A Preliminary Study for Development of Amidoxime-functionalized Silica Adsorbents for Uranium(IV) Extraction from Seawater

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1. Introduction

4 billion tons of uranium, which can supply the electricity for tens of thousands of years, is contained in seawater [1]. Therefore, development of techniques for uranium sequestering from the ocean has been regarded as a great challenging for making nuclear energy to be more economical and sustainable. Despite the inexhaustible uranium resource, it is still hard to produce uranium economically from seawater due to its extremely low level of concentration (3.0 μg/L) and stable complex chemical formation, $UO_2(CO_3)_3^{4-}$ [2].

Various methods for uranium extraction from seawater have been suggested such as precipitation, solvent extraction, ion exchange, adsorption and etc. The most preferred method for extracting uranium is adsorption due to ease of separation from the liquid phase, environment friendliness and cost-effectiveness [2]. Organic or inorganic solids functionalized with amidoxime (AO, $-R-C(NH_2)=NOH$) groups, which has high affinity to uranium species, is the one of candidate material for uranium adsorbents [3]. In 1990's, Japanese scientists had first performed uranium extraction in real seawater using the braid type fibers polymerized with AO functional group, and it showed 1.5 mg/g of uranium loading in 30 days [4]. However, traditional adsorbents still showed poor capacity and kinetics because of the small specific surface area and poorly developed porous structure.

Recently, nanomaterials are the most interesting part of modern chemistry due to its high specific surface area, so they can maximize some kinds of physicochemical properties such as catalysis or adsorption. There also has been lots of trials to develop nanomaterial-based adsorbents for uranium extraction from seawater since around 2010, and high uranium loading capacity and fast adsorption compared to the past research (Table1) have been achieved. [5-11]. Although nanomaterials have enhanced uranium loading capacity by having a large number of AO functional groups on its surface, instinct limitations in chemical properties of uranyl ions and AO functional groups still remain. The presence of carbonate ions, CO_3^{2-} is significantly lower the uranium adsorption kinetics due to the complexation with uranyl ions [12], and the uranium sorption ability of AO group is highly dependent on pH due to the change of charge states [13]. In this study, the strategies which can overcome the problems will be suggested based on the adsorption mechanism, and advanced adsorbent type for improving uranium uptake will be designed.

Table 1. Current research status of uranium adsorbents

Adsorbents Type	Uranium uptake capacity*(mg/g)*
Nanoporous zirconia [5]	3.3
Nanoporous alumina [6]	11
AO-mesoporous carbon [7]	80
AO-mesoporous silica [8]	57
AO-grapheneoxide hydrogel [9]	28
AO-graphene oxide/ magnetic nanoparticle [10]	284.9
AO-graphene nanoribbon [11]	502.6

2. Theoretical Background

2.1. Adsorption mechanism AO-based adsorbents

The mechanism of adsorption on AO-based adsorbents can be summarized in three steps [13]. 1) Diffusion of $UO_2(CO_3)_3^{4-}$ from aqueous solution to the surface of the adsorbent, 2) diffusion of $UO_2(CO_3)_3^{4-}$ from the surface of the adsorbents to the binding sites through pores, and 3) chemical reaction between $UO_2(CO_3)_3^{4-}$ and AO. Among them, it has been observed that the chemical reaction process which is the substitution process from carbonate ions to AO chelating group as shown in below (eq.1) is considered the rate-determining step according to experiments [13] and DFT calculation [14].

$$UO_2(CO_3)_3^{4-} + 2HAO \rightarrow UO_2(AO)_2 + 3CO_3^{2-} + 2H^+ \text{ (eq.1)}$$
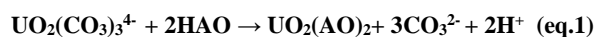
2.2. Effect of pH on sorption efficiency

Acid has both positive and negative effects on uranium adsorption ability of adsorbents [13]: Positive) H^+

promotes the dissociation of carbonate ions from the uranyl ions, and then AO chelating group can access to the center uranium atom, easily. Negative) H^+ competes with uranyl ions on the binding sites of AO chelating group, so it interrupts the formation of the uranyl-AO complex. Therefore, most of the AO-based adsorbents showed the maximum capacity at optimized pH in the range of 4~6. However, the pH of real seawater is around 8.

2.3. Co-grafting acidic group with AO group

 The co-grafted acidic group such as carboxylic group (-COOH) with the AO-based polymers is one of the methods for improving uranium adsorption capacity [15-16]. Especially, Choi et al prepared the fiber copolymerized AO group with carboxylic acid and showed the maximum uranium adsorption capacity when the ratio of carboxylic acid and AO group is 50/50 mol% [17]. These achievements were attributed to the acidic sites of the hydrophilic group which promote decomplexation of $UO_2(CO_3)_3^{4-}$, increase hydrophilicity, and donate the additional binding sites [14-16].

3. Adsorbent design

3.1. Support material selection: Mesoporous silica

  Mesoporous silica is one of the most promising material as adsorbents due to its high specific area (400~1500 m^2/g) and highly ordered pore structures [17]. High specific area indicates the potential to donate space for a large number of functional groups, and ordered pore structure has many advantages for transferring molecules and good accessibility to active sites. Furthermore, silica is chemically inert so that its structure does not change during the performance such as highly acidic elution process for uranium production.

3.2. Co-grafting AO group with the acidic group.

  It was developed AO-functionalized mesoporous silica based uranium adsorbents [8]. Based on previous studies [15-17], it is expected high potential to improve the adsorption efficiency by co-grafting with other acidic groups. Carboxylic group is one of the promising candidates for the acidic group because both AO group and the carboxylic group can be functionalized on mesoporous silica derived from the same functional group, cyanopropyl (- C_3H_8CN) [8, 18]. Also, new types of acidic groups used for the acid-catalytic reaction, so-called solid acids, such as tin hydroxide (-$Sn(OH)_2$) [19] which has both Bronsted and Lewis acid sites would be a critical part of the study.
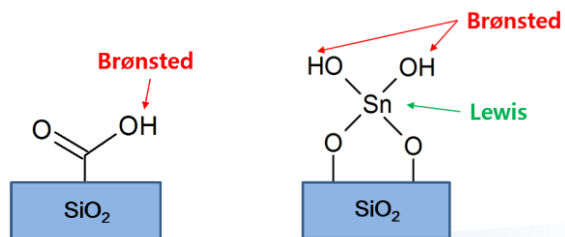

Fig. 1. Carboxylic acid (left) and Sn-based solid (acid)

4. Conclusions

For long-term nuclear power generation, developing uranium extraction technologies from seawater has been a crucial issue. AO-based adsorbent has been considered as the most effective methods for uranium extraction from seawater, and collaboration with nanotechnology has been tried to enhance the traditional adsorbents, recently. Despite the attempts, most AO-based adsorbents were suffered from complexation of uranyl ions with carbonate ions and under the effect of pH. To achieve more efficient uranium uptake, bi-functionalized mesoporous silica with AO group and acidic groups was chosen as a model for this study. In the future, a detailed synthesis method of the adsorbents and establishing an advanced model for uranium adsorption behavior will be necessary.

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