The development of a material for uranium sorption in NH$_3$/N environment

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Abstract – *An efficient hybrid silica (TD-silica) bifunctionalized with trimethyl ammonium (TMAP) and phosphonate (DPTS) for Uranium (VI) extraction in NH$_3$/N media has been developed in this study. The hybrid silica was prepared by a post grafting of N-trimethoxysilylpropyl-N,N,N-trimethylammonium at large-pore silica. The resulting TD-modified silica were observed to possess a good stability and high efficiency for uranium (VI) sorption from solution in coexist with NH$_3$/N. The adsorbed uranium (VI) can be easily desorbed by using 0.05 mol/L HNO$_3$ and reused for at least 4 times. It is suggested that TD-silica could be a promising solid phase sorbent for highly-efficient removal of U(VI) from solution in coexist with NH$_3$/N.*

I. INTRODUCTION

Due to the rapid development of the nuclear power industry, much attention has been paid to novel materials for the efficient and rapid separation, removal and recovery of nuclear fuel associated radionuclides [1,2]. For the fabrication of coated particle fuel of high temperature gas reactor (HTGR), the preparation of ceramic UO$_2$ kernels by total gelation will produce a large amount of basic waste water with U(VI) and high concentration of NH$_3$/N [3]. Despite the potential advantages of mesoporous materials with high efficiency for U(VI) sorption, there have been relative few reports on the sorption materials for uranium in coexist with NH$_3$/N. The reason is that the active groups of reported functionalized sorption materials tend to lose proton when pH > 7, and electrostatically repulse with negative hydrolyzed production of uranyl ion in such conditions.

In this paper, we employed post-synthesis grafting method to prepare TD-silica functionalized with ammonium and phosphonate groups. In NH$_3$/N environment, the positive charged ammonium group will display eletrostatic attraction with negative charged uranium hydrolyzed products. Besides, the complex reaction between phosphonate and U(VI) will also contribute to a satisfactory U(VI) absorption of TD-silica. The obtained functionalized silica was characterized by SEM and ^{13}C NMR spectra.

II. EXPERIMENTAL

II.A. Reagents

Trimethyl [3-(trimethoxysilyl)propyl]ammonium chloride (TMSPA), (2-diethylphosphatoethyl)triethoxysilane (DPTS) were purchased from HWRK chem., China. SiO$_2$ were purchased from Qingdao Chemical Plant, China (particle size: 100-200 μm). U(VI) stock solution (500 mg/g) was purchased from CNNC Beijing Research Institute of Uranium Geology, and diluted to targeting concentrations when needed. Other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Milli-Q water was used throughout the experiment. 1 mM stock solution of PCSA was prepared by dissolving appropriate products in ethanol. Unless otherwise noted, all reagents and solvents used in this paper were analytical grade without further purification.

II.B. Preparation of TD-silica

SiO$_2$ was first dried in vacuum at 102 ^{o}C for 12 h prior to use. 5.0 g SiO$_2$ was added in 100 mL dioxane with 2.25 mL TMSPA and 2.65 mL TMSPA

under an Argon atmosphere, and then refluxed with mechanical stirring for 24 h. The resulting product were collected by filtration, washed by ethanol and water for 3 times, and then dried at 50 °C overnight.

II.C. Sorption experiment

Simulated U(VI) solution was prepared by dissolving $UO_2(NO_3)_2$ and ammonia in deionised water. The initial and final concentrations of U(VI) in the solution were determined by MUA measurements, and the amount of extracted U(VI) per gram of sorbent was accordingly calculated. Adsorption kinetics of U(VI) on all functionalized samples were studied in the range 0.25-72 h. All experiments were done in triplicates.

The U(VI) uptake (q) and sorption percent (E) were defined as follows:

$$q = \frac{C_0 - C_e}{m} \times V$$

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100\%$$

Where C_0 and C_e represent the concentrations of U(VI) in the aqueous phase for the control experiment, respectively. V is the volume of U(VI) solutions and m is the mass of sorbent used in the sorption experiment.

II.D. Feature analysis of TD-silica

The morphology of the TD-silica sample was obtained by SEM. Solid ^{13}C-NMR were used to confirm the grafted organic groups.

III. RESULTS AND DISCUSSIONS

III.A. Characterization

Figure 1 shows the SEM characterization results of TD-silica. The SEM image displayed that the average length of the sample is ca. 50-200 μm. All the signals in ^{13}C-NMR spectra could be assigned to TMAPS and DPTS, clearly indicating that the ammonium and phosphonate bifuncionalized silica has been successfully prepared.
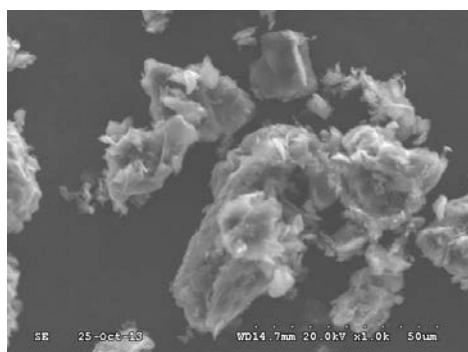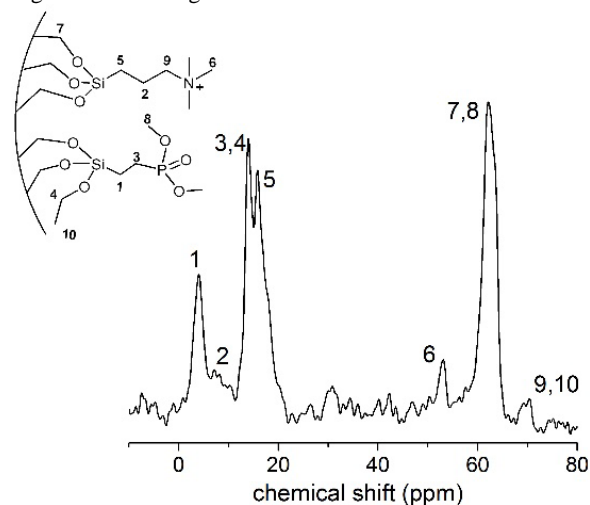

Figure 1 SEM images of TD-silica

Figure 2 ^{13}C-NMR spectra of TD-silica

III.B. Sorption studies

As comparison, the mono-functional silica materials, T-silica and P-silica were also characterized, showing no appreciable sorption to U(VI) in any concentration of NH_3. Alternatively, bi-functional TD-silica, showed quantitative sorption to U(VI) in 0.5-5% NH_3. Therefore, the coordination action and electrostatic attraction between ammonium groups and $UO_2(OH)_3^-$, which is the main species at this pH, and complex reaction between phosphonate groups and $UO_2(OH)_3^-$, could be deduced as the main sorption nature.

At first, the U(VI) sorption by TD-silica for different contact time from 15 min to 60 h in NH_3 and U(VI) was performed to evaluate the sorption rate, in which the sorption time is X-axis, and U(VI) sorption amount (mg/g) is Y-axis. It is clear that the sorption process involves three steps. The first step is from 15 min to 5 h, in which the U(VI) uptake increased sharply. This part of sorption correspond to the surface sorption of U(VI) on the sorbent. The second step is from 5 to 48 h, in which the U(VI) uptake increased slowly. This part of sorption can be attributed to pore sorption of U(VI) in to the sorbent. After 48 h, the sorption seems to be an equilibrium (the third step) with the U(VI) uptake greater than 8.6 mg/g.

III.B. Kinetics studies

It is known that the sorption process on porous sorbents is generally described by four stages, *i.e.* bulk diffusion, film diffusion, intraparticle diffusion and sorprtion of the adsorbate on the surface. One or more of these stages may determine the sorption rate and the amount on the solid surface. Since TD-silica has porous structures, further investigation is needed to find out the effect of intraparticle diffusion to the

entire sorption process. To further clarify the sorption process of U(VI) to TD-silica, three commonly used kinetics models, i.e. intraparticle diffusion model, pseudo-first-order kinetic model and pseudo-second-order kinetic model, were applied to analyze the experimentally observed kinetic data.
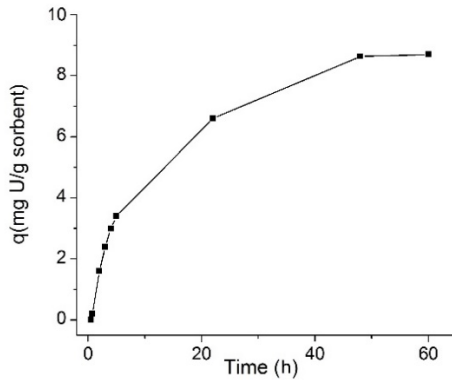

Figure 3 Time effect on the sorption. [U(VI)]initial = 5 ppm, [NH$_3$] = 2.5%.

The intraparticle diffusion model equation by Weber and Morris is expressed as:

$$q_t = k_p \times t^{1/2} \quad [4,5]$$

where q_t (mg/g) is the amount of U(VI) ions absorbed in TD-silica at the time of t (h), and k_p is the intraparticle diffusion constant (mg g^{-1} h^{-1}). The plot of q_t as a function of $t^{1/2}$ gives a straight line, from which k_p can be obtained (Figure 4).
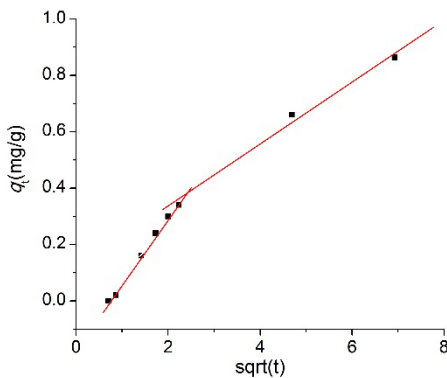

Figure 3 Intraparticle diffusion kinetics of the sorption of U(VI) in TD-silica

It can be seen from Figure 4 that the points are not linearly distributed but give two different slopes. Specifically, the initial steep-slope line suggest that the sorption in the initial hours is controlled by the transportation of U(VI) into the inner sorbent, and the second gently-sloped line represents that of sorption equilibrium. These results suggest that intraparticle diffusion might play a significant role for the rate determination in the sorption process but not the sole rate determining factor.

The linearized form of the pseudo-first-order rate equation by Lagergren is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.3030} \times t \quad [6,7]$$

where q_t has the same meaning as earlier and q_e (mg/g) is the amount of U(VI) ions sorbed in TD-silica at equilibrium, and k_1 is the sorption rate constant (h^{-1}). The plot of $\log(q_e$-$q_t)$ versus t gives a straight line and k_1 can be calculated from the slope. The pseudo-second-order kinetic model is given with the equation below :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad [8,9]$$

where q_e and q_t have the same meaning as earlier and k_2 is the rate constant (g mg^{-1} h^{-1}) of the pseudo-second order kinetic model. The plot of t/q_t versus t shows linearity, and q_e and k_2 can be calculated from the slope and intercept.

The model parameters and the correlation coefficient obtained by pseudo-first-order and pseudo-second-order kinetic model are shown in Table 1.

From table 1 it can be seen that pseudo-second-order model poorly matches ($R^2 < 0.75$) with the experimental kinetics data, whereas pseudo-first order model gives much better correlation coefficient (more than 0.99). The result clearly indicates that the kinetics of U(VI) sorption in TD-silica follows pseudo-first order model.

Table 1 The model parameters and the correlation coefficients

Kinetics model			
pseudo-first-order		pseudo-second-order	
k$_1$(min)	R^2	k$_2$(min)	R^2
0.053	0.9905	-	0.6063

III.C. Sorption isotherm

A sorption isotherm is fundamental in understanding the sorption mode of an adsorbate on sorbent surface once the equilibrium is attained. Herein, the amount of U(VI) adsorbed in TD-silica as a function of U(VI) were determined, and the obtained data were applied to the Langmuir isotherm. The Langmuir isotherm is based on the assumption that the sorption occurs in a monolayer, uniform and finite mode on the sorbent and the sorption energy decreases as the distance from the surface increase.

The sorption isotherm for U(VI) in TD-silica was determined at a constant NH$_3$ concentration of 2.5% by varying the initial U(VI) concentration from 0.5 to 50 ppm. The result is shown in Figure 4.

It is found that the U(VI) uptake increases slowly with the rise of equilibrium concentration (c_e) of U(VI) at the initial range of 0.27-8.6 ppm. It is probably because in the low concentration, the adsorption effect would be decreased by lower target ions and the adsorption driving force. When equilibrium U(VI) concentration further increased to 10.1 ppm, the sorption seems to increase sharply with c_e, and arrived at an equilibrium at 50.3 ppm,

from which the maximum sorption capacity of 23.6 mg/g was obtained. This result suggest that the TD-sorbent is very suitable for U(VI) uptake from relative concentrated solutions in coexisted with NH_3, and it thus has enormous potential from extracting uranium from processing waste water of HTRG.
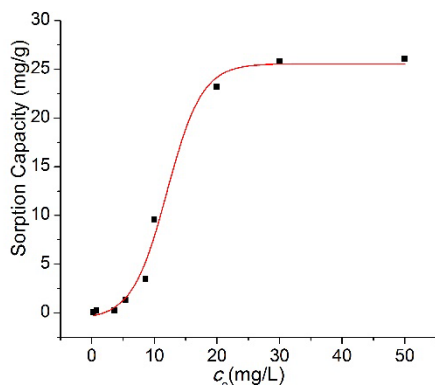

Figure 4 The sorption isotherm for U(VI) in TD-silica

The percentage sorption of TD-silica was investigated at three NH_3 concentrations, namely, 0.5%, 2.5% and 5%. The related results about sorbent amounts were shown in Table 2, the reaction time and the reaction nature were both studied. As shown in the data, as the NH_3 concentration increased, the sorption equivalent time was also increased, while the maximum sorption capacity was decreased. It is concluded that the U(VI) adsorption of TD-silica would be more seriously affected by higher concentration of NH_3.

Table 2 The effect of NH_3

$c(NH_3)$	0.5%	2.5%	5%
equiv. time/h	6	48	72
Equiv. amount/mg g^{-1}	63.7	23.6	12.8

III.D. Desorption and reusability of the sorbent

The desorption of U(VI) from TD-silica was performed using HNO_3 as the eluent. In a typical experiment, 0.5 g TD-silica was contacted with 100 mL U(VI) solution. The eluting agent, HNO_3, was added with 1 h stirring at room temperature. A complete recovery could be achieved using 0.05 mol/L HNO_3 solution.

As for the reusability of TD-silica, the results demonstrate that the sorbent could be used at least 4 times when 0.05 mol/L HNO_3 was used as the eluent. More than 70% sorption could be obtained even after four sorption/elution cycles, of which the sorption percentage decreased gradually from 92% to 73% in first and the fourth cycles.

IV Conclusions

Modification of silica surface was successively achieved with ammonium and phosphonate groups, by using of functional silanes TMAPS and DPTS, respectively. The prepared sorbents were used for sorption of U(VI) from basic aqueous solution in coexist with NH_3, and the sorption results demonstrated high specificity of U(VI). The sorption mechanism could be attributed the electrostatic attraction between negative $UO_2(OH)_3^-$ and positive NH_3^+ group, and chelate formation between U(VI) and phosphonate group. Mono-functionalized silica, on the other hand, displays almost no sorption towards U(VI), indicating the key role of the co-existed bi-functional groups. The advantageous sorption results obtained have boosted further research on the application of the bi-functional TD-silica in the treatment of HTGR fuel processing waste water.

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