

Adsorption of an Uranyl Carbonate Complex onto an Amidoxime Resin

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1. Introduction

Uranium is a major element in the management of spent nuclear fuel or radioactive waste. Uranium is also present in sea water at a trace level (~3ppb)[1]. Usually, an acid medium in a solvent extraction or ion exchange system have been used for the separation of uranium from a radioactive waste solution. Especially, some adsorbents containing amidoxime functional groups selective for the uranyl ion have been developed for the recovery of uranium in sea water [1,2,3,4]. An amidoxime resin as an anion exchanger synthesized using divinylbenzene copolymer as a supporting material was applied for the separation of uranium and plutonium from simulated fission products in carbonate solution [5] by making an uranyltricarboxylate complex, $UO_2(CO_3)_3^{4-}$, in an alkaline solution of a carbonate (pH>8) [6]. A carbonate leaching of uranium from uranium contaminated soils was also successfully performed using a sodium carbonate and a sodium bicarbonate solution[7].

In this work, the distribution coefficients of uranyl ions were measured for the amidoxime resins with a variation of carbonate concentration and the pH of the solutions as a preliminary work for a spent fuel treatment with a strong alkaline carbonate solution because this system has an advantage to reduce a high level waste volume by a selective oxidation and an adsorption of uranium from spent fuels.

2. Experimental

Two different types of amidoxime resins were used. One is a polypropylene grafted with acrylonitrile-methacrylate (7/3)(resin-1). Another is acrylonitrile-divinylbenzene(5/5) copolymer containing amidoxime group. The latter was classified into three different types according to the bead sizes made by the different polymerization processes: fine powder(resin-2), middle size(resin-3) and coarse grain(resin-4).

Sodium carbonate solution was prepared by estimating the concentration of the carbonate using the equation[8] related to the dissociation constants of carbonic acid, partial pressure of carbon dioxide in air and so on.

U stock solution(2.1145 mg U/mL) was prepared by a dissolution of $UNH[UO_2(NO_3)_2 \cdot 6H_2O]$ in 0.072M Na_2CO_3 solution. The distribution coefficients of uranyl ions were measured by a batch method as follows;

Take 50 mL of Na_2CO_3 solution and add 2.5 mL of U stock solution(pH 11.34). Weigh the resin-1(0.3742 g) and put it into the solution(pH 10.35). Total volume was 52.5 mL and the initial U concentration was 100.7 μ g/mL. Control the temperature(30 C) in the shaking

oven(120 rpm). Take 1 mL of sample solution every two hours for 8 hrs as a sampling time and dilute it by 10 times. Measured U concentration by ICP-AES.

For the divinylbenzene resin, the distribution coefficients were measured for three different conditions. That is, 0.0044 M Na_2CO_3 (pH 10.9), 0.072 M Na_2CO_3 (pH11.36) for resin-1, 2, 3, and 0.5 M Na_2CO_3 - $NaHCO_3$ (pH9, 10, 11) for resin-2 only. The resin weights were about 0.75 ~ 1.6 g. The initial concentrations of U were 35 ~ 41 μ g/mL. Other conditions were the same as in the propylene resin(resin-1).

3. Results and discussion

3.1 Measurement of Distribution Coefficients(Kd)

The distribution coefficients(Kd) of the uranyl ions onto amidoxime resins were measured and shown in Fig. 1. As shown in Fig 1, the ion exchange reaction reached an equilibrium within about 2 hr. The distribution coefficients in the propylene resin(1) were about 75. In the case of the divinylbenzene resin(2,3,4), the Kd values increased as the resin bead size decreased and the maximum Kd value was about 65. However, these Kd values for both resins were much lower than those reported in other works(Kd ~130). This lower Kd value seems to be due to the lower capacity of the resin tested in this work. In a higher concentration of the carbonate(0.072M, pH 11.36), the distribution coefficients were much lower(<10) for the three types of resins(resin-2,3,4) even though resin-2 showed the highest value among the three. This seems to be due to the formation of the uranyltricarboxylate complex which would be hindered by hydroxide in a high pH(>11). In the 0.5 M Na_2CO_3 - $NaHCO_3$ solution, the distribution coefficients were also much lower(~10) and the Kd's slightly increased as the pH increased. This means that the adsorption behavior in the carbonate medium containing an additional bicarbonate showed a different phenomenon from that in carbonate only. However, the exact reason is not identified.

3.2 Speciation of Uranyltricarboxylate Complex

Uranyl ion is presented as an uranyltricarboxylate complex only in a carbonate solution over pH 9 and this complex shows four absorption peaks between 400 nm and 500 nm[6]. In this work, the UV-Vis spectra of the uranyl ions were measured for different carbonate solutions

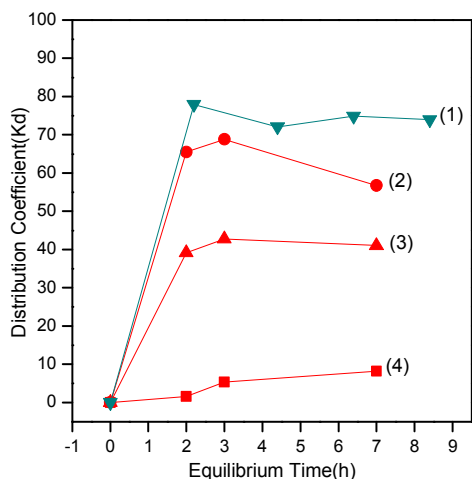


Fig. 1. Distribution coefficients of UO_2^{2+} onto midoxime resin in Na_2CO_3 solution. (1) : PP+(AN/Mac =7/3) 0.3742 g, 0.072 M Na_2CO_3 50 mL(pH 10.5), U 5.3 mg, (2) : AN/DVB=50/50(resin-102) 1.6 g. 0.0044 M Na_2CO_3 25mL(pH 10.9), U 1.06 mg, (3) : AN/DVB =50/50(resin-103) 1.0g, other condition; same as in (2), (4) AN/DVB=50/50 (resin-103) 1.0g, other condition; same as in (2),Temp 30 C, Shaking 120 rpm

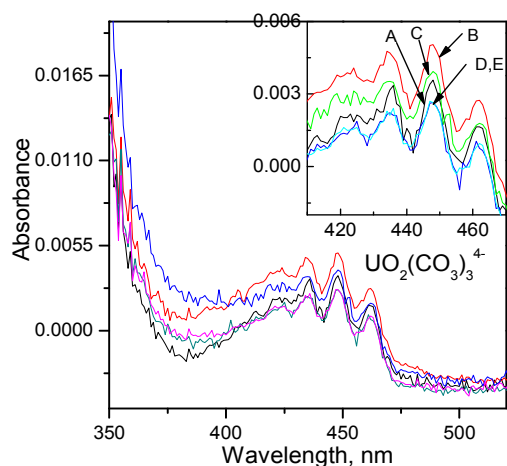


Fig. 2. UV-Vis spectrum of uranyl carbonate complexes. U: 0.2586 mM, A; 0.0044 M Na_2CO_3 (pH 10.9), B; 0.072 M Na_2CO_3 (pH11.36), C; 0.5 M Na_2CO_3 - $NaHCO_3$ (pH9.01), D; 0.5 M Na_2CO_3 - $NaHCO_3$ (pH10.00), E; 0.5 M Na_2CO_3 - $NaHCO_3$ (pH 10.99)

Fig. 2 shows the UV-Vis spectra measured for the carbonate solutions such as 0.0044 M Na_2CO_3 (pH 10.9), 0.072 M Na_2CO_3 (pH 11.36), 0.5 M Na_2CO_3 - $NaHCO_3$ (pH 9, 10 and 11), respectively. As shown in Fig. 2, four absorption peaks were clearly resolved. This confirms that the uranyltricarboxylate complexes were formed. However, the peak heights in the pure carbonate solutions were higher than those in the carbonate-bicarbonate solutions. This means that the uranyltri-carboxylate complex is more easily formed in the Na_2CO_3 solution when compared to the Na_2CO_3 - $NaHCO_3$ solution.

4. Conclusion

The distribution measured coefficients of uranyl ions onto an amidoxime resin in this work showed lower values when compared to other works. This seems to be due to the lower capacities of the resins. This work will be continued for another resin to be synthesized.

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