Exchanges of Uranium(VI) Species in Amidoxime-Functionalized Sorbents

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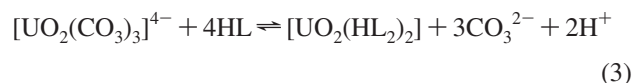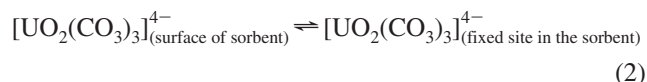
Amidoxime (AO)-functionalized polymer sorbents used in this study were prepared by two different routes involving UV grafting and electron-beam grafting of acrylonitrile (AN) into poly(propylene) fibrous and microporous sheets, and subsequent conversion of AN to AO groups by reacting the precursor sorbent with hydroxylamine. The values of self-diffusion coefficient (D_s) of UO_2^{2+} in fibrous and sheet AO sorbents were found to be 1.1×10^{-6} and 2.3×10^{-10} cm^2 s^{-1}, respectively. The higher diffusion mobility of UO_2^{2+} in the fibrous AO sorbent was attributed to its higher free volume as observed in scanning electron microscopic studies. The water content was also found to be maximum in AO-fibrous sorbent (165−200 wt %) and minimum in AO-sheet sorbent (70 wt %). In fibrous AO sorbent, the values of D_s for Na^+ and Sr^{2+} were found to be comparable to their self-diffusion coefficients in the aqueous medium. This indicated that the retardation in diffusion mobility of the ions was a minimum in the fibrous AO sorbent. However, D_s of UO_2^{2+} in the fibrous membrane was found to be significantly lower than that of Sr^{2+}, which has a self-diffusion coefficient comparable to that of UO_2^{2+} in aqueous medium. This could be attributed to stronger binding of UO_2^{2+} with AO groups as compared to Sr^{2+}. To understand the parameters affecting the U(VI) sorption from seawater, the U(VI) exchange rates between fibrous AO sorbent (S) and seawater (aq) involving $(H^+/Na^+)_S \rightleftharpoons ([UO_2(CO_3)_3]^{4-})_{aq}$ and $(UO_2^{2+})_S \rightleftharpoons ([UO_2(CO_3)_3]^{4-})_{aq}$ systems were experimentally measured. The exchange profiles thus obtained were found to be non-Fickian and much slower than $(H^+)_S \rightleftharpoons (UO_2^{2+})_{aq}$ and $(UO_2^{2+})_S \rightleftharpoons (UO_2^{2+})_{aq}$ exchanges. This seems to suggest that the reaction kinetics involved in decomplexation of $[UO_2(CO_3)_3]^{4-}$ into UO_2^{2+}, which forms a complex with AO groups, is the rate-determining step in sorption of U(VI) from seawater. The kinetics of U(VI) sorption in AO-gel and AO-fibrous sorbents followed the pseudo-second-order rate equation. The density of AO groups in the sorbents and their conditioning were found to influence the U(VI) sorption from seawater.

Introduction

Selective preconcentration of target ions in the membrane from multicomponent ionic systems is highly desirable for many applications, including recovery of valuable metal ions from lean sources and removal of toxic ions from the waste streams. Recovery of uranium from seawater is one of such challenging problems that require considerations of chemical, kinematical, and process design aspects. The concentration of uranium in seawater is of the order of 1.4×10^{-8} mol L^{-1} (3.3 mg m^{-3}) and is found to be present principally as the anionic tricarbonatouranate(VI) $[UO_2(CO_3)_3]^{4-}$ species under the prevailing conditions.[1] The major problems pertaining to the development of a suitable uranium recovery system from seawater are due to its very low concentration, the chemical form tricarbonatouranate(VI), and the large excess of competing ions.[1−3] Because seawater is a low-grade source of uranium, it is not realistic to process large volumes of seawater in continuous membrane or resin separation schemes. The separation process must be able to operate in situ without any manipulation of the chemical condition of seawater.[4,5] Therefore, the on site adsorption based separation scheme would be best suited for the preconcentration of U(VI) from seawater. For success of this scheme, the sorbent should have adequate selectivity toward U(VI) as well as high

functional groups density. This is due to fact that no further preconcentration of U(VI) would occur once the binding sites of the sorbent get saturated.

Tricarbonatouranato(VI) $[UO_2(CO_3)_3]^{4-}$ has a high stability constant that limits the choice of functional groups for uranium recovery from seawater.[1−5] Poly(acrylamidoxime) (AO) has been found to be chemically suitable for uranium recovery from seawater.[1,6] However, the major challenge for making uranium recovery economically viable is to develop a sorbent that has a very high uranium sorption rate. In general, U(VI) sorption from seawater involves the following three steps:

$$[UO_2(CO_3)_3]^{4-}_{(deep\ solution)} \rightleftharpoons [UO_2(CO_3)_3]^{4-}_{(surface\ of\ sorbent)} \quad (1)$$

$$[UO_2(CO_3)_3]^{4-}_{(surface\ of\ sorbent)} \rightleftharpoons [UO_2(CO_3)_3]^{4-}_{(fixed\ site\ in\ the\ sorbent)} \quad (2)$$

$$[UO_2(CO_3)_3]^{4-} + 4HL \rightleftharpoons [UO_2(HL_2)_2] + 3CO_3^{2-} + 2H^+ \quad (3)$$

where HL represents the amidoxime groups (fixed-complexing sites) in the sorbents. The first step involves diffusion of uranium species in seawater up to the surface of the contactor. The aqueous diffusion of bulky $[UO_2(CO_3)_3]^{4-}$ anion is affected by the temperature of the seawater, and motions of seawater and contactor. For example, 10 °C increases in seawater temperature (293−303 K) have been found to give a 3-fold higher sorption rate of uranium onto AO sorbent.[7] The second step involves

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the diffusion of anionic uranium species from the aqueous layer adjacent to the surface of sorbent into the internal matrix of sorbent. Since $[UO_2(CO_3)_3]^{4-}$ species is bulky (10 Å), the diffusion of this species in the sorbent matrix is highly dependent on the physical structure of the sorbent matrix (free volume and tortuosity) and its hydrophilicity.[8] The final step of the sorption of uranium in AO sorbent is the chemical reaction shown in eq 3. This chemical reaction involves decomplexation of $[UO_2(CO_3)_3]^{4-}$ to UO_2^{2+}, followed by complexation of UO_2^{2+} with four AO groups.[9] The decomplexation of $[UO_2(CO_3)_3]^{4-}$ may be the rate-determining step in U(VI) sorption in the AO sorbent from seawater. Zhang et al. have studied the mechanism and kinetics of U(VI) sorption in a fibrous, amidoxime-functionalized polymer matrix at different pH.[10] These studies indicated the sorption of U(VI) in AO sorbent is an endothermic chemical process and dependent on the pH of the equilibrating solution. The sorption of U(VI) in AO sorbent has been found to increase from pH 2 to 6, which is in accordance with eq 3. The sorption of U(VI) under seawater conditions in AO sorbent involves two processes having opposite requirements; i.e., decomplexation of $[UO_2(CO_3)_3]^{4-}$ is catalyzed by H^+ ions, whereas complexation of UO_2^{2+} with AO is retarded by H^+ ions.

In the present work, the U(VI) sorption kinetics has been studied in AO sorbents (gel and grafted sheet) under different conditions. The main objective of this work is to identify the parameters that determine the kinetics of U(VI) sorption in AO sorbent from seawater. For this study, the AO sorbents have been prepared by grafting acrylonitrile (AN) onto poly(propylene) host matrix (fibrous and sheet), and subsequent conversion of AN to AO groups by reacting the precursor sorbent with hydroxylamine. Two different routes have been used for anchoring AN in poly(propylene) host matrix. These are UV initiator based method[11] and post-electron-beam irradiation grafting.[9,12] These AO sorbents have been conditioned using a protocol described elsewhere.[9] The profiles of rates of U(VI) exchanges in the AO sorbents (S) have been measured using ^{233}U radiotracer spiked in the well-stirred seawater/aqueous solution (aq). The kinetics of U(VI) exchanges studied in the present study involve $(H^+/Na^+)_S \rightleftharpoons ([UO_2(CO_3)_3]^{4-})_{aq}$, $(UO_2^{2+})_S \rightleftharpoons ([UO_2(CO_3)_3]^{4-})_{aq}$, $(H^+)_S \rightleftharpoons (UO_2^{2+})_{aq}$, $(UO_2^{2+})_S \rightleftharpoons (H^+)_{aq}$, and $(UO_2^{2+})_S \rightleftharpoons (UO_2^{2+})_{aq}$ systems. The rate profiles of $(M^{n+})_S \rightleftharpoons (M^{n+})_{aq}$ isotopic exchanges are analyzed using an analytical solution of Fick's second law[13] to obtain the self-diffusion coefficients of Na^+, Sr^{2+}, and UO_2^{2+} ions in AO-fibrous sorbents. The self-diffusion coefficient of Sr^{2+} was measured as it has comparable self-diffusion coefficient with UO_2^{2+} in water but expected to have different chemical interactions with AO groups in the sorbent. The results of these studies are discussed in this paper.

Experimental Section

Materials and Reagents. Analytical reagent grade chemicals and deionized water (18 MΩ/cm) purified by model Quantum from Millipore (Mumbai, India) were used throughout the present studies. Acrylonitrile (AN), *N,N*′-methylenebis(acrylamide) (MBA), and α,α′-dimethoxy-α-phenylacetophenone (DMPA) were obtained from Sigma-Aldrich (Steinheim, Switzerland). Hydroxylamine (40% in aqueous solution), tetrahydrofuran (THF), and *N,N*′-dimethylformamide (DMF) were obtained from Merck (Mumbai, India). Locally available thermally bonded nonwoven poly(propylene) macroporous fibrous sheet (NK Filter Fabric, Mumbai, India) was used as a substrate for grafting acrylonitrile. The specifications for this

fibrous substrate were as follows: thickness ≈ 2 mm; density ≈ 0.26 g/cm³; bursting strength = 30−35 kg/cm². The other host substrate used for grafting acrylonitrile was microporous poly(propylene) membrane produced by a thermally induced phase separation process which had pore size of 0.45 μm, thickness of 80 μm, and porosity of 80%. Radiotracers ^{22}Na and $^{85,89}Sr$ dissolved in aqueous solutions were obtained from the Board of Radiation and Isotope Technology, Mumbai, India. The γ-activity of the radiotracer was monitored by a well-type NaI(Tl) or HPGe detector connected to a multichannel analyzer. The α-radioactivity of ^{233}U in equilibrating aqueous solutions were monitored by taking out a 50 μL sample and adding it in a vial containing 5 mL of scintillation cocktail-O. The composition of cocktail-O was as follows: 2,5-diphenyloxazole = 10 g, 1,4-bis(2-(5-phenyloxazolyl)benzene) = 0.25 g, naphthalene = 100 g in 1000 mL of toluene, and 10% (v/v) bis(2-ethylhexyl)phosphoric acid (HDEHP). The liquid scintillation counting was carried out in a home-built liquid scintillation counter with a EMI 9514 photomultiplier tube (13 stages) coupled to an amplifier and a single-channel analyzer via discriminator. The volume and thickness of each sorbent sample in the appropriate ionic form was measured using a pycnometer[14] or a digital micrometer (Mitutoy, Japan) with an accuracy of 0.001 mm. A microprocessor-based pH meter model PHAN from Laboratory India (Mumbai, India) was used for pH measurements. Seawater used in the present work was collected from Andaman and Nicobar Islands.

Sorbent Preparation. The electron-beam grafted sorbent samples were provided by Radiation Technology Development Section (RTDS), BARC, Mumbai, India. This sorbent was prepared by grafting acrylonitrile (AN) on the matrix of poly(propylene) fibrous sheet by post electron-irradiation grafting method as described elsewhere.[9,12] For UV grafting of AN in the sorbent (microporous or fibrous sheet), the samples (6 × 6 cm² area) were soaked for overnight in the polymerizing solution containing monomer (AN), cross-linker (MBA), and an UV initiator (DMPA) dissolved in THF + DMF (1:1) mixture. The amounts of cross-linker and monomer were adjusted in the polymerization solution to get 5 mol % cross-linking. The amount of UV initiator was taken as 1 wt %. The grafting solution filled samples were sandwiched between two transparent polyester sheets to prevent any possible loss of grafting solution filled in the pores. Care was taken to remove excess of grafting solution and air bubbles trapped between sorbent and polyester covering sheet. Finally, the sandwiched sorbent was exposed to 365 nm UV light in a multilamps photoreactor (Heber Scientific, model no. HML-SW-MW-LW-888) for a period of 20 min. After irradiation in the photoreactor, the samples were washed thoroughly with THF, methanol and distilled water to remove the ungrafted components. Acrylonitrile gel was prepared UV-induced homopolymerization of AN in the solution having same composition of AN, MBA, and DMPA in THF + DMF mixed solvent as that used for AN grafting in the poly(propylene) matrix. The precursor sorbents were vacuum-dried to obtained weight of grafted material. The degree of AN grafting in samples was determined from the knowledge of weights of sorbent sample before ($W_{initial}$) and after grafting (W_{final}). The C≡N groups in the precursor sorbents and gel were converted to AO groups by reacting it in the 3 wt % hydroxylamine solution (methanol:water = 1:1) at 60 °C for 8 h. After amidoximation, the gel and sorbent samples were washed thoroughly with a water. The AO-sorbent samples were conditioned by treating them with 0.1 mol L^{-1} NaOH at room temperature (25 °C) for overnight or 80 °C for 1 h.

Characterization. The conversion of AN groups to AO groups was confirmed by FTIR. The sorbent samples were powdered in liquid nitrogen and mixed with KBr for FTIR measurements. FTIR spectra of the samples were recorded using the spectrophotometer (8400 model) procured from Shimadzu, Japan. The KBr powder was used as an internal standard in the measurements. The ratio of the KBr to membrane samples was maintained to be 100:1. Diffused reflectance assembly was used for recording the spectra. The water uptake capacity of the sorbents, defined as the amount of water absorbed per unit dry weight of the sorbent, was obtained from the difference in weight of wet and vacuum-dried sample at room temperature. For measurements of water uptake capacity, the sorbent samples were equilibrated with seawater for 24 h.

The Na^+-exchange capacities of the AO-sorbent samples were measured by using ^{22}Na radiotracer, which emits 511 keV γ-rays. The stock solution of 0.1 mol L^{-1} NaCl was spiked with a known radioactivity of carrier-free ^{22}Na radiotracer. The sorbent samples of known weight (0.2–0.3 g) were equilibrated in 25 mL well-stirred aqueous NaCl solution (0.1 mol L^{-1}) containing known amount of ^{22}Na radioactivity for 4 h. After equilibration, the samples were thoroughly washed with deionized water to remove equilibrating solution clinging to the surface of the samples. The washing cycles were repeated until the radioactivity of ^{22}Na in sorbent became constant. To obtain the moles of Na^+ ions held in the sorbent, the ^{22}Na radioactivity in the samples were measured by γ-counting using a well-type NaI(Tl) detector based γ spectrometer. Filter paper standards were prepared by taking pieces of Whatman-41 filter paper of the same dimensions (1 × 2 cm) as the sorbent samples and adding known volume (50, 100, and 200 μL) of the radiolabeled 0.1 mol L^{-1} NaCl stock solution. NaCl stock solution used for preparing standard samples contained the same ^{22}Na (radioactive) to ^{23}Na (natural) ratio as that in the solution used for equilibrating the sorbent samples. Each standard was prepared in duplicate. The soaked filter papers were dried at room temperature and counted in a well-type NaI(Tl) detector in a counting geometry similar to that of the sorbent samples. The amount of Na^+ ion in the membrane sample was obtained by comparing the γ-activity of ^{22}Na in the samples with filter paper standards as given below:

$$Na^+\text{-exchange capacity} = \frac{A_S}{A_{std}} \times \frac{M_{std}}{W_S} \qquad (4)$$

where A_S and A_{std} are ^{22}Na γ-radioactivity (counts s^{-1}) in sample and standard, respectively. M_{std} is the moles of Na^+ in the standard, and W_S is weight of sample.

The uptake studies of U(VI) in AO sorbents (sheet and gel) from seawater were carried out using a ^{233}U radiotracer, which is an α-emitter. The radioactivity of ^{233}U in the sorbent could not be measured directly as α-particles have a short range in the solid matrix. The uptake of ^{233}U in the AO sorbent was obtained by measuring the α-activity of the solution before and after its equilibration with AO sorbent. Pure ^{233}U radiotracer was used for measuring the uptake efficiency. The amount of ^{233}U spiked in seawater was 10 μg mL^{-1}. This amount of ^{233}U was adjusted to obtain sufficient α-scintillation counts ($\approx$10000 cpm) in a 50 μL sample of aqueous feed added to the liquid scintillation cocktail. To keep the pH of seawater unaltered, the known volume of ^{233}U radiotracer solution was dried under the IR lamp, and 100 mg L^{-1} NaHCO$_3$ solution was added to prevent the precipitation of uranium in seawater. The uptake of U(VI) in the sample (2 × 1 cm^2) was monitored by liquid scintillation counting of samples (50 μL) of feed solution (15

mL) taken before and after 5 h (with stirring) equilibration with the sorbent. The uptake of U(VI) in the sorbent sample was obtained from following equation:

$$\text{U(VI)-uptake efficiency} (\%) = \frac{(A_{before} - A_{after})}{A_{before}} \times 100 \ (5)$$

where A_{before} and A_{after} are the α-scintillation counts (counts s^{-1}) of ^{233}U in the samples taken from the feed solution before and after equilibrating the AO-sorbent sample, respectively. Similar experiment was carried out to measure the loading capacity of the sorbent except that $^{nat}U + {}^{233}U$ was used to saturate the sorbent sample. Fixed volume of the solution containing known concentration of uranyl nitrate ($^{nat}UO_2(NO_3)_2$) spiked with required radioactivity of ^{233}U was dried under IR lamp, and 15 mL of seawater was added to equilibrate the sorbent sample of a known weight for overnight with a constant stirring. ^{233}U radiotracer sorbed in the samples was obtained from the difference in total initial radioactivity of ^{233}U in solution and residual radioactivity of ^{233}U in solution left after equilibrating the sample. The mass balance of ^{233}U was checked by accounting for the total radioactivity taken in the experiment and the total radioactivity distributed in the sorbent and the equilibrating solution, which was found to be within ±5. Since radioactivity of ^{233}U corresponding to the total amount of U(VI) ($^{nat}U + {}^{233}U$) was known, the radioactivity of ^{233}U sorbed in the sample was converted to the total amount of U(VI). The U(VI) loading capacity of sorbent was calculated using the following relation:

$$\text{U(VI)-loading capacity} = \frac{(A_{before} - A_{after})}{W_{sorbent}} \left(\frac{M_{U(VI)}}{A_{before}}\right) \quad (6)$$

where A_{before} and A_{after} are the α-scintillation counts (counts s^{-1}) of ^{233}U in the samples taken from the feed solution before and after equilibrating the AO-sorbent sample, respectively, $W_{sorbent}$ is a weight of the sample ($\approx$0.3 g), $M_{U(VI)}$ is the total moles of U(VI) ($^{nat}U + {}^{233}U$) added in the 15 mL of equilibrating solution.

Self-Diffusion Coefficient. The self-diffusion coefficients (D_s) of the Na^+, Sr^{2+}, and UO_2^{2+} in AO sorbents were measured from analyses of the rates of isotopic exchange rate profiles using nonstationary radiotracer method.[13] The exchange rates of γ-emitting radiotracers (^{22}Na and $^{85,89}Sr$) were monitored by measuring the radioactivity of these isotopes in the sorbent sample itself as a function of equilibration time. In the case of α-emitter (^{233}U), the radioactivity sorbed or desorbed in the equilibrating solution was monitored by taking 50 μL samples of equilibrating solution as a function of time and subjecting these to liquid α-scintillation counting. For measuring rates of isotopic exchanges involving $(Na^+)_S \rightleftharpoons (Na^+)_{aq}$ and $(Sr^{2+})_S \rightleftharpoons (Sr^{2+})_{aq}$ systems, the sorbent samples (2 × 1 cm^2) were converted to appropriate ionic forms (saturation loading) using 0.1 mol L^{-1} relevant salt solution tagged with the known activity of the radiotracers (^{22}Na or $^{85,89}Sr$). These sorbent samples were equilibrated with a well-stirred 25 mL relevant salt solution (0.1 mol L^{-1}) without any radiotracer. During equilibration, the radiotracer of ion diffuses from the sorbent sample to the aqueous solution by isotopic exchange. The exchange rates of γ-emitting radiotracers (^{22}Na and $^{85,89}Sr$) between sorbent sample and equilibrating solution was monitored by taking out the sorbent sample from the equilibrating solution at regular time intervals and counting γ-radioactivity of the radiotracers in the fixed geometry using a well-type NaI(Tl) detector connected to a single-channel analyzer. Before monitoring the radioactivity, the sorbent samples were washed with an excess of deionized water to remove traces of equilibrating solution adhering to its

TABLE 1: Experimental Conditions of U(VI) Species Exchanges between Fibrous AO Sorbent (F-1) and a Well-Stirred Equilibrating Solution

| exchange system	sorbent	equilibrating solution
$(H^+/Na^+)_S \rightleftharpoons ([UO_2(CO_3)_3]^{4-})_{aq}$	alkali treated	seawater (pH = 7.6) spiked with 10× excess of $^{nat}U + ^{233}U$ than saturation; $NaHCO_3$ was added to prevent precipitation
$(UO_2^{2+})_S \rightleftharpoons ([UO_2(CO_3)_3]^{4-})_{aq}$	saturated with $^{nat}U + ^{233}U$	seawater (pH = 7.6) spiked with 10× excess of ^{nat}U than saturation; $NaHCO_3$ was added to prevent precipitation
$(H^+)_S \rightleftharpoons (UO_2^{2+})_{aq}$	conditioned at pH = 2	Clarke-Lubs buffer at pH = 2, spiked with 10× excess of ^{nat}U than saturation
$(UO_2^{2+})_S \rightleftharpoons (H^+)_{aq}$	saturated with $^{nat}U + ^{233}U$	1.0 mol L^{-1} HCl

surface. To ensure the removal of the traces of equilibrating solution adhering to the sorbent surface, the repeated cycles of washing and subsequent γ-counting were carried out until constant γ-activity in the sorbent sample was obtained. The sorbent sample was again placed in the equilibrating solution after counting. The actual residence time of the sorbent in the equilibrating solution was considered for obtaining an isotopic exchange rates profile.

Similar experiments were carried out in the case of α-emitter (^{233}U), except that the radioactivity of the equilibrating solution was monitored by taking out a 50 μL sample at regular intervals. Also, the equilibrating solution was maintained at pH 2 using Clarke-Lubs buffer to avoid hydrolysis of UO_2^{2+} ions. The aqueous samples taken from the equilibrating solution (0.1 mol L^{-1} containing $^{nat}U + ^{233}U$) were subjected to α-scintillation counting after adding it in the 5 mL liquid scintillation cocktail. The fractional attainment of isotopic exchange equilibrium between sorbent sample and equilibrating solution, $F(t)$, was obtained from the ratio of radioactivity of ^{233}U (counts s^{-1}) at equilibrating time t to time ∞ ($F(t) = n_t/n^*$).

Kinetics of U(VI) Species Exchanges. The kinetics of U(VI) species exchanges were studied using samples of the fibrous AO sorbent (F-1). The exchange of ions between sorbent samples and equilibrating solution are listed in Table 1. In all the cases, the radioactivity of ^{233}U in the equilibrating solution was monitored as a function of time by α-scintillation counting of 50 μL samples taken from the equilibrating solution. From the α-radioactivity of ^{233}U in equilibrating solution, $F(t)$ was obtained as a function of equilibration time. For $(UO_2^{2+})_S \rightleftharpoons ([UO_2(CO_3)_3]^{4-})_{aq}$ and $(UO_2^{2+})_S \rightleftharpoons (H^+)_{aq}$ exchanges, U(VI) was loaded in the sorbent samples up to saturation from seawater containing $^{nat}U + ^{233}U$. In equilibrating solutions, the concentration of U(VI) was 10 times in excess of their U(VI) sorption capacity. For $(H^+)_S \rightleftharpoons (UO_2^{2+})_{aq}$ exchanges, the Clarke-Lubs buffer having pH = 2 was used to keep U(VI) as UO_2^{2+} ions in the equilibrating solution. The Clarke-Lubs buffer solution was prepared using 0.1 mol L^{-1} KCl and was adjusted to pH 2 with dilute HCl. An appropriate volume (100−500 μL) of $NaHCO_3$ solution (100 mg L^{-1}) was added to prevent the precipitation of uranium from seawater and to ensure the existence of U(VI) as $UO_2(CO_3)_3^{4-}$. The AO-sorbent sample of 2 × 1 cm^2 dimension was equilibrated with 25 mL of a well-stirred solution.

Results and Discussion

Amidoxime sorbents studied in the present work were prepared by grafting acrylonitrile by two different methods in fibrous and microporous sheets. The maximum grafting of AN obtained in fibrous membranes was 165 wt %. However, high grafting of AN in fibrous poly(propylene) was found to be difficult and could be readily achieved only up to 120−130 wt % by both UV or post-EB-irradiation methods as described in the Experimental Section. These AN-grafted precursor sorbents

SCHEME 1: U(VI)−Amidoxime Complex Formed in the Sorbent
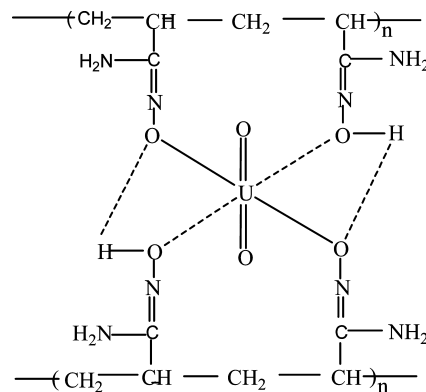
TABLE 2: Properties of AO Sorbents Prepared by Different Methods

ID	host substrate	thickness	grafting method	grafting (wt %)	water uptake[a] (wt %)	U(VI) loading capacity ($\times 10^{-3}$ mol g^{-1})
gel	none	-	UV	-	152	2.8 ± 0.1
F-1	fibrous	2 mm	EB	125 ± 4	190	1.6 ± 0.2
F-2	fibrous	2 mm	EB	165 ± 5	164	1.8 ± 0.1
F-3	fibrous	2 mm	UV	120	200	
S-1	sheet	80 μm	UV	128	70	

[a] In seawater.

were converted to AO sorbent by reacting with hydroxylamine. The conversion of AN (-C≡N) to AO groups (-C(=NOH)NH₂) in the sorbents were confirmed by recording FTIR spectra before and after treating with hydroxylamine (amidoximation). In the FTIR spectra of amidoximated sorbent, the intensity of the band at 2245 cm^{-1} corresponding to C≡N groups was reduced considerably. The additional bands at 1650 cm^{-1} (C=N stretching), 922 cm^{-1} (N−O stretching), and 1560 cm^{-1} (-NH₂) and the broad band at 3000−3600 (N−H, O−H stretching vibrations) were observed in the FTIR spectrum of amidoximated sorbents. The conversion of AN to AO groups with hydroxylamine was not complete as the characteristic band of C≡N did not disappear completely in the FTIR spectra of the sorbent after amidoximation. The elemental analyses indicated that the increase in nitrogen contents in amidoximated sorbents with respect to AN sorbents was on the order of 75−80% conversion of -C≡N to -C(=NOH)NH₂ group. After U(VI) sorption, a shift in the N−O band from 922 to 913 cm^{-1} and appearance of new bands at 1041 and 1134 cm^{-1} (from the alkoxy group) were observed in the AO sorbent. These results may explain that =N−O- groups are coordinated with UO_2^{2+}, as reported elsewhere[8e] and shown in Scheme 1.
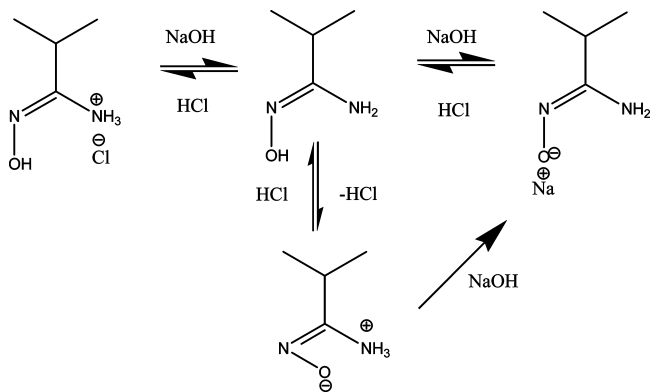
The properties of AO membranes are given in Table 2. The AO sorbents were found to readily take up water from seawater. The dimensions of microporous sheet and fibrous AO sorbent were not changed on the sorption of water. The water uptake

TABLE 3: Effects of Pretreatment Conditions of AO Sorbent (F-1)

S no.	pretreatment conditions	Na^+-exchange capacity (mol g^{-1})	UO_2^{2+}-uptake efficiency[a] (%)
1	1.0 mol L^{-1} HCl for 24 h at 27 °C	1.4×10^{-6}	−
2	HCl equilibrated sorbent conditioned with 1.0 mol L^{-1} NaCl for 24 h at 27 °C	6.5×10^{-6}	67 ± 2
3	HCl equilibrated sorbent conditioned with 0.1 mol L^{-1} NaOH for 24 h at 27 °C	1.9×10^{-4}	97 ± 2
4	HCl equilibrated sorbent conditioned with 0.1 mol L^{-1} NaOH for 1 h at 80 °C	8.8×10^{-4}	98 ± 2

[a] Total ^{233}U spiked in 15 mL seawater was 128 μg that was considerably lower than the uranium loading capacity (0.0726 g) of the F-1 sorbent sample.

SCHEME 2: Change in Chemical Structure of Amidoxime Sorbents on Treatments with Acid and Base

Figure 1. Comparison of fractional attainment of U(VI)-uptake equilibrium ($F(t)$) in AO sorbents from well-stirred seawater spiked with ^{233}U as a function of equilibrating time. Symbols +, ×, ▲, Δ, and □ represent gel, F-2, F-3, F-1, and S-1 sorbents, respectively, which were equilibrated with stirring. Symbol ○ represents F-1 sorbent equilibrated under the same conditions without stirring.

capacity of microporous sheet AO sorbent was significantly lower than fibrous AO sorbent. It is seen from Table 2 that fibrous AO sorbents have high U(VI) sorption capacity, which makes these sorbents suitable in the adsorptive scheme for preconcentration of U(VI) from seawater. The AO sorbents having same degree of grafting but prepared by two different routes (UV and EB) were found to have similar water uptake capacity. The experimental U(VI) sorption capacity of AO sorbent (380.8 mg/g) was found to be in close agreement with that obtained by Zhang et al. using the Langmuir isothermic adsorption equation (384.6 mg/g) in the fibrous sheet AO sorbent, having a similar degree of grafting.[10a]

To understand the effects of conditioning, the membrane sample F-1 was treated sequentially with HCl, NaCl, and NaOH at room temperature (27 °C), and NaOH at 80 °C. After each treatment, the Na^+-exchange capacity and U(VI)-extraction efficiency were measured, and values thus obtained are given in Table 3. The Na^+-exchange capacity of F-1 membrane was found to increase substantially after its treatment with NaOH. This can be attributed to dequaternization of the amidoxime groups in the AO membrane with strong base only, as shown in Scheme 2.[8] Although Na^+-exchange capacity was maximumally increased (8.8×10^{-4} mol g^{-1}) on treatment of the AO membrane with hot NaOH, it was less than the U(VI) loading capacity (1.6×10^{-3} mol g^{-1}) of the sorbent. This is due to the fact that amidoxime is a weak acidic group with $pK_a > 11$.[2] The U(VI)-uptake efficiency of the AO sorbents was not found to be affected by the temperature of the alkali treatment.

The comparison of rates of $F(t)$ in the different AO sorbents as a function of equilibration time in well-stirred seawater are shown in Figure 1. This comparison indicated that (i) the sorption of U(VI) is not affected by the grafting method but strongly affected by the stirring of the equilibrating solution; (ii) the U(VI)-sorption rate is faster in the AO membrane having a fibrous matrix as compared to the microporous sheet; (iii) the increase in the degree of grafting in host membrane increases the U(VI)-sorption kinetics; and (iv) the AO gel itself has slower
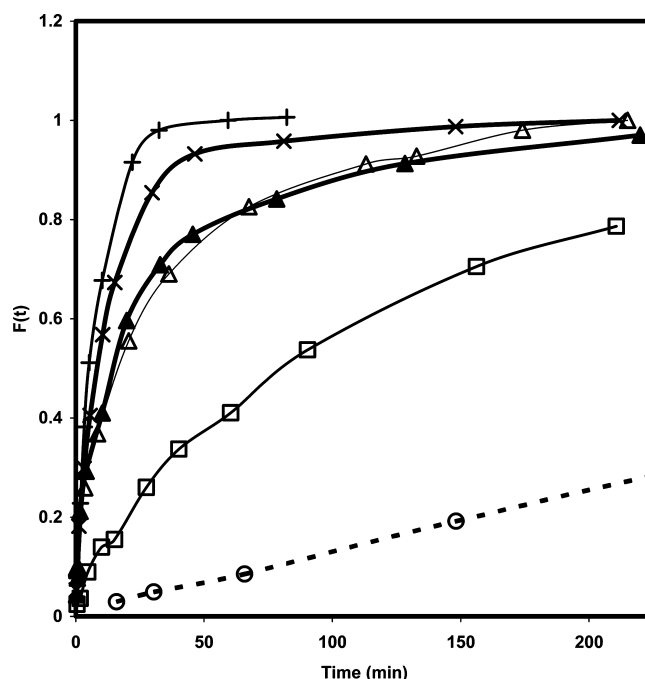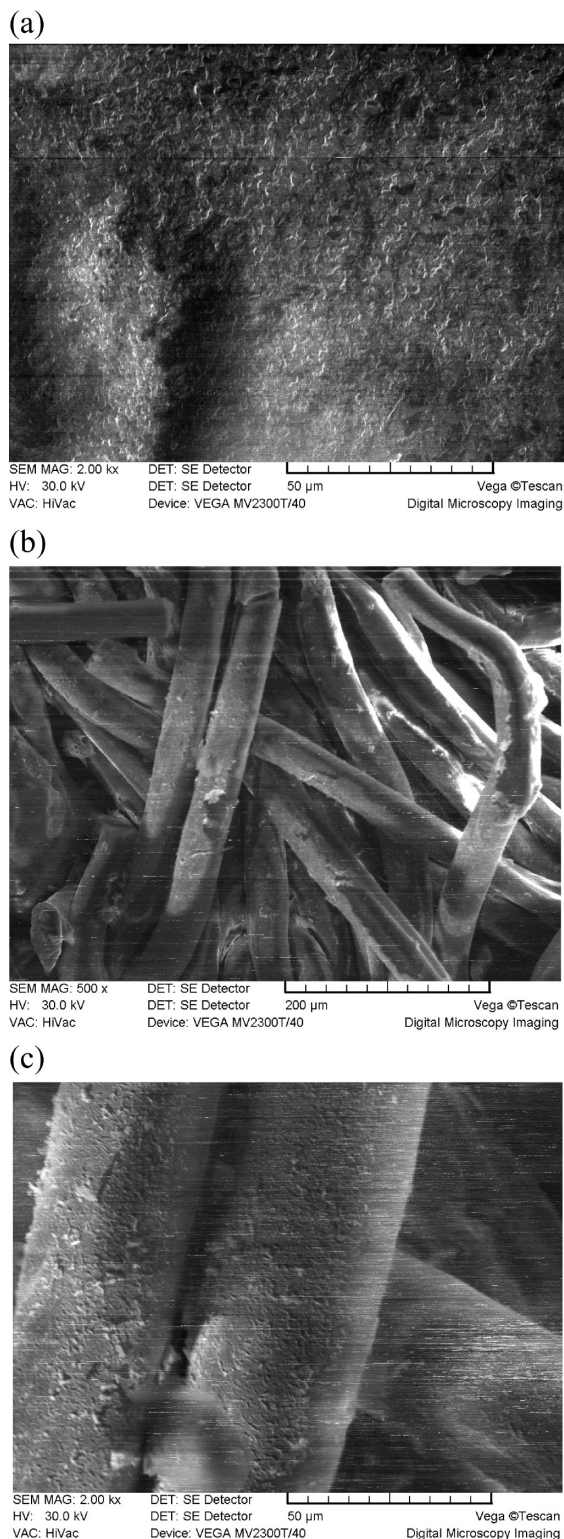
U(VI)-sorption kinetics and poly(propylene) matrix slows it down further. Similar sorption kinetics of U(VI) in EB-beam-grafted and UV-grafted sorbents from seawater is attributed to the fact that the same base fibrous poly(propylene) samples were used in both routes of grafting, and also the degree of grafting was nearly the same in both cases. The higher U(VI)-sorption kinetics in the fibrous sorbent than that in the microporous sheet sorbent could be attributed to the accessibility of $[UO_2(CO_3)_3]^{4-}$ to a large number of binding sites as well as high diffusion mobility of UO_2^{2+} in the fibrous matrix. It can be seen from the scanning electron microscopy (SEM) images given in Figure 2 that fibrous AO sorbent consists of fibers having 30−40 μm diameter and a large void space (free volume) between them. Contrary to this, sheet AO sorbent is highly compact.

Self-Diffusion of Ions in Sorbent Matrix. Self-diffusion takes place in the absence of a chemical potential gradient. The self-diffusion of ions in a homogeneous medium is due to continuous random motion of the ions which gives rise to a definite probability of arrival at some point within a given time. The precise information about the matrix effect on the mobility of ions can be obtained from the self-diffusion coefficient. The self-diffusion coefficients of UO_2^{2+} in the fibrous and microporous sheet AO-sorbent samples were measured. The choice of UO_2^{2+} ions instead of $[UO_2(CO_3)_3]^{4-}$ ions was based on the fact that U(VI) sorption in AO sorbent from seawater involves

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(a)

SEM MAG: 2.00 kx   DET: SE Detector
HV: 30.0 kV   DET: SE Detector   50 µm   Vega ©Tescan
VAC: HiVac   Device: VEGA MV2300T/40   Digital Microscopy Imaging

(b)

SEM MAG: 500 x   DET: SE Detector
HV: 30.0 kV   DET: SE Detector   200 µm   Vega ©Tescan
VAC: HiVac   Device: VEGA MV2300T/40   Digital Microscopy Imaging

(c)

SEM MAG: 2.00 kx   DET: SE Detector
HV: 30.0 kV   DET: SE Detector   50 µm   Vega ©Tescan
VAC: HiVac   Device: VEGA MV2300T/40   Digital Microscopy Imaging

Figure 2. Scanning electron micrographs of sheet AO sorbent S-1 (a) and fibrous AO sorbent F-1 (b and c) having the same degree of grafting.

decomplexation of uranium anionic complex $[UO_2(CO_3)_3]^{4-}$ followed by complexation of UO_2^{2+} with AO groups in the sorbent. This suggests that UO_2^{2+} ions would diffuse in the sorbent. Therefore, the self-diffusion coefficient of UO_2^{2+} ions was measured in the AO sorbents. The self-diffusion coefficients of Na$^+$ and Sr^{2+} were also measured to understand the effects of the valence of ions and their binding with the fixed sites in the AO sorbent. Sr^{2+} and UO_2^{2+} have almost the same self-

TABLE 4: Self-Diffusion Coefficients of Ions in Water and Fibrous AO Sorbent (F-1)

ion	degree of grafting (wt %)	D_{aq} ($\times 10^{-5}$ cm^2 s^{-1})	D_s^c ($\times 10^{-5}$ cm^2 s^{-1})	D_s/D_{aq}
Na$^+$	125 (F-1)	1.33^a	1.20 ± 0.07	0.90
Sr^{2+}	125 (F-1)	0.790^a	0.75 ± 0.04	0.96
UO$_2^{2+}$	125 (F-1)	0.779^b	0.11 ± 0.01	0.14
UO$_2^{2+}$	160 (F-2)	0.779^b	0.18 ± 0.02	0.24
UO$_2^{2+}$	128 (S-1)	0.779^b	2.3 × 10^{-5}	-

^{a} Taken from ref 15. ^{b} Taken from ref 16. ^{c} Obtained from the analyses of isotopic exchange profiles using eq 7.

diffusion coefficients in water; see Table 4. However, the nature of interactions of these ions in the sorbent would be different due to the fact that U(VI) forms a covalent complex with AO groups as shown in Scheme 1, whereas Sr^{2+} electrostatistically binds with the fixed sites.

The self-diffusion coefficients (D_s) of Na$^+$, Sr^{2+}, and UO_2^{2+} ions in the AO sorbents were obtained by analyzing experimentally measured rate profiles of the isotopic exchange between sorbent sample and well-stirred equilibrating solution using the following analytical solution of Fick's second law.[13]

$$n(t_k) = n^* \left[1 - \left(\frac{8}{\pi^2} \right) \left\{ \exp\left(\frac{-D_s \pi^2 t_k}{L^2} \right) + \right. \right.$$

$$\left. \left. \frac{1}{9} \exp\left(\frac{-9D_s \pi^2 t_k}{L^2} \right) + ... \right\} \right] \quad (7)$$

where $n(t_k)$ and n^* are the activity of radiotracer in the equilibrating solution at fixed time t_k and t_∞, respectively, D_s is the self-diffusion coefficient of the ions in the sorbent, and L is the thickness of the sorbent. The details of boundary conditions and the method used for obtaining D_s are described in our earlier paper.[13] The main assumption in eq 7 is that the contribution from aqueous diffusion is not significant in the isotopic exchange rate profiles. Experimentally, this was realized by saturating the ions at the aqueous−sorbent interface by using a higher concentration of the ions in well-stirred equilibrating solution.

The isotopic exchange profiles of $(UO_2^{2+})_S \rightleftharpoons (UO_2^{2+})_{aq}$, $(Sr^{2+})_S \rightleftharpoons (Sr^{2+})_{aq}$, and $(Na^+)_S \rightleftharpoons (Na^+)_{aq}$ were experimentally measured and shown in Figure 3. These exchange rate profiles were analyzed by a nonlinear least-squares fit of eq 7, using n^* and D_s as the free parameters, to obtain self-diffusion coefficients of Na$^+$, Sr^{2+}, and UO_2^{2+} ions in AO sorbents. The comparison of values of D_s of ions and their corresponding self-diffusion coefficient in water is given in Table 4. The values of D_{aq} were taken from the literature.[15,16] It is seen from this table that the values of D_s vary in the order Na$^+$ > Sr^{2+} > UO_2^{2+} in the fibrous AO sorbent.

The value of D_s ions in the sorbent matrix could be related to D_{aq} by the following equation:[17]

$$D_s = D_{aq} \frac{g(\phi)}{Z_i} f(V_p) \quad (8)$$

where $g(\varphi)$ is the electrostatic interaction parameter with φ representing the reduced electrostatic potential, Z_i is the charge on the diffusing ion, and $f(V_p)$ represents tortuosity factor related to polymer volume faction V_p.[18] The ratio D_s/D_{aq} is a measure of retardation in the diffusion mobility of ions in the sorbent matrix. The values of D_s/D_{aq} close to unity in the case of Na$^+$ and Sr^{2+} indicates that the retardation of diffusion mobility of these ions is not significant in the fibrous matrix. The lower self-diffusion coefficient of UO_2^{2+} can be attributed to its strong
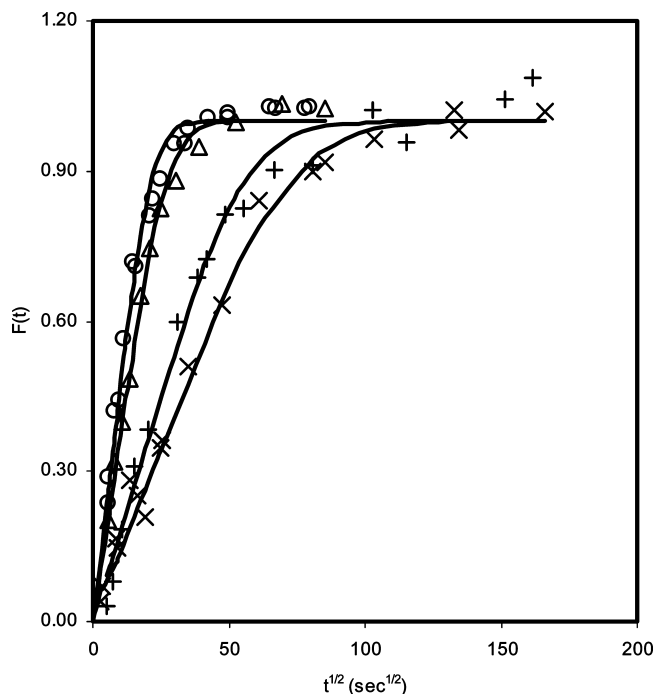
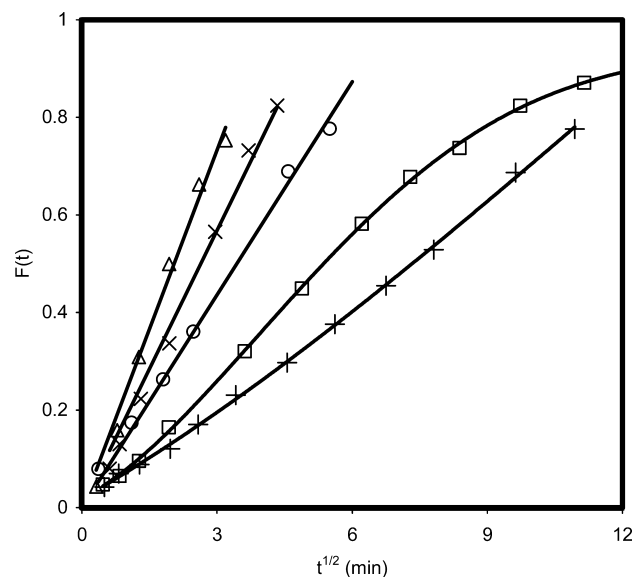**Figure 3.** Isotopic exchanges of Na$^+$, Sr^{2+}, and UO$_2^{2+}$ in fibrous AO sorbent. Symbols O, Δ, and X represent (Na$^+$)$_S$ ⇌ (Na$^+$)$_{aq}$, (Sr^{2+})$_S$ ⇌ (Sr^{2+})$_{aq}$, and (UO$_2^{2+}$)$_S$ ⇌ (UO$_2^{2+}$)$_{aq}$ exchanges between F-1 sorbent and well-stirred equilibrating solution. Symbol + denotes (UO$_2^{2+}$)$_m$ ⇌ (UO$_2^{2+}$)$_{aq}$ exchange with F-2 sorbent. Solid lines are fitted data using eq 7.

Figure 4. Fractional attainment of U(VI)-uptake equilibrium $F(t)$ in AO sorbent (F-1) as a function of time t. Symbols Δ, ×, O, □, and + represents (H$^+$)$_S$ ⇌ (UO$_2^{2+}$)$_{aq}$, (UO$_2^{2+}$)$_S$ ⇌ (H$^+$)$_{aq}$, (UO$_2^{2+}$)$_S$ ⇌ (UO$_2^{2+}$)$_{aq}$, (H$^+$/Na$^+$)$_S$ ⇌ ([UO$_2$(CO$_3$)$_3$]$^{4-}$)$_{aq}$, and (UO$_2^{2+}$)$_S$ ⇌ ([UO$_2$(CO$_3$)$_3$]$^{4-}$)$_{aq}$ exchange systems.

binding with AO functional groups in the sorbent as compared to Sr^{2+}, which forms an electrostatic bond with AO groups. On increasing the grafting from 125 to 165 wt %, the self-diffusion coefficients of UO$_2^{2+}$ were increased from 0.11 × 10^{-5} to 0.18 × 10^{-5} cm^2 s^{-1}. This indicates that the spacing of AO groups also influence the self-diffusion of UO$_2^{2+}$ in the sorbent matrix. The self-diffusion coefficient of UO$_2^{2+}$ in the microporous sheet AO sorbent (S-1) was found to be 2.3 × 10^{-10} cm^2 s^{-1}. The lower diffusion mobility of UO$_2^{2+}$ in the microporous sheet attributed to the dense physical structure of this sorbent as shown in Figure 2. As can be seen from eq 8, the high polymer volume faction in the sheet sorbent would increase the tortuosity factor considerably.

Kinetics of U(VI) Species Exchanges. To understand the U(VI) exchange between the equilibrating solution and the AO-sorbent sample in different ionic forms, the experiments were carried out by equilibrating F-1 sorbent with a seawater (pH = 7.6) or aqueous solution (pH = 2) containing [UO$_2$(CO$_3$)$_3$]$^{4-}$ and UO$_2^{2+}$ ions, respectively. Under the experimental conditions described in the Experimental Section, U(VI)-exchange profiles would be governed by the reaction kinetics at sorbent−aqueous phases and subsequent diffusion in the sorbent matrix. Using appropriate conditions described in the Experimental Section, the U(VI)-exchanges profiles represented by (H$^+$/Na$^+$)$_S$ ⇌ ([UO$_2$(CO$_3$)$_3$]$^{4-}$)$_{aq}$, (UO$_2^{2+}$)$_S$ ⇌ ([UO$_2$(CO$_3$)$_3$]$^{4-}$)$_{aq}$, (H$^+$)$_S$ ⇌ (UO$_2^{2+}$)$_{aq}$, (UO$_2^{2+}$)$_S$ ⇌ (H$^+$)$_{aq}$, and (UO$_2^{2+}$)$_S$ ⇌ (UO$_2^{2+}$)$_{aq}$ systems were studied and shown in Figure 4. As can be seen from this figure, $F(t)$ varies linearly up to 70−80% exchange involving (H$^+$)$_S$ ⇌ (UO$_2^{2+}$)$_{aq}$, (UO$_2^{2+}$)$_S$ ⇌ (H$^+$)$_{aq}$, and (UO$_2^{2+}$)$_S$ ⇌ (UO$_2^{2+}$)$_{aq}$ systems as a function of the square root of the equilibration time ($t^{1/2}$). The kinetics of the exchanges follows the trend (H$^+$)$_S$ ⇌ (UO$_2^{2+}$)$_{aq}$ > (UO$_2^{2+}$)$_S$ ⇌ (H$^+$)$_{aq}$ > (UO$_2^{2+}$)$_S$ ⇌ (UO$_2^{2+}$)$_{aq}$. These are the characteristics of the Fickian diffusion.[19]

It is seen from Figure 4 that (H$^+$/Na$^+$)$_S$ ⇌ ([UO$_2$(CO$_3$)$_3$]$^{4-}$)$_{aq}$ and (UO$_2^{2+}$)$_S$ ⇌ ([UO$_2$(CO$_3$)$_3$]$^{4-}$)$_{aq}$ exchanges are quite slow, and non-Fickian type diffusion as a variation of $F(t)$ as a function of $t^{1/2}$ is nonlinear (S-shaped). The comparison of profiles of exchange rates given in Figure 4 indicates that (H$^+$)$_S$ ⇌ (UO$_2^{2+}$)$_{aq}$ exchange is a diffusion process and (H$^+$/Na$^+$)$_S$ ⇌ ([UO$_2$(CO$_3$)$_3$]$^{4-}$)$_{aq}$ exchange may be controlled by reaction kinetics at the interface of the sorbent. The slower exchange in the (UO$_2^{2+}$)$_S$ ⇌ ([UO$_2$(CO$_3$)$_3$]$^{4-}$)$_{aq}$ system as compared to the (H$^+$/Na$^+$)$_S$ ⇌ ([UO$_2$(CO$_3$)$_3$]$^{4-}$)$_{aq}$ system indicates that U(VI) exchange between [UO$_2$(CO$_3$)$_3$]$^{4-}$ and the UO$_2^{2+}$−AO complex is also a slower process.

Reaction Kinetics in U(VI) Sorptions from Seawater. Various models are used to understand the controlling mechanisms of the adsorption process involving mass-transfer and chemical reaction. Most commonly used kinetics models are pseudo-first-order, pseudo-second-order, and interparticle diffusion model. Lagergren suggested a rate equation for the sorption of solutes from a liquid solution.[20] This pseudo-first-order rate equation is as follows:

$$\ln\left[\frac{(q_e - q)}{q_e}\right] = -K_1 t \qquad (9)$$

where q and q_e are the amounts of solute sorbed in unit weight of the sorbent at time t and at equilibrium, respectively, and K_1 is the rate constant of first-order sorption. Another model reported in the literature for the analysis of sorption kinetics is pseudo-second-order.[21] The rate law for this system in a linear form can be expressed as follows:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (10)$$

where K_2 is the pseudo-second-order rate constant of the sorption, and other symbols are the same as for eq 9. The model based on diffusion can be expressed by Morris−Weber equation as follows:[22]

$$q_e = K_i \sqrt{t} \qquad (11)$$

where K_i represents the intraparticle diffusion rate constant. U(VI)-sorption rate profiles shown in Figure 1 were analyzed

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TABLE 5: Analyses of U(VI)-Sorption Profiles in AO Sorbents from Seawater Using Different Kinetics Models

sorbent	plot	correlation coefficient (R^2)	kinetics of sorption
AO gel	$\ln(q_e - q_t)/q_e$ vs t	0.991	pseudo-first-order
	t/q_t vs t	0.999	pseudo-second-order
	q_t vs $t^{1/2}$	0.967	diffusion controlled
F-1 AO sorbent	$\ln(qe - qt)/qe$ vs t	0.973	pseudo-first-order
	t/q_t vs t	0.999	pseudo-second-order
	q_t vs $t^{1/2}$	0.904	diffusion controlled
F-2 AO sorbent	$\ln(q_e - q_t)/q_e$ vs t	0.964	pseudo-first-order
	t/q_t vs t	0.999	pseudo-second-order
	q_t vs $t^{1/2}$	0.994	diffusion controlled
S-1 AO sorbent	$\ln(q_e - q_t)/q_e$ vs t	0.974	pseudo-first-order
	t/q_t vs t	0.977	pseudo-second-order
	q_t vs $t^{1/2}$	0.990	diffusion controlled

in terms of rate equations of pseudo-first-order (eq 9), pseudo-second-order (eq 10), and interparticle diffusion (eq 11). The results of the analyses are summarized in Table 5. On the basis of correlation coefficients, it can be concluded from Table 5 that the sorption kinetics of U(VI) in gel and fibrous AO sorbents (with high water contents) follow the pseudo-second-order rate equation. The U(VI)-sorption kinetics in the AO-sheet sorbent (S-1) was best fitted with diffusion eq 11. The diffusion-controlled U(VI)-sorption process in the microporous AO-sheet sorbent (S-1) from seawater may be attributed to the physical architecture of sobent leading to the slow mobility of UO_2^{2+} in its matrix. Zhang et al. found that U(VI) sorption from aqueous solution having pH = 6 to fibrous AO sorbent follows pseudo-first-order.[10a] In the present work, the $^{233}U(VI)$ concentration in seawater was kept as 10 ppm, which is significantly lower than the concentration of U(VI) (184 ppm) used in the study of Zhang et al. Azizian has evaluated the theoretical basis for the pseudo-first-order and pseudo-second-order kinetics models, which predict the sorption process obeys pseudo-first-order kinetics at high initial concentration of solute and pseudo-second-order kinetics at lower initial concentration of solute.[23] Therefore, a change in the concentration of U(VI) may cause switching of the U(VI)-sorption profile from pseudo-first-order to pseudo-second-order.

Conclusions

The fibrous AO sorbent was found to be better than the microporous sheet AO sorbent for U(VI) sorption from seawater. The experimentally measured self-diffusion coefficients indicated that the mobility of UO_2^{2+} ions increases in the fibrous AO sorbent with an increase in functional group density. The study on the kinetics of U(VI) sorption in AO sorbents revealed (i) that the self-diffusion coefficient of ions in the fibrous AO sorbent was close to their self-diffusion mobility in the aqueous medium (ii) but that U(VI)-sorption profiles of $(H^+/Na^+)_m \rightleftharpoons ([UO_2(CO_3)_3]^{4-})_{aq}$ and $(UO_2^{2+})_m \rightleftharpoons ([UO_2(CO_3)_3]^{4-})_{aq}$ exchanges were significantly slower than that for $(H^+)_m \rightleftharpoons (UO_2^{2+})_{aq}$ and $(UO_2^{2+})_m \rightleftharpoons (UO_2^{2+})_{aq}$ exchanges under identical laboratory conditions. The analyses of U(VI)-sorption profiles from seawater indicated that the sorption process in fibrous AO sorbent involves non-Fickian diffusion and follows pseudo-second-order rate equation. These observations indicated that decomplexation of $[UO_2(CO_3)_3]^{4-}$ at AO-sorbent surface is a major factor that is responsible for the slower sorption kinetics in AO sorbents.

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