectrometry (XRD), infrared spectrometry (IR), N_2 adsorption/desorption measurements, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA), which confirm the successful modification of amino groups and the maintenance of porous structures. The sorption performances of these materials toward U(VI) from aqueous solution were investigated in detail. It was found that all the amine-grafted MOFs were highly efficient in capturing U(VI) compared to the raw MIL-101. The sorption capacity of these MOFs for U(VI) sorption follows the order of MIL-101-DETA>MIL-101-ED>MIL-101-NH_2>MIL-101, in which MIL-101-DETA possesses the highest sorption capacity of 350 mg/g at pH ~5.5. Moreover, the sorbed U(VI) can be easily desorbed by controlling a lower pH (pH$\leqslant$3.0), and the prepared materials also display desirable selectivity toward U(VI) in the solution containing a range of competing ions. Based on the FTIR and EXAFS characterizations, the sorption mode of U(VI) onto the MOFs are fully discussed. This work promises to provide a facile approach for developing acid-resistant MOFs toward highly efficient and selective extraction of radionuclides from aqueous solutions.

Introduction

The sustainable energy supply is one of the most significant events concerning the development of human beings. Considering the global climate change and the shortage of fossil fuels in the near future, nuclear power, a kind of high efficient and clean energy with no greenhouse gas emission, has been regarded to be a plausible alternative to the traditional energy sources. Rapid development of the nuclear power industry, however, brings environmental concerns associated with nuclear fuel cycle, including the removal and recovery of radionuclides from nuclear waste solutions[1-5]. Uranium, as an essential element in nuclear fuel cycle, its separation and recovery are of great significance from point of view of sustainable utilization of uranium resources and environmental protection.[6-8] The versatile materials that can remove the radionuclides and remediate the environment are therefore anticipated, in which porous materials have gained extensive attention in recent years.[9]

Metal-organic frameworks (MOFs) are a family of porous materials constructed by bridging organic ligands linked with metal ionic centers. One of the merits of MOFs is that organic groups can vary according to different needs,[10] which makes it possible to tune their physicochemical properties. Therefore, various MOFs with different properties have been synthesized for gas separation and storage,[11-13] catalysis,[14, 15] drug delivery,[16, 17] and chemical sensing,[18, 19] etc. Recently, it was reported that MOFs could be used as solid sorbents to sorb uranium, providing a potential avenue for actinide extraction. MOF-76[20] and UiO-68[21], for example, have been shown to efficiently capture U(VI) from aqueous solution.

As in many cases radionuclides are present in acidic aqueous solutions, the sorbents that possess adequate stability in acidic aqueous solutions are thus anticipated. Keep this in mind, a chromium-based MOF, MIL-101, prepared by a hydrothermal method at 220 °C, was selected as a potential substrate due to its outstanding stability in acidic solution and even in concentrated acid.[22-25] Moreover, MIL-101 possesses two types of zeotypic mesoporous pores with diameter of ca. 29 and 34 Å defined by pentagonal and hexagonal windows, with free opening of ca. 12 and 16 Å, respectively. The apertures are large enough to facilitate the transportation of actinide ions into pores. In addition, nitrogen atoms are well known soft donors that have good affinities toward light actinides,[26, 27] functionalization of the MIL-101 substrate with N-containing groups, e.g. amino groups, is probably an effect way for achieving enhanced sorption and directed selectivity toward actinide cations. Up to now, two different pathways to introduce amino groups into MIL-101 have been reported. A first route consists of a direct modification of the aromatic rings present in MIL-101 by covalent grafting, which creates the amino-MIL-101[23]. Although the amino groups were evidenced to be firmly anchored onto the framework of MIL-101, steric hindrance of the aromatic rings and rigidity of the amino group as well as lower activity of the aromatic amines are probably unfavorable to capture actinide cations from aqueous solution. A second pathway for amine modification of MIL-101 use coordinatively unsaturated metal centers (CUS) as anchoring points for the chosen amine ligands. Several kinds of amines were incorporated into the MOFs by using this method, and the prepared MOFs were successfully applied in catalysis[28], metal and organic molecules encapsulation[25] and recent gas sorption[29] with encouraging results. To the best of our knowledge, however, the utility of these materials on the metal ions sorption from aqueous solution is fairly unexplored, and it is yet interesting topic.

In this work, three amino functionalized MIL-101, i.e. MIL-101-NH_2, MIL-101-ED and MIL-101-DETA as U(VI) sorbents were prepared by the two post-grafting methods as mentioned above. The products were sufficiently characterized by X-ray diffraction (XRD), FT-IR, N_2 sorption, SEM, and TGA. The sorption of U(VI) onto the raw MIL-101 and three amino functionalized materials as a function of solution pH, contact time, and initial U(VI) concentration were studied in detail. The influences of different post-grafting methods and the coverage of grafted ligands on the U(VI) sorption, as well as the sorption mode of U(VI) on the sorbents were fully discussed. Finally, selective sorption properties of MIL-101-ED and MIL-101-DETA toward U(VI) in the presence of other competing ions were determined, and the vast opportunity of MOFs for the treatment of actinide containing aqueous waste were highlighted based on the present results.

Experimental

Chemical and reagents

All chemicals (analytical grade) were obtained from commercial sources and used without further purification. The stock U(VI) solution was prepared by dissolving appropriate amount of uranyl nitrate hexahydrate ($UO_2(NO_3)_2{\bullet}6H_2O$, Merck, Germany) in deionized water. The pure U(VI) solutions (5–200 mg L^{-1}) were prepared by appropriate dilution of the stock solution. The multi-ion solution containing nine competing ions besides U(VI) as listed in Table S1 (SI) was prepared by dissolving their nitrates in aqueous solution. The concentration of all the metal ions was identical as ca. 0.5 mmol L^{-1}. Deionized water used in all experiments was obtained from the Milli-Q water purification system.

Preparation of MIL-101 MOFs

Synthesis of MIL-101

MIL-101 MOF was synthesized according to a procedure as reported previously [22]. Specifically, 1.63g of chromium(III) nitrate ($Cr(NO_3)_3 \cdot 9H_2O$, Aldrich, 99%), 0.7g of 1,4-benzene dicarboxylic acid (H_2BDC, Aldrich, 99%), 0.18 mL of fluorhydric acid (HF, Beijing Chemical Works, > 40%) and 20 mL H_2O were sealed in a 50 mL teflonlined stainless steel autoclave and then heated to 220 ^oC in an oven. After being maintained for 8 h, the mixture was cooled down to room temperature naturally. Most of the recrystallized unreacted H_2BDC was eliminated by filtration using two glass filters with a pore size between 40 and 100 μm. Then, the MIL-101 powder was obtained by separating the filtrate using a 0.45 μm filter membrane. To remove the residual H2BDC present both outside and within the pores of MIL-101, a thermal treatment was sequentially performed using water at 70 ^oC for 24 h, ethanol at 80 ^oC for 24 h and 1 M of NH_4F solution at 70 ^oC for 24 h. Then, the mixture was immediately filtered and washed with hot water. The solid was finally dried overnight at 80 ^oC under air atmosphere.

Amino-group functionalization

The synthesis of MIL-101-NH_2 consists of two steps as reported previously[23]. First, nitro groups are introduced to the benzene rings of the organic framework by a direct covalent post-grafting method. Specifically, 14 mL of concentrated sulfuric acid and 10 mL of concentrated nitric acid were added into 200 mg MIL-101 and the mixture was stirred for 5 h in ice bath. Then the mixture was warmed to room temperature naturally and poured into 100 mL ice. The isolated raw material was subsequently activated by thermal treatment using water and ethanol at 80 ^oC for 12 h, and Green MIL-101-NO_2 solid was thus obtained. Second, the $SnCl_2 \cdot 2H_2O$ was used to reduce the nitro groups to amino groups. Typically, the solid MIL-101-NO_2 and 6.52 g $SnCl_2 \cdot 2H_2O$ were suspended in 40 mL ethanol. The mixture was heated at 70 ^oC for 6 h. After filtration, the greenish solid was suspended in 40 mL concentrated hydrochloric acid. Afterwards, the solid was filtered, washed three times with H_2O and one time with ethanol. The product was dried in air at 70^oC for 12 h. MIL-101-ED and MIL-101-DETA were prepared according to the reported procedure.[28] In a typical preparation, 200 mg MIL-101 dehydrated at 150 ^oC for 12 h was suspended in 12 mL anhydrous toluene in a flask. Then an appropriate amount of ethylenediamine (ED, 0.1 mL), or diethylentriamine (DETA, 0.18 mL) was added to the suspension and the mixture was refluxed at 120 ^oC with stirring under N_2 atmosphere for 12 h. The product was recovered by filtration and washed three times with ethanol, and then dried at 70 ^oC for 12 h.

Characterizations of the synthesized MOFs

X-ray diffraction (XRD) patterns of the materials were obtained on a Bruker D8-Advance X-ray Diffractometer with a Cu Kα radiation (λ=1.5406 Å) at a step size of 0.02º. The morphologies and microstructures of the prepared samples were examined with a field emission scanning electron microscopy (SEM, Hitachi S-4800). Thermogravimetric curve was recorded on a thermal gravimetric analyzer (TGA, TA Instruments, Q500) from 20-800 ^{o}C by using a heating rate of 5 ^{o}C min^{-1} under air flow. CHN content was determined by an elemental-analysis device (Elementar Vario MICRO CUBE). Data of fourier transform infrared (FTIR) spectra of the prepared samples were recorded on a Bruker Tensor 27 spectrometer with a potassium bromide pellet method. The N_2 sorption experiments were measured at a liquid nitrogen temperature (-196 ^{o}C) using a micromeritics ASAP 2020 HD88 instrument. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method with prior degassing under vacuum at 120 ^{o}C for 12 h. For the quantitative determination of U(VI) in single component sorption experiments, the UV–Visible spectrometry with arsenazo-III as the chromogenic agent was used at the wavelength of 656 nm, while Inductively coupled plasma optical emission spectrometer (ICP-OES, HORIBA, JY 2000-2) was used to determine the residual concentration of tested ion(s) in supernatants in the selectivity test experiment.

U(VI) sorption experiments

All sorption experiments were carried out using a batch method in air at room temperature, with initial concentration of U(VI) ranging from 5 to 200 mg L^{-1}. The solution pH was adjusted by using negligible volume of dilute HNO_3 or NaOH. The control experiment was performed simultaneously using the identical U(VI) solution in the absence of the sorbent. A detailed experimental procedure is described in Supporting Information (SI-1) with experimental conditions presented in the related figure and table captions for clarity. Sorption amount q_e (mg g^{-1}) and distribution coefficient K_d (mL g^{-1}) were calculated by following equations:

$$q_e = \frac{(c_o - c_e) \times V}{m} \qquad (1)$$

$$K_d = \frac{(c_o - c_e) \times V}{c_e \times m} \qquad (2)$$

Where c_0 and c_e are the initial concentration and equilibrium concentration of metal ions (mg L^{-1}), respectively. V denotes the volume of the testing solution (mL), and m corresponds to the amount of the sorbent (g). All values were measured in duplicate with the uncertainty within 5%.

Results and Discussion

Characterizations of the synthesized MOFs

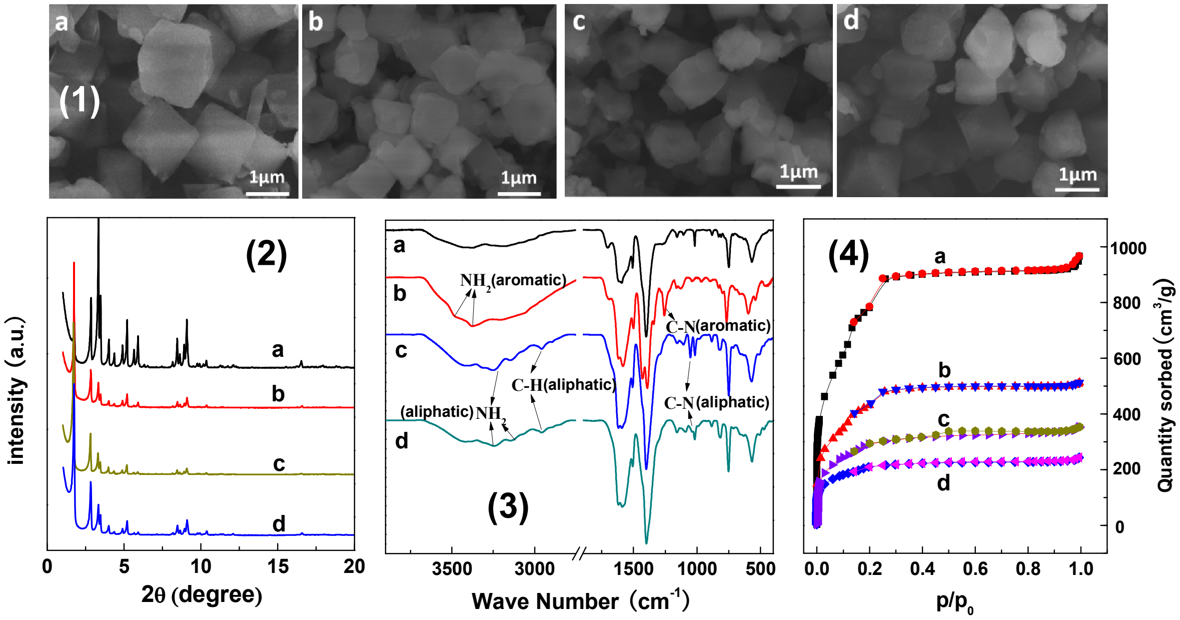

Fig. 1 Characterizations of MIL-101(a) and its amino derivatives MIL-101-NH_2 (b), MIL-101-ED (c) and MIL-101-DETA (d).

(1) SEM image; (2) XRD pattern; (3) FTIR spectra; (4) N_2 sorption/desorption isotherm;

Fig. 1 gives the characterization results of MIL-101(a) and its amino derivatives. The SEM images demonstrate that all the materials possess discrete octahedral morphologies with a dimension of approximate 1 μm per side, and no significant morphological changes were observed following amine-grafting. The maintenance of the morphology seems to be an indication that the MIL-101 framework keeps stable during functionalization process. The XRD patterns of four materials are shown in Fig. 1 (2). The comparability of the related peak pattern of MIL-101 with the result of reported work[22] indicates the successful synthesis of the material. The amine-grafted materials show almost the same X-ray diffraction patterns with the raw MIL-101, which confirms that the amine grafting occurs with no apparent loss of crystallinity, while the change in the relative reflection intensities is in agreement with a partial pore filling of the functional groups.

The successful modification of MIL-101 by amine is also evidenced by comparing FTIR spectra of MIL-101, MIL-101-NH_2, MIL-101-ED and MIL-101-DETA (Fig.2 (3)). For all the amine-grafted materials, the asymmetric and symmetric N–H-stretching vibrations appears at the range of 3250-3500 cm^{-1},[23, 28] which confirms the presence of amino groups. The C–N stretching vibration for

MIL-101-NH_2 is revealed at 1260 cm^{-1}. A peak split at ~1400 cm^{-1} is clear an indication of intermolecular hydrogen bonding occurring between grafted amino and carboxyl group in MOF framework, with the lower energy peak being the C-O stretching vibrations affected by hydrogen bonding and the higher energy peak considered “free” of these interactions. For MIL-101-ED and MIL-101-DETA, as a result of introduction of alkylamines, the absorption band assigned to C-H(aliphatic) stretching mode and C-N(aliphatic) stretching mode are observed at 2950 and 1050 cm^{-1}, respectively. All these characteristic peaks clearly suggest that the expected amine-grafted MIL-101 were successfully prepared.

The specific surface areas of the four materials were determined by N_2 sorption/desorption experiments at the temperature of -196 ^oC, as shown in Fig.1 (4). The N_2 sorption/desorption isotherms for all the materials are found to be reversible type I, typical for a microporous material. Compared with the bare MIL-101, the anime-grafted materials exhibit a significant decrease of the N_2 amount adsorbed at $P/P_0 > 0.01$. The BET surface area decreases from 3065 $m^2\ g^{-1}$ for MIL-101 to 1645 $m^2\ g^{-1}$ for MIL-101-NH_2, 753 $m^2\ g^{-1}$ for MIL-101-ED and 1074 $m^2\ g^{-1}$ for MIL-101-DETA, respectively. The pore volumes (1.437 $cm^3\ g^{-1}$ for MIL-101, 0.779 $cm^3\ g^{-1}$ for MIL-101-NH_2, 0.363 $cm^3\ g^{-1}$ for MIL-101-ED and 0.528 $cm^3\ g^{-1}$ for MIL-101-DETA) are also decreased after grafting, which confirm again the successful pore modification of MIL-101. Moreover, the N_2-sorption results seem to give a hint that MIL-101-ED has the largest coverage of grafting reagent since it has the lowest BET surface area and pore volume. However, the pores of all the MOFs are still maintained and accessible by U(VI) species, which facilitates the entrance of U(VI) and coordination with amino groups so as to enhance the U(VI) sorption.

In addition, thermal analysis for the prepared materials was performed to assess thermal stability of the MOFs and determine coverage of the functional groups. The result is shown in Fig. 2. As can be seen, the weight loss of all the grafted materials with the increase in temperature shows three distinct stages. The first stage is from room temperature to ca. 100 ^oC, in which the weight loss could be ascribed to the evaporation of physically adsorbed water and some residual solvent on the surface and/or in the pore channels. The second stage lies in the temperature range of 100 ^oC - 290 ^oC, the slow weight loss reasonably corresponds to the pyrolysis of the grafted functional groups on the surface of MOFs. At temperature above 290 ^oC, the weight loss sharply increases owing to the decomposition of MOFs frameworks since MIL-101 decomposes at the same temperature range. The most significant weight loss occurs at temperature of ca. 300 ^oC for MIL-101-NH_2 and ca. 350 ^oC for the other materials, suggesting a good thermal stability of all the prepared MOFs. The relatively lower decomposition temperature of MIL-101-NH_2 is probably attributed to the harsh synthesis procedure in which the concentrated HNO_3 and H_2SO_4 were used. At or near 500 ℃, the TGA profile for all the materials reaches a plateau, and the coverage of functional groups could be obtained from TGA curves by comparing the total weight loss of grafted materials with their substrate. To eliminate the interference of physically adsorbed water and solvent, all the material were heated at 120 ^{o}C for 2 h before each TGA measurement (Fig.5 b-d), and then the differences of weight loss between the grafted materials and MIL-101 substrate at the temperature range of 120 -500 ^{o}C were obtained, from which the coverage of the amino groups in MIL-101-NH_2, MIL-101-ED, and MIL-101-DETA were calculated to be 1.63, 1.28, and 0.72 mmol g^{-1}, respectively. This result is in agreement with the corresponding data (1.35 mmol g^{-1} for MIL-101-ED and 0.86 mmol g^{-1} for MIL-101-DETA) evaluated by the fluctuation of N content between raw MIL-101 and amine-grafted MIL-101 through CHN element analysis (MIL-101-NH_2 was not analyzed here because of the disturbing of nitrate ions). Hwang and coworkers[28] have assumed that the grafted amino groups are present mainly at the center of pore cages, thus higher amino group coverage in MIL-101-ED cause more decrease of BET surface area and pore volume than MIL-101-DETA as confirmed by N_2 sorption experiment. For MIL-101-NH_2, however, the highest amino group coverage corresponds to the highest BET surface area and pore volume among the three grafted materials. This is understandable from the fact that for MIL-101-NH_2 bare amino group with little size was directly anchored to the aromatic rings present in MOF framework, while for MIL-101-ED and MIL-101-DETA the alkylamine group with larger size was grafted onto coordinatively unsaturated metal centers of MOFs.

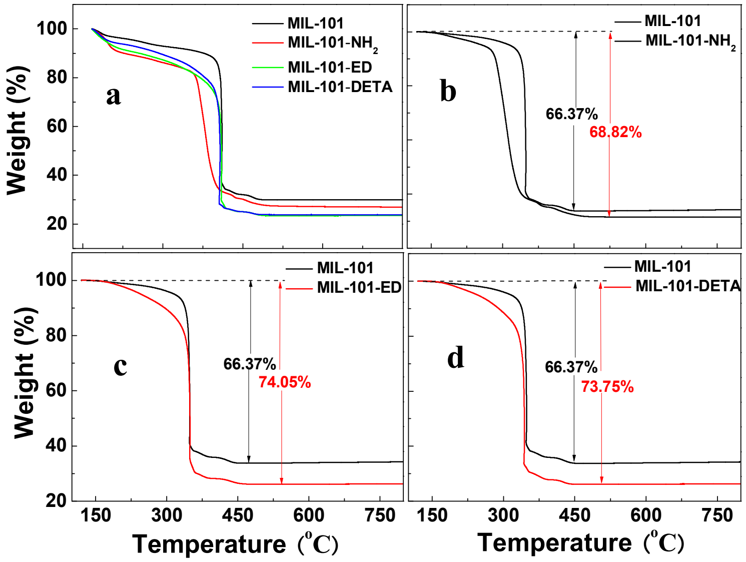

Fig. 2 The TGA profile for the as-prepared MOFs (a) and the TGA profile of MIL-101-NH_2 (b), MIL-101-ED (c) and MIL-101-DETA (d) compared with MIL-101 after heating at 120 °C for 2 h.

U(VI) sorption by the prepared MOFs

To evaluate the adsorbability of MIL-101 and its amino derivatives, the sorption of U(VI) from aqueous solution into the four prepared MOFs materials was performed at various conditions of pH, contact time, initial U(VI) concentration and absence/presence of competing metal ions. The U(VI) sorption performances of bare MIL-101 and the three different amine-grafted MIL-101was compared, and the sorption mode of U(VI) into the MOFs sorbent was discussed in detail based on EXAFS and FTIR characterizations combined with DFT calculations.

Effect of solution pH on U(VI) sorption

The solution pH is an important parameter for the metal ion sorption, because it remarkably affects the speciation of metal ions as well as the surface charge and binding sites of the sorbent. Herein, the U(VI) sorption by the prepared MOFs at pH ranging from 3 to 6 was performed to assess the effect of pH. As shown in Fig. 3, except that raw MIL-101 shows no obvious U(VI) sorption at the test pH range, the sorption of U(VI) by MIL-101-NH_2, MIL-101-ED and MIL-101-DETA is strongly pH-dependent and increase rapidly with the increase of solution pH. At pH below 4.0, for example, almost no U(VI) sorption occur for all the test materials, whereas the sorption amount reaches more than 200 mg/g for MIL-101-DETA at pH 5.5. The similar pH- dependent U(VI) sorption was also observed in our previous works in which amine [30] and dihydroimidazole [31] functionalized SBA-15 were used as sorbent. One reasonable explanation might be associated with the pH induced protonation and deprotonation of grafted amino groups on MOFs. Besides, it is well known that

U(VI) cations can hydrolyze or precipitate at higher pH. The transformation of U(VI) from free UO_2^{2+} to multi-nuclear hydroxide complexes with the increase of pH might be another reason of the pH-dependent sorption, considering that multi-nuclear hydroxide complexes of U(VI) available at higher pH may be more favored by the MOFs sorbent. To avoid severe hydrolysis and precipitation of U(VI) from the solution at higher pH and achieve higher sorption capacity, pH 5.5 was selected for further sorption experiments.

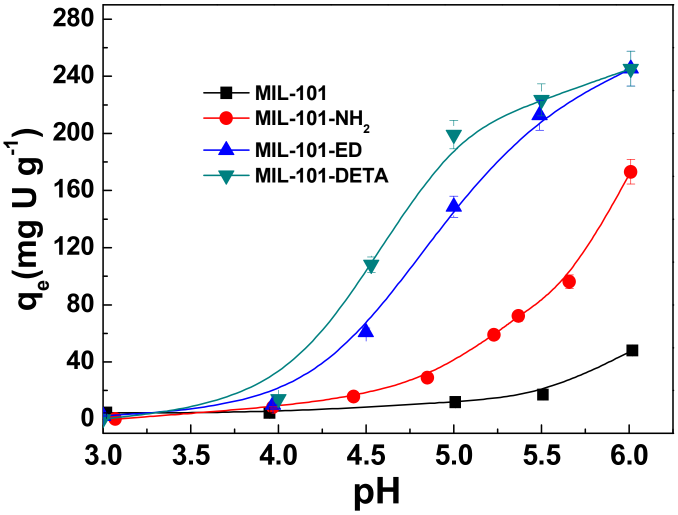

Fig. 3. Effect of pH on the U(VI) sorption onto MIL-101, MIL-101-NH_2, MIL-101-ED and MIL-101-DETA; t = 240 min, $m_{sorbent}$ = 4.0 mg, $V_{solution}$ = 10 mL, c_0 = 100 mg L^{-1}, T = 25 ± 0.5 °C.

Sorption kinetic

In order to evaluate the sorption rate of U(VI) by the four MOFs sorbents, sorption experiments covering different contact time (1 min to 4 h) were performed at initial U(VI) concentration (c_0) of 100 mg L^{-1}. As shown in Fig. 4, the U(VI) sorption rates for all the MOFs are ultra-fast especially in initial 30 min, except that raw MIL-101 shows no obvious U(VI) sorption even after 4 h contacting. The sorption process for all the materials reaches equilibrium at around 2 h. The equilibrium time in this case is comparable with that of less than 2 h in functionalized mesoporous silicas [6, 30, 31] but extremely shorter than that of 20 h in MCM-41[32], 24 h in nanoporous carbon[33] and 24 h in MWCNT-g-CMC[34]**.** To get more information regarding the sorption process, the pseudo-first-order and pseudo-second-order kinetic models were applied to fit the experimental data. The model details and parameters, as well as the correlation coefficient obtained by the three models are listed in Supporting Information (SI-2, Fig. S1 and Table S1). From the good fitting with correlation coefficient of more than 0.99 for all amine-grafted materials and the fact that the sorption capacity (q_e) obtained from pseudo-second-order model (101, 187, and 235 mg g^{-1} for MIL-101-NH_2, MIL-101-ED, and MIL-101-DETA, respectively) is very close to the experimentally observed equilibrium capacity, it can be clearly concluded that the sorption of U(VI) in test MOFs follows pseudo-second order model regardless of reaching equilibrium or not. This result can be expected because a chelating exchange process, unlike a ordinary exchange process, is always considered to be controlled either by particle diffusion mechanism or by a second-order chemical reaction[35]. The MOFs sorbent with its porous structure and amino groups present on its surface most probably behaves like a chelating exchanger, thus second-order chemical reaction kinetics is expected to be followed in the sorption processes. To ensure the complete sorption of U(VI), the mixture of the sorbent and the solution was stirred for at least 2 h in subsequent experiments.

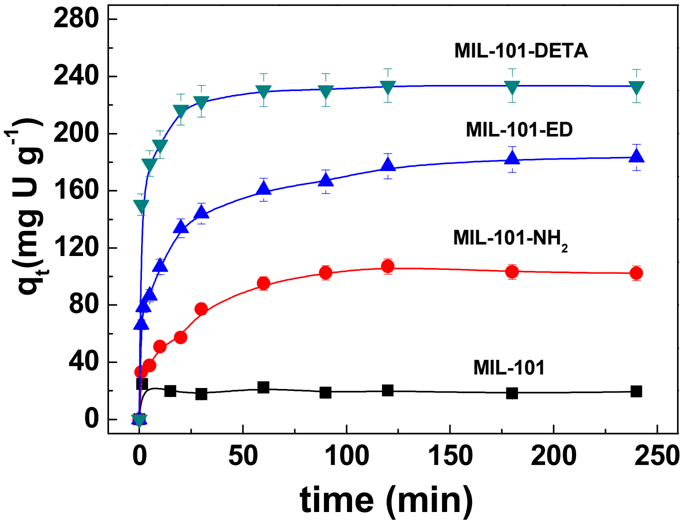

Fig. 4 Effect of contact time on the U(VI) sorption onto MIL-101, MIL-101-NH$_2$, MIL-101-ED and MIL-101-DETA; pH = 5.5, $m_{sorbent}$ = 4.0 mg, $V_{solution}$ = 10 mL, c_0 = 100 mg L^{-1}, T = 25 ± 0.5 °C.

Sorption isotherms

The amount of U(VI) sorbed by the four MOFs sorbent as a function of U(VI) concentration in supernatant at the equilibrium state (C_e), i.e. sorption isotherms, were determined at a constant pH of 5.5±0.1 by varying the initial U(VI) concentrations from 5 μg/mL to 200 μg/mL (Fig. 5). As can be seen, a continuous increase of U(VI) sorption with augmentation of initial U(VI) concentrations was observed for all the amine-grafted MOFs, whereas bare MIL-101 shows negligible U(VI) sorption regardless of U(VI) concentrations. At a U(VI) concentration over 180 μg/mL corresponding to a C_e of > 60 mg L^{-1}, the U(VI) sorption for all the MOFs reached equilibrium, from which the saturated sorption capacities were obtained under the experimental conditions, as shown in Table 1. The results clearly suggest that amine-functionalized MOFs are much more efficient in U(VI) capture compared to bare MIL-101. And the adsorbability of amine-functionalized MOFs follows the order of MIL-101-DETA> MIL-101-ED> MIL-101-NH_2. It is also noted from Table 1 that the coverage of functional groups in the grafted MOFs follows the order of MIL-101-NH_2> MIL-101-ED> MIL-101-DETA. Such an order is reversed to that of the adsorbability, which we considered can be rationalized from the amount and the nature of accessible amine sites on the MOFs. For MIL-101-NH_2, amino groups were directly anchored to the aromatic rings present in MIL-101 framework. Although its more coverage of functional groups and larger surface area, the availability of amino groups is much lower because of steric hindrance of the aromatic rings and formation of intermolecular hydrogen bond between the carboxyl group present in the MOF and the grafted amino group (as evidenced in Fig. 2). Moreover, aromatic amines are always less active than aliphatic amines. All these issues make a lowest U(VI) sorption among the three functionalized MOFs. For MIL-101-ED and MIL-101-DETA, however, ethylenediamine (ED) and diethylenetriamine (DETA) were grafted on coordinatively unsaturated metal centers (CUS) of MIL-101, respectively. That is, one amino group of ED or DETA was linked to a CUS of chromium (III) of MIL-101 by direct ligation, while the other one (for MIL-101-ED) or other two (for MIL-101-DETA) amino groups capture U(VI) ions through complexation. This kind of grafting mode and the flexibility of the alkylamine greatly increase the availability of amino groups and thus increase the U(VI) sorption. MIL-101-DETA (0.72 mol g^{-1} DETA corresponds to 1.42 mol g^{-1} free amino group) has more accessible amine sites and larger surface area than MIL-101-ED (1.28 mol g^{-1} ED corresponds to 1.28 mol g^{-1} free amino group), which make it become the most effective U(VI) sorbent among the functionalized MOFs. Besides, it is clear from Table 1 that the U(VI) sorption in amine-grafted MIL-101, particularly in MIL-101-ED and MIL-101-DETA, is comparable and even more efficient than that in previously reported MOFs, which is another indication of the high performance of amimo-grafted MIL-101 on sequestrating U(VI) from aqueous solution.

Table 1 A summary of U(VI) uptake by MIL-101 series in this work and by other MOFs previously reported, as well as functional groups coverages and structural parameters of the sorbents.

Samples	Saturation capacities (mg U/g)	Functionality coverages (mmol/g)	BET surface area (m²/g)	Pore volume (cm^3 /g)
MIL-101	20	-	3065	1.437
MIL-101-NH_2	90	1.63	1645	0.779
MIL-101-ED	200	1.28	753	0.363
MIL-101-DETA	350	0.72	1074	0.528
MOF-76[20]	300 [a]	nm	nm	nm

UiO-68[21]	217 [b]	nm	1350	65.7%[c]

[a] The value were obtained at pH 3.0 and decreased to ~100 at pH 5.5; [b] The value were obtained at pH 2.5 and decreased to 152 at pH 5.0; [c] Solvent accessible volume calculated with PLATON; nm = not be measured

To explore the sorption mode of U(VI) onto the amino group functionalized MOFs, the sorption data were fitted to Langmuir and Freundlich models, which are frequently used to describe the mechanism of sorption. The details of the two models and the fitting results are provided in Supporting Information (SI-3, Fig. S2, and Table S2). From the better correlation coefficient (> 0.99) and the fact that the equilibrium sorption capacity (Q) obtained from Langmuir model (220 mg/g for MIL-101-ED and 410 mg/g for MIL-101-DETA) is close to the experimentally observed saturation capacity, it can be concluded that the U(VI) sorption by both MIL-101-ED and MIL-101-DETA follows Langmuir sorption model very well, revealing a monolayer uniform sorption mode. This result supports our expectation that U(IV) sorption by MIL-101-ED and MIL-101-DETA mainly occur through complexation with the amino group on surface of the sorbents. For MIL-101-NH_2, however, the sorption data are not regarded to properly fit both the Langmuir (R^2 < 0.9) and Freundlich models (R^2 < 0.92), which suggests a complex U(VI) sorption mode. Perhaps a physical sorption and/or a multilayer sorption are involved due to the steric hindrance of the aromatic rings and the formation of intermolecular hydrogen bond as mentioned above.

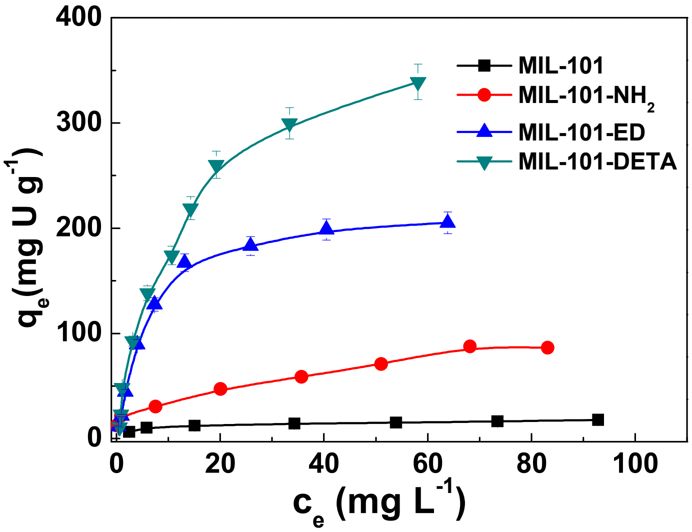

Fig. 5 Effect of initial U(VI) concentration on the U(VI) sorption onto MIL-101, MIL-101-NH_2, MIL-101-ED and MIL-101-DETA; pH = 5.5, t = 120 min, $m_{sorbent}$ = 4.0 mg, $V_{solution}$ = 10 mL, T = 25 ±0.5 °C.

Sorption mode studies

FTIR and EXAFS spectra of U(VI)-loaded MIL-101-NH$_2$, MIL-101-ED and MIL-101-DETA were recorded for further understanding the sorption behavior of U(VI) on the MOFs. The comparison of the FTIR spectra (see Supporting Information SI-4, Fig. S3, S4, S5) shows no discernible changes in both absorption position and intensity following U(VI) sorption at various pH except that a new peak assigned to asymmetric stretching vibration of the O=U=O unit appears at ~912 cm^{-1}. The absence of absorption bands at ~1520 cm^{-1}, ~1280 cm^{-1}, ~1030 cm $^{-1}$ [36] and no intensity increases at ~1380cm $^{-1}$ are the clear indications that no nitrate ions as counter ions were sorbed onto the MOFs during U(VI) sorption, which is consistent with the fact that U(VI) ions typically occurs in the hydroxide complexes form at pH > 4.

Fig. 6 shows the comparison of L$_{III}$-edge EXAFS spectra of U(VI) sorbed onto the amine-grafted MOFs. As reference, the spectra of as-prepared U(VI) hydroxide precipitate were also provided (details on the preparation and EXAFS measurement are present in Supporting Information SI-5). It is observed that, on the one hand, spectra B and C have almost the same oscillation mode and the same intense FT peaks at the range of 1~6 Å, whereas spectra A shows a clear difference in intensity of the FT peak at ~2 Å (not phase correction). This indicates that the U(VI) sorption on MIL-101-ED and MIL-101-DETA occur in a same way but are slightly different from that on MIL-101-NH$_2$. On the other hand, all these spectra are distinct from spectra D for the reference one of U(VI) hydroxide precipitate, revealing the absence of such an incidental species under the experimental conditions.

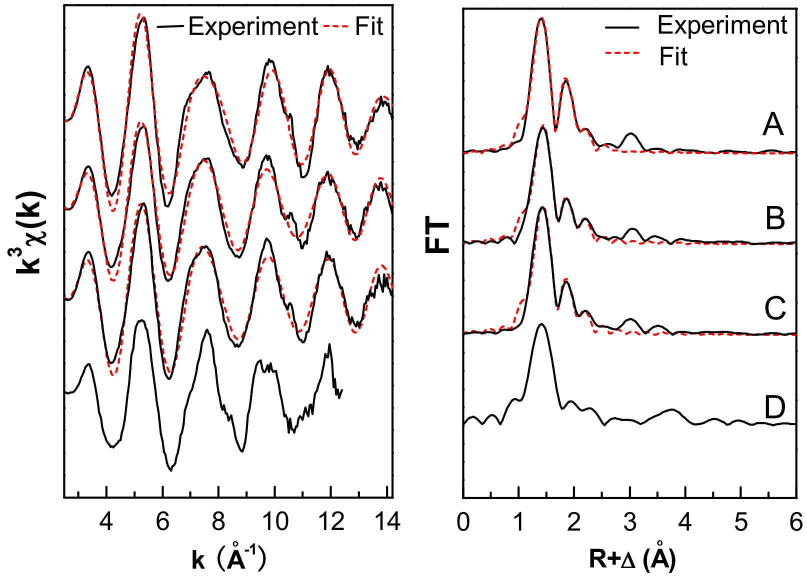

Fig. 6 Left: Raw U L$_{III}$-edge k^3 weighted EXAFS spectra of U(VI) sorbed onto MIL-101-NH$_2$ (A) , MIL-101-ED (B) and MIL-101-DETA (C) including the best theoretical fits and as-prepared U(VI)

hydroxide precipitate (D) as reference. Right: Corresponding Fourier transforms. The FT spectra are not corrected for phase shift.

Reasonable fittings of spectra A, B and C are then followed and the metric parameters are presented in Table 2. During the fit procedure, the coordination number (N) of axial oxygen atoms (O_{ax}) was fixed to two, and the energy shift (E) was linked for all the paths. As can be seen from Table 2, U(VI) sorbed on MIL-101-ED (spectra B) and MIL-101-DETA (spectra C) have almost the same metric parameters, which further confirm a similar type of coordination. Specially, U-O_{ax} distances of ~1.79 Å obtained are typical of uranyl compounds[37], and the UO_{ax} σ^2 value (0.003 $Å^2$) are consistent with the reported value for uranyl (0.001-0.003 $Å^2$).[38, 39] Four oxygen atoms at a range of 2.3-2.5 Å (two at ~2.3 Å and other two at ~2.48 Å) and one nitrogen atom at ~ 2.43 Å comprise the first equatorial shell of the U(VI) ions. The U-N and U-O distance obtained in this work is in agreement with that in $[UO_2][NH_2]_2O_2[H_2O]_3$ cystal[40] and U(VI) hydroxo complex[41] reported previously. These results seems to suggest that U(VI) ions are surround by hydroxy and water molecules except the amine group on the surface of the MOFs. From charge balance and the fact that no nitrate ions as counter ions were sorbed onto the MOFs as evidenced by FTIR, it is deemed that two hydroxy ions (U-O_{eq1}) act as both counter ions and coordinating ligand that bind U(VI) ions in a closer distance, while one amine group (U-N_{eq}) and two water molecules (U-O_{eq2}) as ligand coordinate with U(VI) ions in a little farther distance. For MIL-101-NH_2, however, such a sorption structure changes slightly. One U-O_{eq1} distance increases from 2.29 Å to 2.47 Å, whereas U-N_{eq} distance slightly reduces from 2.43 Å to 2.36 Å. Such a change is understandable from the fact that amino groups in MIL-101-NH_2 are directly anchored to the aromatic rings present in MIL-101 framework and the steric hindrance of the aromatic rings promotes rearrangement of the coordination of U(VI) sorbed on MIL-101-NH_2.

Table 2 Metric parameters extracted by Least-Squares fitting analysis of EXAFS spectra

Sample	Shell	CN	R/Å[b]	σ^2/ $Å^2$[c]	E/eV[d]	R-factor[e]
MIL-101-NH_2	U-O_{ax}	2[f]	1.79	0.003	9.8	0.0069
	U-O_{eq1}	1.1	2.29	0.004	9.8	
	U-N_{eq}	1.1	2.36	0.001	9.8	
	U-O_{eq2}	3.1	2.47	0.006	9.8	
MIL-101-ED	U-O_{ax}	2[f]	1.79	0.003	9.8	0.0072

	U-O_{eq1}	2.0	2.29	0.007	9.8	
	U-N_{eq}	0.9	2.43	0.012	9.8	
	U-O_{eq3}	1.8	2.48	0.006	9.8	
MIL-101-DETA	U-O_{ax}	2^{f}	1.79	0.003	9.6	0.0076
	U-O_{eq1}	2.1	2.29	0.006	9.6	
	U-N_{eq}	0.9	2.43	0.006	9.6	
	U-O_{eq2}	1.9	2.48	0.007	9.6	

[a] Coordination number. N ± ~20%. [b] Interatomic distance. R ± ~0.03 Å. [c] Debye–Waller factor. [d] Energy shift linked for all the paths. [e] Goodness of fit parameter. [f] fixed parameter.

Application assessment

The above results highlight the vast opportunities of amine-grafted MOFs especially MIL-101-DETA on the U(VI) sorption from aqueous solution. To be successful in such application, however, the sorbents should keep stable during the practical sorption process. To verify the stability of prepared MOFs during U(VI) sorption, firstly, the sorbents loaded with U(VI) were subjected to XRD analysis and SEM observation (see Supporting Information, SI-6 and SI-7). The comparison of XRD patterns of the MOFs before and after U(VI) sorption indicates that there is no apparent loss of crystallinity and no supplementary Bragg peaks appear, but the intensities of same peaks of MIL-101 changed, confirming the introduction of U(VI) ions into the pores. The SEM images show that no significant morphological changes occur for all the materials following U(VI) sorption, which also support the maintenance of the MOFs framework during sorption process. Then, leaching test of the sorbed U(VI) from the sorbent and assessment of reusability of the reclaimed sorbent were followed. As mentioned above, the U(VI) sorption in the MOFs is greatly dependent on the solution pH due to the pH-dependent U(VI) speciation and surface charge of the sorbent. Accordingly, the desorption of U(VI) from the sorbent was performed by controlling a lower pH. It is found that a complete U(VI) leaching (> 99%) can be achieved using a solution with pH$\leqslant$3.0. The reclaimed sorbents were then reused to sorb U(VI) at the same conditions as that for fresh sorbents, and the results show that for MIL-101-NH_2, no remarkable decrease of sorption capacity occur after the U(VI) desorption, whereas there is a ca. 30% reduction of sorption capacity for reclaimed MIL-101-ED and MIL-101-DETA compared to the fresh one. This probably can be rationalized from the fact that the functional groups in MIL-101-ED and MIL-101-DETA were grafted on coordinatively unsaturated chromium centers (CUS) of MIL-101. Chromium is known to be a hard lewis acid and prefer coordination with hard bases, such as H_2O. Some amine groups were replaced by water molecules in abundant amount during sorption/desorption of U(VI), thus leading to a reduction of sorption capacity. However, the U(VI) adsorbability of MIL-101-ED and MIL-101-DETA even after a sorption/desorption cycle is still much stronger than that of fresh MIL-101-NH_2 and unfunctionalized MIL-101.

Besides, selectivity is always anticipated for the practical applications of a sorbent. Herein, the U(VI) sorption by MIL-101-DETA, which shows the strongest adsorbability among the four materials, from the aqueous solution containing a range of competing metal ions as listed in supporting information SI-9 (Table S3) was performed at pH 4.4 and 5.5, respectively. The results are shown in Fig. 9. As can be seen that at pH 4.5, the sorption capacity of U(VI) in MIL-101-DETA is more than 80 mg g^{-1}, while that of other metal ions is less than 10 mg g^{-1}. When increased to pH 5.5, the amount of U(VI) sorbed by MIL-101-DETA reached about three times of that at pH 4.5. The sorption capacity here is comparable with that in the absence of competing ions, which reveals an insignificant influence of ionic strength on the U(VI) sorption. This result is of great importance because the independent ionic strength sorption of U(VI) is a critical issue for assessing the feasibility of a sorbent applied in removal or recovery of U(VI) from wastewater with high concentration salts. In addition, it is noticed that the selectivity for U(VI) to all the test competing metal ions at pH 5.5 clearly enhanced compared to that at pH 4.5, which seems to give a hint that solution pH is probably a key factor for determining the selectivity for U(VI). The distribution coefficient (K_d) is usually used to reflect the binding affinity of a metal ion to a sorbent. higher K_d value such as more than 5000 always means the stronger binding affinity and thus higher performance of a sorbent.[4, 42] Herein, the K_d of the test ions on MIL-101-DETA at pH 5.5 were calculated from sorption data to explore the binding affinities of MIL-101-DETA to these metal ions. As shown in inset of Fig. 9, a high value of K_d (> 6000 mL g^{-1}) for U(VI) is obtained even at a high U(VI) concentration (0.5 mmol L^{-1}), whereas the K_d for other coexistent ions (< 100 mL g^{-1}) are fairly low. The significant disparity of K_d between U(VI) and other ions clearly suggests desirable selectivity of MIL-101-DETA toward U(VI).

When MIL-101-ED was tested under the same condition as used for MIL-101-DETA, a similar selectivity toward U(VI) was observed (see supporting information SI-8, Fig. S9), which reveals the important role of the grafted amino groups on the selective sorption of U(VI). It is well known that amino groups always serve as soft donors for actinides and thus have better affinity toward U(VI) over other test metal ions. Moreover, at the test pH, the hydrolysis of U(VI) occurs by transformation of free UO_2^{2+} to hydroxide complexes such as $(UO_2^{2+})_3(OH)_5^+$. These hydroxide complexes may be more favored by the sorbent by forming hydrogen bond with amino groups, thus increases the affinity toward U(VI). Further works based on DFT calculations are in progress to explore the intrinsical reasons of the selectivity of amine-grafted MOFs.

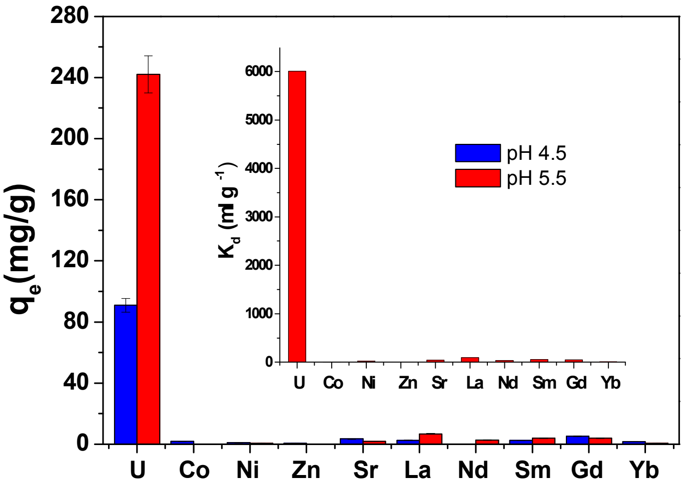

Fig. 9 Competitive sorption of coexistent ions by MIL-101-DETA. Inset shows the K_d of the test ions at pH 5.5 on MIL-101-DETA; the initial concentration of all metal ions was 0.5 mmol L^{-1}.

Conclusions

We report here the first study of enhanced U(VI) sorption by using a series of facilely synthesized amine-grafted MIL-101 MOFs. The MOFs sorbents, with octahedral morphology, ordered porous structure and large surface area, were successfully prepared by different modification method using different amine precursors, and were fully characterized. The adsorbability of the MOFs for U(VI) was systematically studied and was compared with that of raw MIL-101, which clearly suggests that the introduction of amino group greatly enhances U(VI) capture by MIL-101 from aqueous solution. From the fast sorption kinetics of less than 2 hr, large sorption capacity of more than 350 mg/g at a relatively low pH, desirable selectivity for U(VI) ions over a range of competing metal ions and the fact that the sorbed U(VI) can be readily desorbed by using a solution with pH$\leqslant$3.0, it is concluded that amine-grafted MIL-101 MOFs are indeed efficient and feasible sorbent for U(VI) uptake from wastewater. This study indicates a better scope by introducing functional groups into porous MOFs for the separation, removal or recovery of actinides ions from environment. Further works are in progress to fabricate more effective actinides sorbents by varying different functional groups into different MOFs matrix, and to assess reusability and radiation stability of these new materials for further assessing their feasibility applied in separation of actinides.

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TOC art

Amine grafting on the framework of MOFs greatly enhances adsorbability of Cr-MIL-101 towards U(VI) from aqueous solution, and the enhancement dependents on the coverage and flexibility of the grafted amino group.