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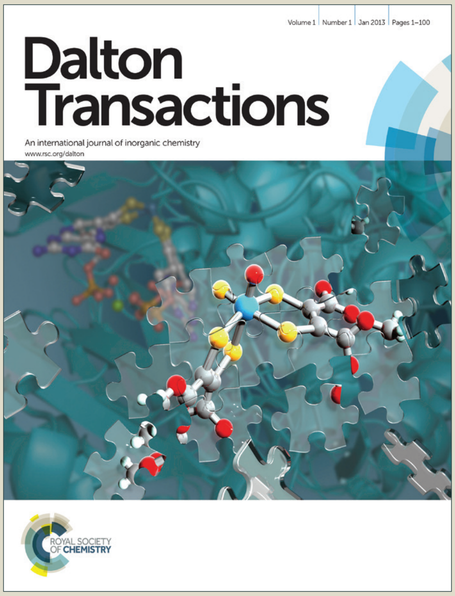

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Carbonate-H_2O_2 Leaching for Sequestering Uranium from Seawater

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Abstract

Uranium adsorbed on amidoxime-based polyethylene fiber in simulated seawater can be quantitatively eluted at room temperature using 1M Na_2CO_3 containing 0.1 M H_2O_2. This efficient elution process is probably due to formation of an extremely stable uranyl-peroxo-carbonato complex in the carbonate solution. After washing with water, the sorbent can be reused with little loss of uranium loading capacity. Possible existence of this stable uranyl species in ocean water is also discussed.

Introduction

Developing techniques for extracting uranium from seawater is of considerable current interest because land-based uranium sources would be depleted by the end of this century.[1, 2] Our ocean contains a very large quantity of uranium (about 1000 times more than terrestrial ores) which is sufficient to support nuclear power production in the next few centuries.[3] Uranium exists in seawater at a low concentration (~3 ppb) and as the very stable uranyl tris-carbonato complex, $UO_2(CO_3)_3^{4-}$.[3] Screening studies conducted in the 1980s with more than 200 functionalized adsorbents show that the sorbent materials with the amidoxime group $RC(NH_2)(NOH)$ were most effective for uranium adsorption from seawater.[4-6] Recent research efforts in Japan and in the USA are focused on using amidoxime-based adsorbents for sequestering uranium from seawater.[4] The amidoxime-based fiber can be prepared by a radiation-induced graft polymerization method which involves acrylonitrile (CH_2=CH-CN) grafting onto polyethylene fabrics and chemical conversion of the -CN groups with hydroxylamine to the amidoxime groups. This type of sorbents show good mechanical strength and high capacity for uranium sorption from seawater. If this uranium sequestering technology could be made economically favorable and environmentally sustainable, our ocean would provide virtually an inexhaustible source of uranium for nuclear power production. The amidoxime groups formed in the polymer sorbent by the synthesis method described above may exist in two different structures as illustrated in Fig. 1. Both the cyclic imide dioxime and the open-chain diamidoxime on the sorbent can form strong complexes with uranium.[7, 8] Tian et al. recently reported that the open-chain diamidoxime is a weaker competing ligand than the cyclic imide dioxime for complexation with U(VI) under the seawater conditions.[8] The uranium sequestering process may be illustrated by the following reaction

$$[UO_2(CO_3)_3]^{4-} + 2H_2A \rightarrow UO_2(HA)A^- + 3HCO_3^- \qquad (1)$$

where H_2A represents either glutarimidedioxime or glutardiamidoxime shown in Fig. 1.

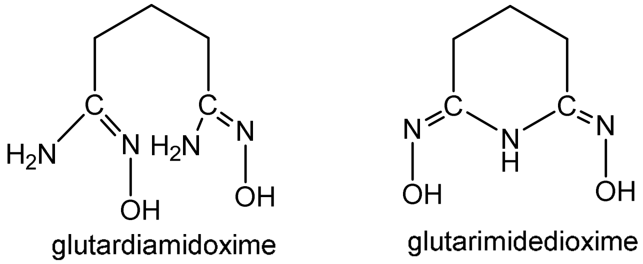


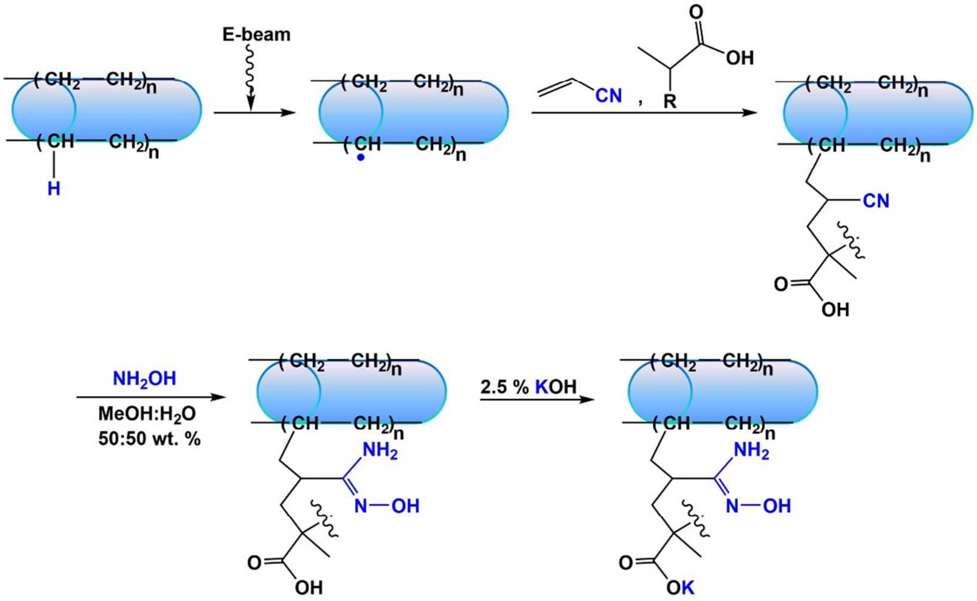
Fig. 1. Structures of open chain diamidoxime (left) and cyclic imide dioxime (right).

Uranium collected by the amidoxime-based sorbents is recovered typically by elution with an acid such as 1.0 M hydrochloric acid (HCl). After the acid elution, the sorbent requires a KOH reconditioning process, which involves heating the sorbent in 2.5% KOH solution at 80°C for 3 hours, to regenerate the active functional groups for reuse.[9, 10] A serious drawback of the acid elution process is deterioration of the sorbent caused by acid hydrolysis making its reusability rather limited. Sorbent durability appears to be an important factor determining economic competitiveness of the current amidoxime-based sorbent collection system for sequestering uranium from seawater.[2, 4] This paper describes a new desorption method utilizing a mixture of sodium carbonate and hydrogen peroxide as eluent for recovering uranium from amidoxime-based polymer sorbent. The high efficiency of this elution process is attributed to the formation of an extremely stable uranyl-peroxo-carbonato complex. The carbonate-peroxide desorption process creates little damage to the sorbent and requires only water rinse to regenerate the sorbent for its reuse. This new elution method may provide a simple and benign process for recycling the sorbent for sequestering uranium from seawater. Because hydrogen peroxide is known to exist in ocean water surface, the possibility of formation of uranyl-peroxo-carbonato complex in seawater is also discussed.

Experimental Section

Preparation of amidoxime-based polyethylene fiber

The amidoxime-based polyethylene adsorbent fibers were prepared by the radiation-induced graft polymerization method[11] as illustrated in scheme 1, which involves four processing steps: electron beam irradiation of polyethylene fibers; co-grafting polymerizable monomers containing nitrile groups and hydrophilic groups to form grafted side chains throughout the fiber; conversion of nitrile groups to amidoxime groups; and alkaline conditioning of the grafted fibers.



Scheme 1. Reaction scheme for preparation of amidoxime-based polyethylene fibers.

1. Irradiation of polyethylene fibers

Prior to irradiation, the polyethylene fibers were placed inside a plastic bag and sealed under nitrogen. The bag was then put inside an insulated container and placed on top of dry ice and irradiated to a dose of 200 kGy using 4.9 MeV electrons and 1 mA current from an electron beam machine.

2. Grafting of polymerizable monomers containing nitrile groups and hydrophilic groups

After irradiation, the fibers were immersed in a flask containing a previously de-gassed solution of acrylonitrile and methacrylic acid in dimethylsulfoxide and placed in an oven at 65 °C for about 18 hours. After the grafting reaction was complete, the fibers were drained from the solution and washed with dimethylformamide (DMF) to remove any monomers or co-polymer by-products.

The fibers were then washed with methanol to remove the DMF and dried at 50 °C under vacuum for 72 hours.

3. Conversion of nitrile groups to amidoxime groups

The irradiated and grafted polyethylene fibers were placed in a flask containing 10% hydroxylamine hydrochloride in 50/50 (w/w) water/methanol at 80 °C for 72 hours. The fibers were then washed with deionized water followed by a methanol rinse and allowed to dry at 50 °C under vacuum for 72 hours.

4. Alkaline conditioning of grafted fibers

After the amidoximation reaction the polyethylene fibers were added to a flask containing 2.5 % KOH and heated for 3 hours at 80 °C then washed with deionized water until the pH was neutral.

Adsorption of uranium in simulated seawater

Uranium sorption was performed using simulated seawater spiked with 9 ppm of uranium. The simulated seawater contained Na^+ (10,118 ppm), Cl^- (15,573 ppm), and HCO_3^- (140 ppm) at pH=8.0. The uranium sorption experiment was conducted with 20 mg of the amidoxime-based polyethylene fiber suspended in 400 mL of the simulated seawater with stirring for 24 hours. At the end of this period, sorption of uranium was found to reach equilibrium. The evolution plot of the sorption of uranium from simulated seawater is given in the Supporting Information (Fig 1S).

Uranium in the simulated seawater was analyzed by a spectrophotometric method using Arsenazo III as a complexing agent and the absorbance of the uranyl-arsenazo complex was monitored at 653 nm with a UV-Vis spectrometer.[12, 13] The UV-Vis spectra of the urany-arsenazo complex are shown in the Supporting Information (Fig 2S, left). According to the literature[13], Arsenazo III reacts with uranium (VI) in acidic media to give a uranyl-arsenazo complex (green-blue complex, $\lambda_{max} = 653$ nm) which is very sensitive for determination of U (limit of detection ~ 0.50 μg/L.). The pH value of the solution for spectrophotometric determination of uranium utilizing Arsenazo III was adjusted to one in this study. Under this acidic condition (pH = 1), either $UO_2(CO_3)_3^{4-}$ or $UO_2(O_2)(CO_3)_2^{4-}$ should be converted to $UO_2(H_2O)_5^{2+}$. The linear regression equation for uranium in the concentration range 0–5.38 ppm was Abs = 0.19265 X ($R^2 = 0.99966$, n = 7) where X is the uranium concentration in ppm (Supporting Information, Fig 2S, right). The capacity of uranium adsorption on the sorbent under our experimental conditions was about 6 wt %.

Elution with carbonate or carbonate–H_2O_2 solution

Elution of uranium from the fiber was performed with the uranium loaded fiber immersed in 10 mL of a sodium carbonate solution with or without hydrogen peroxide at room temperature (21 °C) with stirring for one hour. Uranium in the leaching solution at appropriate time intervals was measured during the elution process using the same Arsenazo spectrophotometric method. After the elution, uranium remaining in the sorbent was checked by washing the fiber in concentrated HCl followed by analyzing the acid solution. For repeated sorption experiments, the sorbent after the elution was rinsed with de-ionized water several times and then filtered and dried in a chemical fume hood at room temperature. No other treatment is needed for reusing the sorbent.

Results and Discussion

Using sodium carbonate (Na_2CO_3) solution for leaching uranium from amidoxime-based sorbent has been reported previously. Das et al.[14] showed that uranium could be recovered over 95% from amidoxime-based membranes by leaching with sodium carbonate at room temperature. A report by Rivas et al.[15] showed that only 67% recovery of uranium from an amidoxime-based sorbent could be achieved and the elution efficiency did not change significantly in the carbonate concentration range 0.5 to 2 M. According to the literature, the solubility of sodium carbonate in water is about 2.59 M at 25 ^{o}C.[16] We have recently re-examined the carbonate leaching of uranium from amidoxime-based polymer fiber fabricated at the Oak Ridge National Lab. Our carbonate leaching results agree with those reported by Rivas et al. A significant observation in our elution study is that when a small amount of hydrogen peroxide is added to sodium carbonate, the efficiency of uranium elution from the amidoxime-based sorbent is significantly improved to near 100%. The sorbent can be reused after rinse with water without other treatment. The recycled sorbent exhibits a minimal loss (about 3%) of uranium loading capacity per sorption-desorption cycle which is significantly lower than the conventional acid elution process known in the literature.

The results of our sodium carbonate and hydrogen peroxide elution of uranium from the amidoxime-based sorbent are given in Fig. 2. Using 1 M sodium carbonate, elution of uranium from the sorbent at room temperature (21 ^{o}C) reaches a near constant value around 77% after one hour. Hydrogen peroxide alone (1 M) is not effective for eluting uranium from the sorbent. When a small amount of hydrogen peroxide is added to 1 M sodium carbonate, there is a significant increase in the efficiency of uranium elution. Even with 0.01 M of H_2O_2 in 1 M sodium carbonate, the uranium elution efficiency is increased from 77% to over 90%. The elution of uranium from the sorbent by 1 M sodium carbonate with 0.1 M of H_2O_2 is near quantitative (Fig. 2).

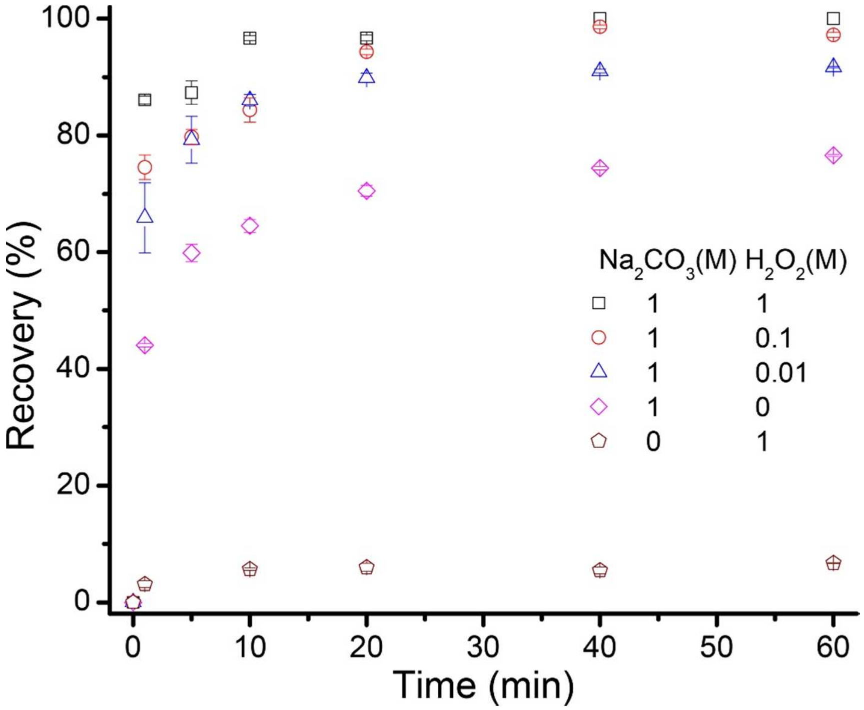


Fig. 2. Rates of uranium elution from the sorbent with sodium carbonate and hydrogen peroxide solutions

The carbonate elution of uranium from the amidoxime-based sorbent with 1 M Na_2CO_3 (pH ~ 11.0) may be expressed by the following equation:

$$UO_2A_2^{2-} + 3CO_3^{2-} \rightarrow [UO_2(CO_3)_3]^{4-} + 2A^{2-} \qquad (2)$$

At a high carbonate concentration the equilibrium of equation (2) tends to shift to the right favoring formation of the uranyl tris-carbonato species. The synergistic elution of uranium by hydrogen peroxide and sodium carbonate may be attributed to the formation of an extremely stable uranyl-peroxo-carbonato complex as illustrated by equation (3).

$$UO_2A_2^{2-} + 3CO_3^{2-} + H_2O_2 \rightarrow [UO_2(O_2)(CO_3)_2]^{4-} + 2A^{2-} + HCO_3^{-} + H^{+} \qquad (3)$$

Fig. 3. Structures of $UO_2(CO_3)_3^{4-}$ and $UO_2(O_2)(CO_3)_2^{4-}$. (The structure of $UO_2(CO_3)_3^{4-}$ is from reference 17;[17] the structure of $UO_2(O_2)(CO_3)_2^{4-}$ is built by crystallographic data from reference 18 using molecular modeling software, Spartan.)

A recent report by Goff et al. shows that the uranyl-peroxo-carbonato complex is thermodynamically much more stable than the uranyl tri-carbonate complex.[18] The apparent formation constant of $[UO_2(O_2)(CO_3)_2]^{4-}$ from $[UO_2(CO_3)_3]^{4-}$ according to the following equation

$$[UO_2(CO_3)_3]^{4-} + HO_2^- \rightarrow [UO_2(O_2)(CO_3)_2]^{4-} + HCO_3^-$$

is about 5×10^4.[18] Therefore even with the addition of 0.01–0.1 M hydrogen peroxide, the efficiency of carbonate elution of uranium from the sorbent can be significantly improved. Under the experimental conditions used by Goff et al.[18] and by us, only monoperoxo uranyl complex, $UO_2(O_2)(CO_3)_2^{4-}$, should be formed in the solution according to the DFT calculations reported by Odoh and Schreckenbach.[19] The DFT calculations also indicate that the reaction energies are -59.8 and 6.3 kcal/mol for $UO_2(O_2)(CO_3)_2^{4-}$ and $UO_2(O_2)_2(CO_3)^{4-}$, respectively, which suggests that the diperoxo uranyl complex, $UO_2(O_2)_2(CO_3)^{4-}$ should not be formed in the solution. In fact, Grenthe et al. reported that no diperoxo uranyl complex, $UO_2(O_2)_2(CO_3)^{4-}$, was found even at a high concentration of H_2O_2.[20]

The reusability of the amidoxime-based polymer sorbent after the sodium carbonate-hydrogen peroxide elution of uranium is illustrated in Fig. 4. Reduction of uranium loading capacity of the recycled sorbent depends on the concentration of the hydrogen peroxide used in the carbonate-peroxide elution process. For uranium elution with 0.1 M H_2O_2 in 1 M Na_2CO_3, the decrease in loading capacity was about 3% for each cycle after 3 consecutive cycles. Elution with 1 M H_2O_2 and 1 M Na_2CO_3 resulted in about 10% decrease in uranium loading capacity after each sorption-desorption cycle. We also tested uranium elution from the sorbent with hydrochloric acid. Using 0.5 M hydrochloric acid, elution of uranium from the sorbent at room temperature (21 ^{o}C) reaches a near constant value around 94% after 20 minutes. The rate of uranium elution from the sorbent with 0.5 M HCl is given in the Supporting Information (Fig 3S). The sorbent was regenerated in 2.5% KOH at 80 ^{o}C for 3 hours followed by rinsing with water and drying. The recycled sorbent after the acid elution showed a reduction in uranium sorption capacity by about 20% per cycle based on our experiments (Fig. 4).

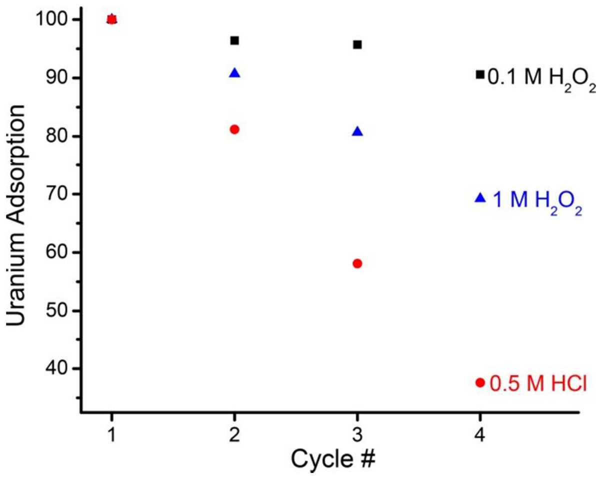


Fig. 4. Uranium loading capacity of the amidoxime-based polymer sorbent after each cycle of sodium carbonate-H_2O_2 and 0.5 M HCl leaching. (Note: For 0.5 M HCl leaching, the sorbent required a KOH reconditioning process after each cycle according to the literature.[9, 10])

The oxime group –C=N–OH on the amidoxime-based fiber is suggested to form a chelate complex with UO_2^{2+} via the η^2 binding with N–O bond (open-chain)[21] or by the two oxime oxygen atom and the imide nitrogen atom of the delocalized –O–N=C–N–C=N–O− group (the cyclic form)[7]. The oxime group containing carbon–nitrogen double bonds (C=N–OH) may be cleaved by oxidation, reduction, or acid hydrolysis to the corresponding carbonyl group (C=O) which would not complex with UO_2^{2+} in seawater.**[22, 23]** The oxidation power of hydrogen peroxide at high concentrations could cause cleavage of the C=N bond.[24] At low concentrations, hydrogen peroxide apparently causes little damage to the oxime group allowing formation of the stable uranyl-peroxo-carbonato complex and leading to enhanced elution of uranium from the sorbent. Lin and co-workers recently reported that maximizing electron density at the binding site of amidoxime-based ligands through resonance of conjugated π orbitals of electron donating groups (e.g. imidazole–oximate) can improve binding strength for uranyl and stability of ligands.[25] On the basis of this concept, future development of amidoxime-based sorbents with conjugated π orbitals of electron donating groups may lead to new sorbent materials with improved stabilities under carbonate-H_2O_2 leaching conditions.

The feasibility of forming stable uranyl-peroxo-carbonato complex in carbonate solutions raises a question about the possibility of formation of this uranium complex in natural seawater because hydrogen peroxide is known to exist in ocean surface. The concentrations of hydrogen peroxide in open ocean surface may vary from several nM to several hundred nM depending on season and time.[26-30] Hydrogen peroxide probably exists in seawater as one of final products of free radical chemistry in the photochemical decomposition processes of dissolved organic matter. Another hypothesis is that a photochemically-initiated formation mechanism may be involved which was used to explain seasonal variation of H_2O_2 concentrations in open ocean sea surface.[27] We have examined the possibility of formation of uranyl-peroxo-carbonato based on the available thermodynamic data of the following equations:

$$UO_2^{2+} + H_2O_{2(aq)} + 2CO_3^{2-} \rightarrow UO_2(O_2)(CO_3)_2^{4-} + 2H^+ \qquad (4)$$

$$UO_2(CO_3)_3^{4-} \rightarrow UO_2^{2+} + 3CO_3^{2-} \qquad (5)$$

$$UO_2(CO_3)_3^{4-} + H_2O_{2(aq)} \rightarrow UO_2(O_2)(CO_3)_2^{4-} + 2H^+ + CO_3^{2-} \qquad (6)$$

According to the literature[20, 31], the equilibrium constants of reactions (4) and (5) are $10^{4.03}$ and $10^{-21.8}$, respectively. Combination of reactions (4) and (5) results in reaction (6), the most probable dominanting reaction that represents the formation of the $UO_2(O_2)(CO_3)_2^{4-}$ species under seawater conditions. The equilibrium constant K of reaction (6) is calculated to be $10^{-17.8}$.

$$K = \frac{[UO_2(O2)(CO_3)_2^{4-}]\,[H^+]^2\,[CO_3^{2-}]}{[UO_2(CO_3)_3^{-4}]\,[H_2O_2]}$$

The ratio of $[UO_2(O_2)(CO_3)_2]^{4-}/[UO_2(CO_3)_3]^{4-}$ is determined by equation (7) with the given concentrations of H^+, H_2O_2, CO_3^{2-} and the equilibrium constant of reaction (6),

$$\log\left(\frac{[UO_2(O_2)(CO_3)_2^{4-}]}{[UO_2(CO_3)_3^{4-}]}\right) = -17.8 + \log[H_2O_2] - 2\log[H^+] - \log[CO_3^{2-}] \qquad (7)$$

Using $K=10^{-17.8}$, $[H_2O_2]= 4\times10^{-7}$ M, pH=8.1, $[CO_3^-]=2.4\times10^{-4}$ M[32], and a total uranium of 3.3 ppb, the $[UO_2(O_2)(CO_3)_2]^{4-}/[UO_2(CO_3)_3]^{4-}$ ratio in ocean water should be about 4.2×10^{-5} even as the concentration of H_2O_2 is near the maximum found in seawater ($[H_2O_2]$= 400 nM). According to this simple ideal solution calculation, there could be a trace amount of uranyl-peroxo-carbonato complex present in ocean water with high concentrations of H_2O_2. In real ocean water, the situation may be complicated because the mechanisms of hydrogen peroxide formation are not totally understood yet. It should be noted that there is no report in the literature regarding the existence of the uranyl-peroxo-carbonato complex in ocean water. The very low concentrations of this stable uranyl-peroxo-carbonato complex in ocean water according to our estimate should not affect the sequestering of uranium from seawater using amidoxime-based sorbents.

Conclusion

In summary, the sodium carbonate–H_2O_2 elution process described in this paper offers an efficient new method of recovering uranium from amidoxime-based polymer sorbents for sequestering uranium from seawater. The synergistic effect is attributed to the formation of an extremely stable uranyl-peroxo-carbonato complex known in the literature. The efficiency of uranium elution offered by the carbonate–H_2O_2 method is comparable to that of the hydrochloric acid elution but damage to the sorbent material is much less for the former. The carbonate-H_2O_2 elution also does not require any elaborate step to recycle the sorbent. Rinsing with water is sufficient to regenerate the sorbent for reuse. The acid elution method requires boiling of the leached polymer sorbent in a KOH solution for several hours to regenerate the active functional groups for reuse. The carbonate–H_2O_2 elution appears to offer a new approach for sequestering uranium from seawater by simplifying recycling procedure and improving durability of the sorbents. Our thermodynamic calculation indicates that formation of uranyl-peroxo-carbonato complex in ocean water is possible but its concentration is very low even at high concentration of hydrogen peroxide. Its effect on sequestering uranium from seawater using amidoxime-based sorbents appears negligible.

Acknowledgement

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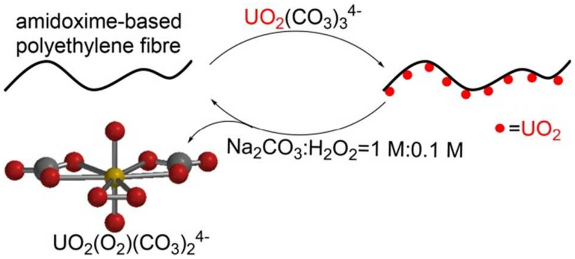

Uranium adsorbed on amidoxime (AO)-based polyethylene fiber in simulated seawater can be quantitatively eluted at room temperature using 1M Na_2CO_3 containing 0.1 M H_2O_2 without significant damage to fiber.