Functionalized magnetic mesoporous silica nanoparticles for U removal from low and high pH groundwater

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ABSTRACT

U(VI) species display limited adsorption onto sediment minerals and synthetic sorbents in pH < 4 or pH > 8 groundwater. In this work, magnetic mesoporous silica nanoparticles (MMSNs) with magnetite nanoparticle cores were functionalized with various organic molecules using post-synthetic methods. The functionalized MMSNs were characterized using N₂ adsorption-desorption isotherms, thermogravimetric analysis (TGA), transmission electron microscopy (TEM), ¹³C cross polarization and magic angle spinning (CPMAS) nuclear magnetic resonance (NMR) spectroscopy, and powder X-ray diffraction (XRD), which indicated that mesoporous

silica (MCM-41) particles of 100-200 nm formed around a core of magnetic iron oxide, and the functional groups were primarily grafted into the mesopores of ~3.0 nm in size.. The functionalized MMSNs were effective for U removal from pH 3.5 and 9.6 artificial groundwater (AGW). Functionalized MMSNs removed U from the pH 3.5 AGW by as much as 6 orders of magnitude more than unfunctionalized nanoparticles or silica and had adsorption capacities as high as 38 mg/g. They removed U from the pH 9.6 AGW as much as 4 orders of magnitude greater than silica and 2 orders of magnitude greater than the unfunctionalized nanoparticles with adsorption capacities as high as 133 mg/g. These results provide an applied solution for treating U contamination that occurs at extreme pH environments and a scientific foundation for solving critical industrial issues related to environmental stewardship and nuclear power production.

Keywords:

Magnetic mesoporous silica nanoparticles

Surface functionalization with organic molecules

Uranium removal

Acidic and alkaline groundwater

1. Introduction

Uranium (U) is the most common radioactive contaminant in the Department of Energy (DOE) complex, at U mining and processing sites, and spent fuel storage basins. U(VI) is normally more mobile, bioavailable and toxic than U(IV). The aqueous U(VI) species exhibit

weak adsorption to sediment minerals under acidic conditions ($\text{pH} < 4$) or naturally-occurring basic carbonate rich ($\text{pH} > 8$) conditions [1], which hampers remediation efforts. Existing technologies for U contaminant treatment often involve biotic or abiotic chemical reduction [2, 3]. However, the redox processes have several shortcomings in applications: (1) electron donors (e.g., acetate, ethanol) need to be available to stimulate the microbial population for its sustained effectiveness, (2) biogenic or chemically reduced U compounds (e.g., uraninite) are susceptible to re-oxidation in natural environments, and (3) they are not applicable to the very low pH systems. There is, therefore, a need to develop more robust technologies for remediation of acidic or alkaline U-contaminated systems.

Functionalized mesoporous silica nanomaterials have been developed and demonstrated as effective sorbents for the removal of organic and inorganic pollutants [4-8], such as toxic metal anions (e.g., CrO_4^{2-} and AsO_4^{3-}) [6], lanthanides [9, 10] and actinides (e.g., Pu [11, 12], Np [11], and U [11-24]). For example, “Hard Lewis base” ligands (e.g., salicylic acid, glycine, phosphine ligands) incorporated as self-assembled monolayers on mesoporous supports (SAMMS) are effective for selective removal of “Hard Lewis acid” lanthanides [9, 10] and actinides (e.g., Am, Pu, U and Th) [12]; while hydroxypyridinones (HOPO)-SAMMS performed well for the selective sequestration of actinides (Pu, Np, and U) [11]. In addition, there are several functionalized mesoporous silica nanoparticles that have been shown to be effective at binding aqueous U, including amino-modified MCM-41 [13] and SBA-15 [21], dopamine-functionalized SBA-15 [24], amidoxime-modified MCM-41 [23-26] and quartz [27], dihydroimidazole functionalized SBA-15 [15], monoamide resins with porous silica support [28], phosphonate or phosphine oxide-incorporated MCM-41 [16, 23], SBA-V [17], KIT-6 [18] and carboxymethylated polyethyleneimine functionalized MSU-H [29]. However, among these

studies, most of the functionalized mesoporous silica nanoparticles were evaluated under near-neutral pH conditions (pH 5-8) in which aqueous U species tend to precipitate or strongly adsorb onto various sorbents.

More recently, magnetic mesoporous silica nanoparticles (MMSNs) and zeolites have been developed for removal and magnetic separation of heavy metals (primarily Hg, CrO_4^{2-} , and U(VI)) from contaminated water by combining the enhanced absorptive properties of mesoporous silica or zeolites and the magnetic characteristics of iron oxide nanoparticles [30-39]. The objective of this study was to develop functionalized MMSNs with high U(VI) uptake under acidic or alkaline conditions and advantages for magnetic separation [30, 32, 37]. Our approach was to functionalize the MMSNs with benzoylthiourea (BT), dihydroimidazole (DIM), polyacryloamidoxime (AD), phosphonate (PP), phosphonate-amino (PPA), poly(propylenimine) dendrimer (PPI), and poly(amidoamine) dendrimer (PAMAM), to characterize the functionalized nanoparticles using the N_2 adsorption-desorption isotherms, TGA, TEM, ^{13}C CPMAS NMR spectroscopy, and powder XRD, and to conduct a series of batch U uptake studies from the pH 3.5 and 9.6 AGW.

2. Materials and methods

2.1 Materials

3-Aminopropyltriethoxysilane (APTES), benzoyl thiourea (BT), acrylonitrile, hydroxylammonium chloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), 3-(trihydroxysilyl)propyl methylphosphonate (PP), (3-chloropropyl)triethoxysilane (CPTS), polyamidoamine dendrimers (PAMAM),

polypropylenimine dendrimers (PPI), tetraethoxysilane (TEOS), hexadecyltrimethyl-ammonium bromide (CTAB), 1,4-dioxane, ferrous chloride, and ferric chloride were purchased from Sigma Aldrich. Nitric acid, sodium hydroxide, dichloromethane, and diethyl ether were purchased from Fisher Scientific. N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (DIM) and diethylphosphatoethyltriethoxysilane (DPTS) were purchased from Gelest, boric acid (99.8%) was purchased from Alfa Aesar, and hydrofluoric acid (51% in water) was purchased from Acros Organics. All chemicals were used as received.

2.2 Synthesis of magnetite (Fe_3O_4) nanoparticles

Ferric chloride (4.80 g) and ferrous chloride (2.00 g) were dissolved in deionized water (30 ml) and were allowed to stir under nitrogen atmosphere at the temperature of 90 °C. Ammonium hydroxide (20 ml) was added to precipitate the iron sources, and the suspension was aged for 2.5 h, then filtered and washed with deionized water and dried at 100 °C [40].

2.3 Synthesis of MSNs and MMSNs

Mesoporous silica nanoparticles (MSNs) and magnetic mesoporous silica nanoparticles (MMSNs) were synthesized using an approach previously described in detail [37, 41]. In this approach, typically, hexadecyltrimethylammoniumbromide (CTAB, 1 g), NaOH (3.5 mL, 2M), and water (500 mL) were mixed with Fe_3O_4 nanoparticles (300 mg) and sonicated. The contents were heated at 80 °C and the silica source tetraethylorthosilicate (TEOS) was added. The reaction mixture was aged for 2 h and then was filtered, washed with deionized water and

methanol, and dried at 120 °C overnight. The CTAB template was removed by calcining the product at 600 °C **in flowing compressed air** for 6 h to obtain MMSNs. The mesoporous silica nanoparticles (MSNs) were also prepared in the same manner without the addition of Fe₃O₄ nanoparticles.

2.4 Functionalization with aminopropyl group

Calcined MSNs or MMSNs (1 g) were refluxed with (3-aminopropyl)triethoxysilane (APTES, 4 mmol) in toluene at 120 °C for 6 h. The reaction mixture was filtered and washed with 1:1 mixture of diethylether and dichloromethane, and then dried overnight in an oven at 100 °C [42].

2.5 Functionalization with benzoylthiourea (BT) group

The aminopropyl functionalized MSNs or MMSNs (1 g) was refluxed with benzoyl thiourea (MPTMS, 4 mmol) in toluene at 120 °C for 6 h. The reaction mixture was filtered, washed with toluene and 1-propanol, and then dried at 100 °C overnight [43, 44].

2.6 Functionalization with dihydroimidazole (DIM) group

Calcined MSNs or MMSNs (1 g) were refluxed with N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (DIM, 4 mmol) in toluene at 120 °C for 4 h. The reaction mixture was filtered,

washed with 1:1 mixture of diethyl ether and dichloromethane, and then dried at 100 °C overnight [15].

2.7 Functionalization with polyaryloamidoxime (AD) group

Aminopropyl functionalized MSNs or MMSNs (1 g) were refluxed with acrylonitrile (8 mmol) in methanol at 65 °C for 12 h under N₂ atmosphere. The reaction mixture was filtered and washed with 1:1 mixture of diethyl ether and dichloromethane, and then dried at 50 °C overnight in an oven. The product obtained from the above reaction was then mixed with 0.5 g of NH₂OH•HCl and 50 ml of methanol. The pH of the reaction was adjusted to 8 and it was equilibrated at 70 °C for 24 h. The reaction mixture was filtered, washed with methanol and then dried at 50 °C overnight [45].

2.8 Functionalization with phosphonate (PP) group

Calcined MSNs or MMSNs (1 g) were refluxed with 3-(trihydroxysilyl)propyl methylphosphonate (4 mmol) in 1,4-dioxane at 100 °C for 4 h. The reaction mixture was filtered, washed with 1:1 mixture of diethyl ether and dichloromethane, and dried at 100 °C overnight [23].

2.9 Functionalization with phosphonate-amino (PPA) group

Calcined MSNs or MMSNs (1 g) were refluxed with APTES and diethylphosphatoethyltriethoxysilane (DPTS) (4 mmol of each functional group) in toluene at 120 °C for 6 h. The reaction mixture was filtered, washed with 1:1 mixture of diethyl ether and dichloromethane, and then dried at 100 °C overnight [46].

2.10 Functionalization with chloropropyl group

Calcined MSNs or MMSNs (1 g) were refluxed with (3-chloropropyl)triethoxysilane (CPTES, 2 mmol) in toluene at 120 °C for 12 h under N₂ atmosphere. The reaction mixture was filtered, washed with 1:1 mixture of diethyl ether and dichloromethane, and dried at 100 °C overnight [47].

2.11 Functionalization with poly(propylenimine) (PPI) dendrimer group

Chloropropyl functionalized samples were refluxed with polypropylenimine (PPI) dendrimer in methanol for 24 h. The reaction mixture was filtered, washed with methanol, and dried at 100 °C overnight [47].

2.12 Functionalization with poly(amidoamine) (PAMAM) dendrimer group

Chloropropyl functionalized samples were refluxed with polyamidoamine dendrimers (PAMAM, 2mmol) dendrimer in methanol for 24 h. The reaction mixture was filtered, washed with methanol, and dried at 100 °C overnight [47].

2.13 Characterization methods

A variety of techniques were used to characterize the physical and chemical properties of the calcined MSN and MMSN materials.

Powder XRD (Siemens D5000 X-ray diffractometer with Cu K α and a nickel filter) was used to verify the mesoporous silica and iron oxide structure. High angle patterns ($2\theta = 10-80^\circ$ with a 0.02 step size, 1 s/step) and a small angle pattern ($2\theta = 1-10^\circ$ with a 0.02 step size, 1 s/step) were collected.

Surface areas, porosities and pore diameters of the materials were measured using N₂ adsorption and a Nova 1200 Nitrogen Adsorption Instrument (Quantachrome). Calcined MSNs and MMSNs (100 mg) were evacuated overnight at 100 °C and then a 7-point BET isotherm and a 50-point adsorption/desorption isotherm were measured. The data were used for calculation of the surface area, pore volume and pore diameter. The pore volume (V_{tot}) and pore diameter were calculated by measuring the amount of adsorbed nitrogen at 0.97 P/P₀ using Barrett-Joyner-Halenda (BJH) analysis.

The percentage of Fe and Si in the solid MSN and MMSN was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Varian 720-ES) of the dissolved particles. For the solid samples, a 70:30 HCl : HF solution was added to the solid sample and the suspension was sonicated for 15 minutes until all of the material was completely dissolved. Next, highly concentrated HNO₃ and 5% boric acid solutions were added, and the total volume was adjusted to 10 mL with DI water prior to ICP-OES analysis.

For TEM imaging (JEOL JEM-1230 transmission electron microscope), a drop of dilute sample suspension in ethanol was placed on a copper grid with thin polymer coating and dried at room temperature prior to analysis.

Thermogravimetric analysis (TGA) was conducted (TA instruments, Q 5000), and a heating rate of 5 °C/min was used to quantify the amount of functional groups grafted onto the MMSN sample.

¹³C cross polarization magic angle spinning (CPMAS) NMR experiments were conducted on the functionalized MSNs using a 4 mm rotor and the spinning speed of 10 kHz.

2.14 Uranium adsorption

Batch U(VI) sorption experiments were conducted at an initial U(VI) concentration of 2.5×10^{-5} M in artificial groundwater (AGW) solution under ambient atmospheric CO₂ and temperature (22 °C) unless specified otherwise. The AGW solution was made based on the monitoring survey results for uncontaminated groundwater samples at the Savannah River Site (SRS) [48]. The chemical composition (in mg/L) of AGW was Na 1.25, K 0.25, Ca 0.93, Mg 0.66, Cl 5.51, and SO₄ 0.73, with a pH ~6.3 [49]. For each set of experiments, a solid-free control was included as the initial U concentration for K_d calculation and to provide an indication of U sorption to the reaction tube during the experiment. Approximately 0.075 gram of MSNs or MMSNs and 7.5 mL AGW that had been allowed to equilibrate with air for 4 days were added to 15 mL polypropylene centrifuge tubes prior to U spiking. Uranyl nitrate hexahydrate (²³⁸U, Electron Microscopy Sciences, Hatfield, PA) was used to make the U stock solution (5×10^{-3} M, pH 3.6, Eh 433 mV). After spiking with 0.0375 mL of the U stock solution and then pH adjusting with 1 M NaOH or 1 M HNO₃, the suspensions were equilibrated on a reciprocating

shaker for 6 days. During equilibration, all tubes were open to the lab atmosphere without shaking twice per day for 1 h to promote equilibration with atmospheric CO₂. The solution pHs were also adjusted daily until the change in pH was < 0.1 pH unit (Radiometer Copenhagen PHM 95 pH meter). After equilibration, each suspension was filtered using 0.2 µm pore size nylon membrane syringe filters. The filtrate was acidified with 2% HNO₃ in a typical 1:10 ratio and analyzed for U by inductively coupled plasma mass spectrometry (ICP-MS; NexION 300X, Perkin Elmer, Inc.). The ICP-MS analyses had an uncertainty of ±10%, but our repeatability test indicated that this uncertainty was often within ±5%. The extent of U sorption was calculated using a distribution coefficient (K_d, mL/g), the U concentration ratio of the sorbent to solution, and the mass of U sorbed onto the sorbent (q_e, mg/g). The K_d and q_e values were calculated using equations 1 and 2, respectively:

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{M} \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (2)$$

where C₀ (mg/L) is the initial U concentration in the control samples, C_e (mg/L) is U concentration in the solution at equilibrium, V is the volume of the solution (mL) and M is the mass of the sorbent (g).

Batch experiments for the adsorption kinetics of U onto the functionalized MMSNs were conducted using an initial U concentration of 2.5 × 10⁻⁵ M, 0.075 gram of MMSNs and 7.5 mL AGW.

Batch experiments for obtaining the adsorption isotherm curves (the mass (q_e, mg/g) of U sorbed onto the sorbent versus U concentration in solution at equilibrium) were conducted at

initial U concentration ranged from 6.7×10^{-5} M (15.9 ppm) to 5×10^{-4} M (119 ppm), 0.0075 gram of MMSNs and 7.5 mL AGW. These isotherm data were analyzed using the Langmuir isotherm model (see equation 3) that assumes that adsorption occurs as a monolayer on an energetically homogeneous surface without interaction between the adsorbates on adjacent sites:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{K_L q_{max}} \quad (3)$$

where q_e is the mass of U sorbed onto the sorbent at equilibrium, q_{max} is the saturation sorption capacity, C_e is the U(VI) concentration in solution at equilibrium, and K_L is the Langmuir constant that is directly related to the binding site affinity. Values for q_{max} , K_L and coefficient of correlation (R^2) that measures how well the Langmuir model fits to the experimental data were obtained by plotting C_e/q_e versus C_e .

3. Results and discussion

3.1 Characterization of functionalized MMSNs

The nanoparticles studied in this work are summarized in Table 1. All functionalized MMSNs were characterized by using N_2 adsorption isotherms, TGA, and elemental analysis. N_2 adsorption isotherms for all functionalized mesoporous silica were included in Fig. S1. The pore size distributions for representative MMSNs and dihydroimidazole-functionalized MMSNs (MMSNs-DIM) were calculated from the N_2 adsorption isotherms using Barrett-Joyner-Halenda (BJH) analysis and density functional theory (DFT) method (Fig. S2). The surface areas, pore volumes, pore sizes, the loadings of functionalized molecules and Fe contents of the functionalized MMSNs, in comparison with the unfunctionalized MSNs and MMSNs, are

summarized in Table 1. The pore volumes and sizes given in Table 1 were calculated using standard BJH method, which gave average values for all pores. However, the pore size distribution for our MMSNs calculated by BJH method was consistent with that of similar magnetic iron oxide/mesoporous silica nanoparticles reported in literature [37, 41]. In general, the average pore sizes of MMSNs and all functionalized MMSNs were primarily in the range of 3.0-3.3 nm; however, a small portion of micropores (< 2 nm) may also be present in these samples (Fig. S2B). Compared to non-functionalized MMSNs, the surface areas and pore volumes of functionalized MMSNs decreased significantly, which indicates that the functionalized molecules were primarily grafted into the mesopores (~3 nm) and less onto external surfaces of MMSNs, which is confirmed by the pore size distributions of MMSNs and MMSN-DIM (Fig. S2B) and is also consistent with previously reported data [37, 42]. However, the pore size essentially remained unchanged, as has been observed previously [37]. The loadings of functionalized molecules ranged from 0.2-0.8 mmol/g (Table 1). The loading of PAMAM dendrimer was lower (0.035 mmol/g) compared to the other functional groups, presumably because it has a larger size and molecular weight. The Fe content of functionalized MMSNs were 10-23 weight %, which is consistent with magnetite cores of 5-10 nm encapsulated by MSNs of ~100 nm that were observed in the TEM images of these materials (see Fig. 1B below).

The functionalized MSNs were analyzed by ^{13}C CPMAS NMR because magnetite in MMSN interferes with NMR measurements. The ^{13}C CPMAS NMR spectra for the functionalized MSNs were used to confirm that the corresponding molecules are functionalized onto MMSN, as well as MSNs. The ^{13}C CPMAS NMR spectrum of MSNs-DIM is shown in Fig. 1A, which demonstrated that dihydroimidazole was grafted onto MSNs and is consistent

with previously published data [15]. The ^{13}C CPMAS NMR spectra of the other functionalized MMSNs, along with schematic representation of the functionalized molecules on MMSNs, are presented in Fig. S3.

TEM images of all functionalized MMSNs were collected. These TEM images were fairly similar to each other among the functionalized MMSNs. The TEM image of MMSNs-DIM as a representative sample is presented in Fig. 1B, in comparison with the TEM image of unfunctionalized MMSNs, which shows that the particle size of both MMSNs and MMSNs-DIM was 100-200 nm, and the magnetite core of 5-10 nm was encapsulated by MSNs. The TEM images shown were visibly similar each other, with the measured pore size was ~ 3 nm, which is in agreement with the calculated pore size based on N_2 adsorption isotherms (Table 1). However, in general, when the material was functionalized with dihydroimidazole or other functional groups, the effective pore sizes decreased, due to the functional groups grafted in the materials.

The high and small angle powder XRD patterns of all functionalized MMSNs were also collected. The high angle powder XRD patterns were fairly similar to each other among the functionalized MMSNs. The high angle powder XRD pattern of MMSNs-DIM as a representative sample in the range of $2\theta = 10\text{--}80^\circ$ is shown in Fig. 1C, along with XRD patterns for magnetite and MMSNs. The XRD patterns of both MMSNs and MMSNs-DIM were characterized with a single broad peak at $2\theta = \sim 20^\circ$, which is consistent with published XRD pattern for MCM-41 [50]. As shown in Fig. S4, the PXRD patterns of as synthesized and calcined iron oxide were similar; however, the higher resolution PXRD pattern for calcined iron oxide shows distinct peaks at $2\theta = \sim 15^\circ$, 18.5° and 23.9° which are characteristic of maghemite [51] (Fig. S4, inset). The PXRD patterns of as synthesized and calcined MMSNs were also similar (Fig. S4); however, the broad peak for MCM-41 at $2\theta = \sim 20^\circ$ might mask the

characteristic peaks for maghemite, we could not confirm whether there was maghemite in the calcined MMSNs or not. As a result, the distinct peaks in the PXRD pattern of MMSN-DIM and other functionalized MMSN indicated that the magnetic iron oxide could be magnetite and/or meghemite ($\gamma\text{-Fe}_2\text{O}_3$), but for simplification, magnetite was used throughout the context. Further, the intensity of magnetite peaks in the XRD patterns of MMSNs and MMSNs-DIM decreased relative to corresponding magnetite because magnetite was just 13 wt % of MMSNs. This confirms that the iron oxide nanoparticles are present inside the core-shell particles.

Small angle XRD patterns for MMSNs and MMSNs-DIM are shown in Fig. 1D. The peak (100) at $2\theta \approx 2^\circ$ characterizes the hexagonal ordering of the pores in the MCM-41 framework, which is consistent with published data [37]. In addition, two weak peaks corresponding to (110) and (200) at $2\theta = 4\text{-}5^\circ$ were observed in the MMSNs pattern, but not observed for MMSNs-DIM. The characteristic (100) peak is shifted slightly relative to MSNs (or MCM-41) when iron nanoparticles are present in the cores, as observed in previous publications [37, 42]. Small angle XRD patterns for the other functionalized MMSNs are shown in Fig. S5. The characteristic (100) peak for most of the other functionalized MMSNs was also shifted slightly toward lower 2θ relative to MMSNs, especially for MMSNs-AD, MMSNs-PPA, and MMSNs-PAMAM, but this peak was shifted toward to higher 2θ for MMSNs-PP and MMSNs-PPI (Fig. S5), indicating that the functionalized molecules were primarily grafted into the mesopores and this functionalization slightly altered the hexagonal ordering of the pores in the MCM-41 framework.

3.2 Uranium removal from acidic groundwater

Previous studies have demonstrated that U exists primarily as the uranyl (UO_2^{2+}) species in $\text{pH} < 4$ aqueous solution (also see Fig. S6), and this species displays limited adsorption to common sediment minerals and synthetic sorbents, primarily because under such a low pH condition the sediment minerals and sorbents are positively charged and electrostatically repel the positive uranyl (UO_2^{2+}) species [1, 37, 52]. Functionalization of MMSNs with select organic ligands alters their surface charge properties and can provide high affinity binding sites for U adsorption. In order to evaluate the performance of the functionalized MMSNs for U removal from acidic groundwater, batch adsorption experiments were conducted. Sorption coefficients (K_d , mL/g) of U onto the functionalized MMSNs from the $\text{pH} = 3.5$ AGW were calculated using equation 1 and these data are shown in Fig. 2, along with the K_d values for unfunctionalized MMSNs, MSNs, and silica. The K_d values for functionalized MMSNs were up to 6 orders of magnitude greater than those of unfunctionalized nanoparticles and silica. MMSNs-DIM and MMSNs-PPI exhibited the highest K_d values, nearly 1×10^5 mL/g.

The adsorption kinetics of U onto the functionalized MMSNs at $\text{pH} 3.5$ was studied using an initial U concentration of 2.5×10^{-5} M and the results obtained are shown in Fig. 3. Uranium adsorption by MMSNs-PP, MMSNs-PPA, and MMSNs-PPI generally achieved the equilibrium within one hour. However, U adsorption reaction by MMSNs-BT, MMSNs-DIM, and MMSNs-AD was demonstrably slower, with equilibrium achieved at ~ 8 h. The U adsorption onto mesoporous silica, like functionalized MMSNs, has been suggested to be diffusion-controlled [53] and through chemical bonding.

The adsorption isotherms of U onto the functionalized MMSNs in $\text{pH} 3.5$ AGW are shown graphically in Fig. 4. Equilibrium data for UO_2^{2+} adsorption onto all functionalized MMSNs, except for MMSNs-BT, were well described by the Langmuir model (equation 3).

Representative Langmuir fits of equilibrium data for U adsorption onto MMSNs-DIM, MMSNs-PP, and MMSNs-PPI are shown in the inset of Fig. 4. Values for $1/q_{\max}$ (slope) and $1/K_L q_{\max}$ (intercept) were obtained through fitting the linearized form of the Langmuir model (equation 3) to the experimental data and are summarized in Table 2. Further, the saturation sorption capacity ($q_{\max}$) and the Langmuir constant (K_L) were calculated, and the $q_{\max}$ and K_L values are also summarized in Table 2. MMSNs-PP exhibited the highest $q_{\max}$ of ~38 mg of U per gram of sorbent in pH 3.5 artificial groundwater, which is in agreement with the maximum U adsorption capacities of phosphonated SBA-15 (45-52 mg/g) and KIT-6 (54-56 mg/g) at pH = 4 [18]. For MMSNs-BT, batch data for U adsorption in pH 3.5 AGW were better fitted using a simple K_d model ($q_e = K_d \times C_e$), rather than by Langmuir model (equation 3). The K_d value obtained through the K_d model fitting was 160 mL/g and is in a good agreement with the K_d value obtained in batch tests, ~201 mL/g (Fig. 2).

3.3 Uranium removal from alkaline groundwater

Uranium exists primarily as the uranyl carbonate ($\text{UO}_2(\text{CO}_3)_3^{4-}$) species in pH > 8 aqueous solution in equilibrium with the atmosphere (Fig. S6), and this species displays limited adsorption to common sediment minerals and synthetic sorbents, primarily due to electrostatic repulsion [1, 37, 52]. However, functionalized MMSNs can provide high affinity binding sites for U adsorption. Batch experiments were conducted to evaluate the adsorption of U onto the functionalized MMSNs in pH 9.6 AGW, and the K_d values for U adsorption onto these MMSNs are shown in Fig. 5, in comparison with unfunctionalized MMSNs, MSNs and silica. The K_d values for functionalized MMSNs were 2-4 orders of magnitude greater than that for silica. Compared to unfunctionalized MSNs and MMSNs, the K_d values for U adsorption onto

MMSNs-BT, MMSNs-AD, MMSNs-PP, and MMSNs-PPA in pH 9.6 AGW did not differ substantially. In contrast, the K_d values for MMSNs-DIM, MMSNs-PPI, and MMSNs-PAMAM increased by nearly two orders of magnitude.

The U adsorption onto all functionalized MMSNs in pH 9.6 AGW was rapid, with equilibrium generally achieved within an hour, except for MMSNs-BT for which the reaction was demonstrably slower, reaching equilibrium at ~ 8 h (Fig. S7). The mass (q_e , mg/g) of U sorbed onto the functionalized MMSNs from pH 9.6 AGW was determined using batch experiments and equation 2, with the adsorption isotherms shown in Fig. 6. Among all functionalized MMSNs, the isotherm data tends to congregate into two groups, which are plotted in Fig. 6A and 6B, respectively. Fig. 6A shows the isotherm data for MMSN-BT, MMSNs-PP, and MMSNs-PAMAM, along with representative Langmuir fits for MMSNs-BT and MMSNs-PAMAM in the inset, which indicated that the sorption capacities of these functionalized MMSNs were < 50 mg/g. Fig. 6B shows the isotherm data for MMSNs-DIM, MMSNs-AD, MMSNs-PP, and MMSNs-PPI, along with representative Langmuir fits for MMSNs-DIM and MMSNs-PPA in the inset, which indicated that the sorption capacities of these functionalized MMSNs were as high as 120 mg/g. However, it is noted that although the isotherm data for these samples tend to approach plateaus, the Langmuir plateaus might not be attained. As a result, the sorption capacities of these functionalized MMSNs obtained are conservative estimates. In addition, although the estimated sorption capacity data are essentially in agreement with the K_d values of these functionalized MMSNs, it is unclear why K_d values for MMSNs-AD and MMSNs-PPA were moderate, but their capacity was high, while MMSNs-PAMAM was opposite.

The isotherm data for U adsorption from pH 9.6 AGW were fitted using Langmuir model (equation 3), and the Langmuir parameters obtained from these fittings are summarized in Table 3. The $q_{\max}$ values for MMSNs-PPI, MMSNs-AD, MMSNs-DIM, and MMSNs-PPA were > 100 mg/g, while the $q_{\max}$ values for the other three functionalized MMSNs were ≤ 55 mg/g. The functionalized MMSN with the highest adsorption capacity for U removal at pH 9.6 was MMSNs-PPI, with a maximum capacity of 133 mg/g. The maximum U adsorption capacities of all functionalized MMSNs were in good agreement with reported literature data (65-185 mg/g) of mesoporous silica functionalized with various organic molecules at pH = 8.3 [23]. The fitting of the Langmuir model had significant correlation coefficients ($R^2 > 0.93$), indicating that the model generally fit the data. However, the sorption plateaus for some of these samples might not completely be achieved. As such, some of the calculated sorption maximum values provide conservative estimates and the actual maximum sorption capacities for these samples may be higher.

4. Conclusions

Mesoporous silica nanoparticles (MSNS) were synthesized with a core of nano-size magnetite to obtain magnetic mesoporous silica nanoparticles (MMSNs). The magnetite cores could permit MMSNs to be recovered from suspensions by magnetic separation. The mesoporous silica (MCM-41) offers advantages of high surface area and high affinity adsorption sites, and the mesoporous structure allows for the grafting of functional groups of various molecules. In this work, the MMSNs were further functionalized by grafting selected organic molecules that have high binding affinities for aqueous U species. We expect that the majority of

functional molecules were grafted into the ~3 nm mesopores, and to a lesser extent on external surfaces; however, the relative functionalization of the external surfaces versus the internal pores were not quantified. Some of the functionalized MMSNs exhibited high capacities of U removal, even in environments that have been problematic for U removal in the past, e.g., very low- or high-pH groundwater. Among these functionalized MMSNs, phosphonate-, polyaryloamidoxime- and dihydroimidazole-functionalized MMSNs exhibited the highest capacities for U removal from pH 3.5 artificial groundwater, with $q_{\max}$ values of 38, 31 and 25 mg/g, respectively. Poly(propylenimine) dendrimer-, polyaryloamidoxime-, dihydroimidazole-, and phosphonate-amino-functionalized MMSNs exhibited the highest capacities for U removal from pH 9.6 artificial groundwater, with $q_{\max}$ values of 133, 125, 110 and 109 mg/g, respectively.

Uranium contamination is widespread in the environment, especially within the DOE complex, U mine and processing sites, and DoD installations. Very often the U contamination occurs under oxidizing condition, in either highly acidic (e.g., DOE Savannah River Site F-area) or highly alkaline systems (e.g., DOE Hanford Sites) in the presence of naturally-occurring carbonate. Under these conditions, U(VI) exhibits limited adsorption to sediments, which leads to high environmental mobility and difficulties in its remediation. These developed functionalized magnetic mesoporous silica nanoparticles may potentially be applicable to U remediation from such low- or high-pH groundwater systems that are common at various contaminated sites.

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Table 1

Physiochemical characterization of functionalized magnetic mesoporous silica nanoparticles (MMSNs)

Samples	Functional molecules		Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Fe content (%)
	Name and acronym	Loading (mmol/g)				
MSNs	Mesoporous silica nanoparticles	-	1210	0.61	3.2	-
MMSNs	Magnetic MSNs	-	1010	0.33	3.3	13
MMSNs-BT	Benzoylthiourea (BT)	0.79	541	0.09	3.1	9.7
MMSNs-DIM	Dihydroimidazole (DIM)	0.64	529	0.13	3.0	9.9
MMSNs-AD	Polyaryloamidoxime (AD)	0.36	602	0.28	3.3	15
MMSNs-PP	Phosphonate (PP)	0.23	512	0.05	3.0	23
MMSNs-PPA*	Phosphonate-amino (PPA)	0.19-A 0.30-PP	475	0.08	3.3	19
MMSNs-PPI	Poly(propylenimine) (PPI) dendrimer	0.48	592	0.11	3.3	13
MMSNs-PAMAM	Poly(amidoamine) (PAMAM) dendrimer	0.04	635	0.10	3.3	20
* A = amino; PP = phosphonate						

Table 2

Langmuir parameters for U(VI) adsorption onto functionalized MMSNs in pH 3.5 artificial groundwater

Samples	$1/q_{\max}$	$1/K_L q_{\max}$	$q_{\max}$ (mg/g)	K_L (mL/mg)	R^2
MMSNs-BT	Isotherm curve was better modeled by K_d model: $q_e = 160 \times C_e$, $R^2 = 0.946$				
MMSNs-DIM	0.040 ± 0.005	0.745 ± 0.292	24.9 ± 3.0	0.054 ± 0.021	0.957
MMSNs-AD	0.033 ± 0.005	0.859 ± 0.333	30.6 ± 4.9	0.038 ± 0.015	0.951
MMSNs-PP	0.027 ± 0.001	0.014 ± 0.030	37.5 ± 0.8	1.867 ± 3.951	0.998
MMSNs-PPA	0.049 ± 0.006	1.124 ± 0.398	20.6 ± 2.7	0.043 ± 0.015	0.952
MMSNs-PPI	0.105 ± 0.012	1.067 ± 0.782	9.5 ± 1.0	0.099 ± 0.072	0.965
MMSNs-PAMAM	Isotherm curve was not determined due to low U(VI) adsorption				

Table 3

Langmuir parameters for U(VI) adsorption onto functionalized MMSNs in pH 9.6 artificial groundwater

Samples	$1/q_{\max}$	$1/K_L q_{\max}$	$q_{\max}$ (mg/g)	K_L (mL/mg)	R^2
MMSNs-BT	0.031 ± 0.002	0.014 ± 0.007	32.5 ± 1.6	2.184 ± 1.432	0.993
MMSNs-DIM	0.009 ± 0.001	0.015 ± 0.006	109.9 ± 8.5	0.623 ± 0.269	0.982
MMSNs-AD	0.008 ± 0.001	0.015 ± 0.003	125.0 ± 10.9	0.523 ± 0.116	0.980
MMSNs-PP	0.018 ± 0.002	0.115 ± 0.059	55.0 ± 5.1	0.158 ± 0.081	0.976
MMSNs-PPA	0.009 ± 0.0003	0.004 ± 0.001	108.7 ± 3.6	2.359 ± 0.726	0.997
MMSNs-PPI	0.008 ± 0.001	0.051 ± 0.015	133.3 ± 6.2	0.148 ± 0.043	0.933
MMSNs-PAMAM	0.034 ± 0.001	0.094 ± 0.028	29.4 ± 0.4	0.378 ± 0.113	0.999

Fig. 1. ^{13}C CPMAS NMR spectrum of MSNs-DIM (A), and TEM image (B) in comparison with the TEM image of MMSNs, powder XRD pattern in the range of $10\text{--}80^\circ$ (C), and small angle powder XRD pattern (D) of MMSNs-DIM

Fig. 2. Sorption coefficient, K_d (mL/g), of functionalized MMSNs for U removal from pH 3.5 artificial groundwater, in comparison with unfunctionalized MSNs, MMSNs and silica

Fig. 3. Adsorption kinetics of U onto the functionalized MMSNs in pH 3.5 artificial groundwater

Fig. 4. Adsorption isotherms of U onto the functionalized MMSNs in pH 3.5 artificial groundwater, and representative Langmuir fits for MMSNs-DIM, MMSNs-PP, and MMSNs-PPI are shown in the inset.

Fig. 5. Sorption coefficient, K_d (mL/g), of functionalized MMSNs for U removal from pH 9.6 artificial groundwater, in comparison with unfunctionalized MSNs, MMSNs and silica

Fig. 6. Adsorption isotherms of U onto the functionalized MMSNs in pH 9.6 artificial groundwater