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Organo-functionalized mesoporous silicas for efficient uranium extraction

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ABSTRACT

A series of new mesoporous silica (MS) sorbents were developed by functionalizing a large-pore 2-D hexagonal MS material, MSU-H, with amidoxime, imide dioxime, phosphonate, and carboxylate functional groups, and characterized by nitrogen adsorption, ζ-potential, infrared spectroscopy, and thermogravimetric analysis. These MS materials have a grafting density of 0.75 to 1.38 mmol/g, and exhibit BET surface areas of 186–526 m^2/g and average pore sizes of 3.8–7.8 nm. The uranyl sorption by the functionalized MS sorbents was investigated in basic water and artificial seawater at pH = 8.3 ± 0.1. The MS materials exhibited a high U sorption capacity in water (>40 μg U/mg sorbent) with Langmuir isotherms suggesting a saturation U sorption capacity of 185.2 μg U/mg sorbent for the phosphonic acid-modified MS material (MSPh-III). The U sorption capacity in artificial seawater was reduced to 12.1 μg U/mg sorbent for MSPh-III. Langmuir isotherms indicated a saturation sorption capacity of 66.7 μg U/mg sorbent for MSPh-III, which also had the greatest binding affinity for U of all sorbents tested, followed by the imide dioxime-functionalized material MSCA-I. Kinetics studies show rapid uranyl sorption and equilibration in less than 40 min. The U was quantitatively eluted from the MS sorbents by washing with strong acid (>0.1 M HCl). This work represents the first comprehensive study of organo-functionalized MS materials for U extraction, and shows that phosphonic acid- and imide dioxime-functionalized MS materials provide excellent platforms for developing novel sorbents for efficient U extraction from seawater.

1. Introduction

The current annual global energy consumption of 13 Terrawatts [1] is projected to double by 2050 due to the increase in global population and standard of living [2]. While 81% of the current power need is supplied from burning fossil fuels [3], a shift towards renewable energy supplies is urgently needed in order to sustain global economic growth and to mitigate the climate change caused by a rapid rise of the atmospheric carbon dioxide level. While efficient solar power generation provides a long-term, sustainable solution to the global energy need, nuclear power remains the only mature, large-scale, non-intermittent, and carbon–neutral means to meet this growing energy demand in the coming decades (and centuries). Development of stable and clean energy supplies through nuclear power is a responsible pursuit.

Among all radionuclides, uranium is the predominant fuel for nuclear reactors. For that reason, the extraction and enrichment of uranium has important strategic and economic value. As the uranium in terrestrial ores is limited, extraction from other sources such as waste coal ash and seawater is actively being explored [4–6]. The oceans contain 4.5 billion tons of uranium, equivalent to 1000 times the currently available terrestrial uranium that can be economically mined. Efficient extraction of uranium from seawater represents an attractive solution for the development of sustainable nuclear fuel cycles [4,7]. Sequestration of uranium from seawater would greatly improve its availability and sustain the fuel supply for nuclear energy, thus removing an important hurdle for increasing nuclear power supply.

Because uranium is present at an extremely low concentration of 3 ppb in seawater, economical extraction of uranium from seawater presents a major scientific and technological challenge. Several methods for uranium collection have been introduced and evaluated over the past decades, including ion exchange, solvent extraction, foam separation, co-precipitation, biomass collection, and adsorption [4,5]. Materials such as ion-exchange resins, titanium oxide, activated carbon, galena, and polymers have been used [4,8–11]. However, none of these techniques have been practical for reasons such as ion selectivity, long term stability, and cost effectiveness. Recent research has focused on sorbents containing organic functional groups (such as amidoxime) as promising candidates for uranium sorption [7–16]. Uranium is typically found as

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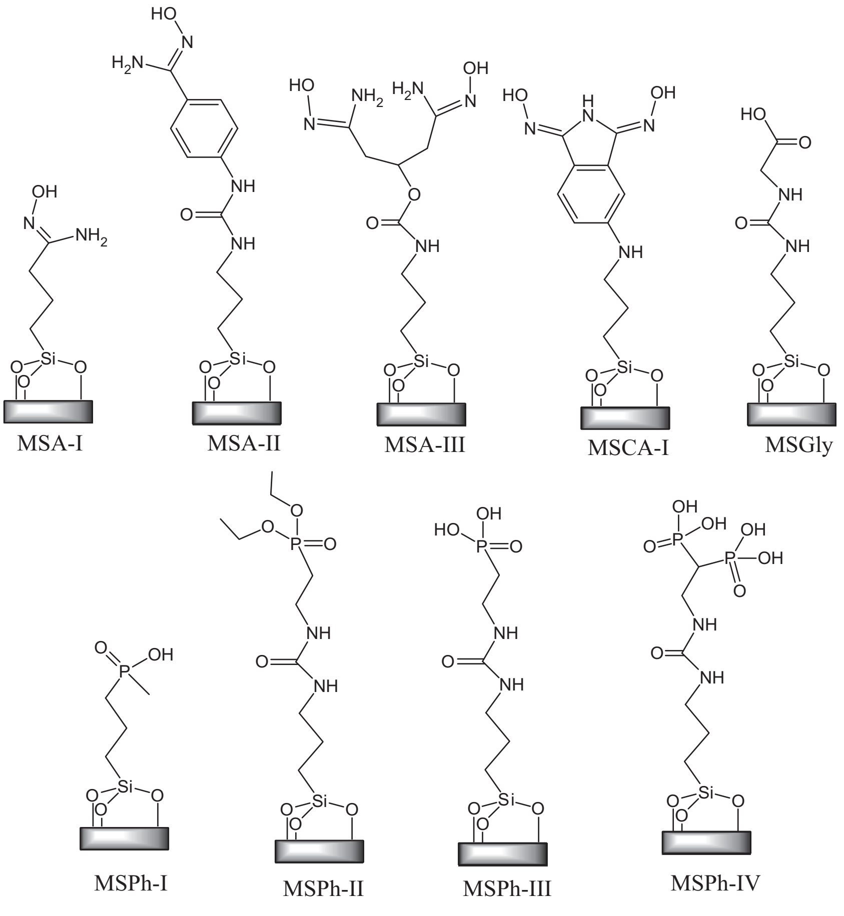
the uranyl ion (UO_2^{2+}) in aqueous solutions, which is a hexavalent U species [17,18]. Simple amidoximes are known to bind the uranyl ion in aqueous solution, with recent data suggesting an η^2-binding mode when grafted onto polymer braids [19–21]. Polymer beads and fibers functionalized with amidoxime groups have shown uranium sorption capacities as high as 1.5 μg U/mg and 6.0 μg U/mg adsorbent in seawater and laboratory conditions, respectively [4]. Further improvements to uranium collection systems in areas of selectivity, loading capacity, sorption kinetics, as well as chemical and mechanical stability must be made in order to make uranium extraction from seawater economically feasible.

Mesoporous silica (MS) materials have attracted attention in recent years due to their useful features such as large surface area, tunable pore volume and size, and facile modification of physical and chemical properties through surface functionalization [22,23]. These characteristics make MS materials an ideal platform for generating a variety of hybrid materials for applications ranging from catalysis to nanomedicine [24–29]. MS materials have also been successfully tested in the removal of several heavy metal ions, oxyanions, and toxic organic species from aqueous solutions [30,31]. In the area of actinide sequestration, Fryxell and others recently used surface-modified MS materials for selective U sequestration under acidic conditions [32–35]. Comprehensive studies and comparisons of U extraction with organo-functionalized MS materials have not been carried out to date. Herein we report the synthesis and characterization of a series of surface-modified MS materials and their application as sorbents for U extraction from seawater. A series of amidoxime-, imide dioxime-, phosphonate-, and carboxylate functional groups were grafted onto commercially available MSU-H mesoporous material (Scheme 1), and their sorption performances were investigated in slightly basic water and artificial seawater. The sorption kinetics, U desorption, and sorption isotherm studies were measured under similar conditions. The phosphonic acid-modified MS material (MSPh-III) exhibited a very high saturation capacity for U sorption in water (185.2 μg U/mg sorbent) and in artificial seawater (66.7 μg U/mg sorbent) according to the Langmuir adsorption model. Our goal is to compare the performance of these MS materials with different functionalities, thus identifying the best candidates for more thorough evaluations of their potential in uranium extraction from seawater.

2. Experimental

2.1. Materials and methods

All reagents including the MSU-H material were purchased from Aldrich and used without further purification, except for 3-(isocyanatopropyl)triethoxysilane (ICP-TES), 3-(cyanopropyl)triethoxysilane (CP-TES), and 3-(iodopropyl)trimethoxysilane (IP-TMS) which were purchased from Gelest. Thermogravimetric analysis (TGA) was carried out with a Shimadzu TGA-50 equipped with a platinum pan and using a heating rate of 5 °C/min under air. The surface charge of the synthesized MS materials was measured in 1.0 mM phosphate buffered saline solution on a Malvern ZetaSizer dynamic light scattering instrument. NMR spectra were recorded on a Bruker NMR 400 NB at 400 MHz. Mass spectrometric analyses were conducted using positive-ion electrospray ionization on a Bruker BioTOF Mass Spectrometer. The IR spectra were obtained using an Alpha-T Bruker Fourier Transform Infrared Spectrometer in attenuated total reflectance (ATR) mode. For all the experiments, uranyl concentration (UO_2^{2+}) in solution was



Scheme 1. Organo-functionalized mesoporous silica sorbents for U sorption from water and artificial seawater.