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ARTICLE

Development of Fluorinated Ligands for Uranium Recovery from Radioactive Liquid Waste

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Radioactive liquid waste containing nuclear fuel materials and chemical reagents is being stored at Japan Atomic Energy Agency (JAEA) while a treatment method is being established. This waste includes uranyl nitrate solutions and organic solvents contaminated with uranium, which were generated during engineering-scale solvent extraction tests at the Engineering Demonstration Facility-1 (EDF-1) of JAEA. For removing nuclear fuel materials from the radioactive liquid waste to reduce the radioactivity of the waste, we developed RFIDA, a new perfluoroalkyl (RF)-based ligand with a basic structure of iminodiacetic acid (IDA). This study involved conducting an adsorption test by impregnating RFIDA into porous silica with a polymer to confirm that the synthesized RFIDA adsorbs uranium. The distribution coefficient (K_d) of the RFIDA adsorbents in uranyl nitrate solution ranged from approximately 1 to 3. The results confirmed that RFIDA exhibits the ability to adsorb or elute uranium depending on the nitric acid concentration.

KEYWORDS: fluorous compound, iminodiacetic acid, RFIDA, radioactive liquid waste, STRAD project

I. Introduction

Nuclear facilities store radioactive liquid waste containing nuclear fuel materials and chemical reagents. The Japan Atomic Energy Agency (JAEA), in collaboration with several organizations, launched the Systematic Treatment of Radioactive Liquid Wastes for Decommissioning (STRAD) project to develop appropriate treatment procedures for such radioactive liquid waste.[1,2)] **Figure 1** shows an overview of the process flow of the radioactive liquid waste treatment. Radioactive aqueous and organic liquid wastes, containing radioactive materials, are generated through solvent extraction experiments involving nuclear fuel materials. Nuclear fuel materials recovered from radioactive waste can be safely stored through stabilization processes such as conversion into oxides. Furthermore, the radioactive liquid waste after the removal of nuclear fuel materials can be safely stored by implementing stabilization processes such as mineralization, if it contains organic solvents or organic compounds, followed by solidification. In the Chemical Processing Facility (CPF) of JAEA, the treatment of organic solvents and analytical waste liquids containing nuclear fuel materials were a challenge, albeit in relatively small volumes of the radioactive liquid waste.[1,2)] Furthermore, engineering-scale solvent extraction tests using nuclear fuel materials were performed at the Engineering Demonstration Facility-1 (EDF-1) of JAEA.[3)] As a consequence of these tests, uranyl nitrate solution and uranium-containing extraction solvent at a 1000 L scale are storing in EDF-1. Although incineration and denitrification/conversion processes are promising for the treatment of such liquid wastes, they require the installation of large-scale equipment. Treatment of liquid wastes generated from the reprocessing experiments is one of the key objectives of this project, and technologies for recovering nuclear materials from aqueous and spent solvents have been developed.[4-10)] Based on these studies, the spent solvent accumulated in the CPF was effectively treated.[11)] However, the recovery of trace amounts of nuclear fuel materials from aqueous solutions across a wide pH range remains a challenging task. In our previous study, porous silica particles with a high specific surface area and bearing the iminodiacetic acid (IDA) functional group were shown to be capable of recovering cations.[7)] Although the IDA group was introduced into adsorbents that exhibited an excellent adsorption reaction from the aqueous solution, further improvements in chemical resistance and adsorption amount are essential for their application in radioactive liquid treatment. Hence, we focused on fluorous compounds, which are difficult to mix with both water and oil phases and exhibit excellent chemical resistance, and developed a new perfluoroalkyl (RF)-based ligand incorporating the basic structure of IDA. The developed ligand is termed RFIDA. In our related work, the metal ion adsorption performance and adsorption behavior of RFIDA were investigated.[12,13)] In addition, the IBIL, PIXE and EXAFS analyses revealed that RFIDA adsorbed cations in nitric acid solutions and that it adsorbs Eu by adsorption onto

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solid adsorbents.

Based on these results, adsorption studies of UO_2^{2+} from uranyl nitrate solution by RFIDA were conducted. To understand the adsorption performance of UO_2^{2+} ions, adsorption-elution tests were performed by impregnating RFIDA into porous silica with a polymer (SiO_2–P). Two RFIDA molecules with different structures, RFIDA-1 and RFIDA-2, are shown in **Fig. 2**.

In this study, to investigate the adsorption performance of the synthesized adsorbents toward nitric uranyl solutions, adsorption-elution tests were performed. The performance of the newly synthesized adsorbents was evaluated by measuring the uranium concentration in the process solutions before and after the experiments, as well as by measuring the material balance.

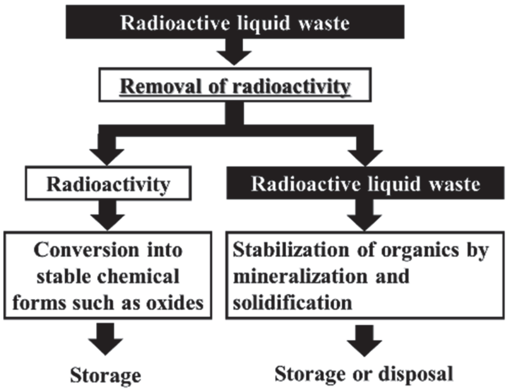
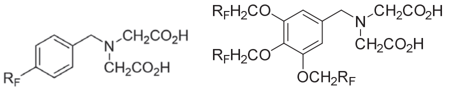


Fig. 1 Overview of the process flow of radioactive liquid waste treatment



RFIDA-1 RFIDA-2

R_F: n-C_6F_{13}

Fig. 2 Structures of RFIDA-1 and RFIDA-2

II. Experimental

1. Preparation of Adsorbent

Two RFIDA molecules with different structures, RFIDA-1 and RFIDA-2, were synthesized based on the previous study.[12,13] An adsorbent RFIDA/SiO_2–P was prepared by impregnating 1 g of RFIDA-1 or RFIDA-2 into 4 g of styrene–divinylbenzene copolymer coating around porous silica particles (referred to as SiO_2–P). The content of REFID-1 and REFID-2 per gram of solid adsorbent is 0.4 mmol/g-SiO_2-P and 0.2 mmol/g-SiO_2-P, respectively. An overview of the RFIDA/SiO_2–P adsorbents is shown in **Fig. 3**, and the preparation procedure of the adsorbent is shown in **Fig. 4**.

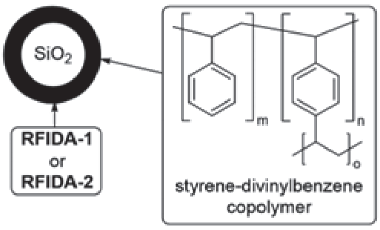


Fig. 3 Overview of RFIDA/SiO_2–P adsorbent

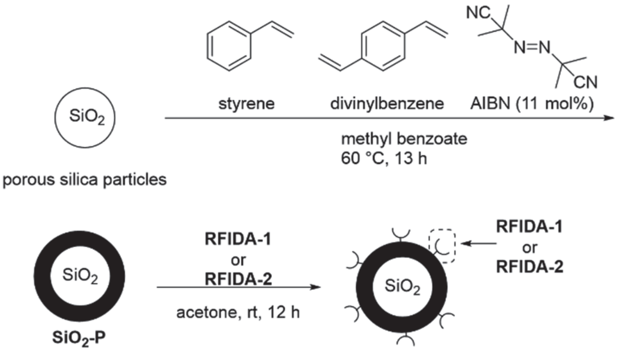


Fig. 4 Preparation procedure of the RFIDA/SiO_2-P adsorbent, where SiO_2–P refers to styrene–divinylbenzene copolymer coating around porous silica particles[12)]

2. U adsorption and Elution Tests

Based on previous studies[12,13)], adsorption and elution conditions were set using nitric acid concentrations of 1 M and 5 M, respectively. The adsorption test conditions are shown in **Table 1**. To evaluate the adsorption behavior, the amount of U in the test solution used was about 1 to 2 times greater than the amount of RFIDAs used in the adsorption tests. In the batch-wise adsorption tests, 0.3 g of RFIDA/SiO_2–P adsorbent was brought into contact with 3 mL of a nitric acid solution containing U (13.3 g/L-U in 1 M HNO_3) in a vial and shaken for 90 min at room temperature (10–15°C). After phase separation, the adsorbent was washed twice with 3 mL of 1 M nitric acid solution. The washings were removed by decanting, 3 mL of eluent (5 M nitric acid) was added to the adsorbent and shaken for 1.5 hours. After shaking, the eluent and adsorbent were separated by decanting. The U concentration in the aqueous solutions was analyzed by ICP–AES.

Table 1 Test conditions of U adsorption tests

Adsorbent	Amount of RFIDA	Weight of adsorbent	Test solution		
			U Concentration	Volume	Amount of U
RFIDA-1	0.12 [mmol]	0.3[g]	0.3	3 [mL]	0.17 [mmol]
RFIDA-2	0.06 [mmol]				

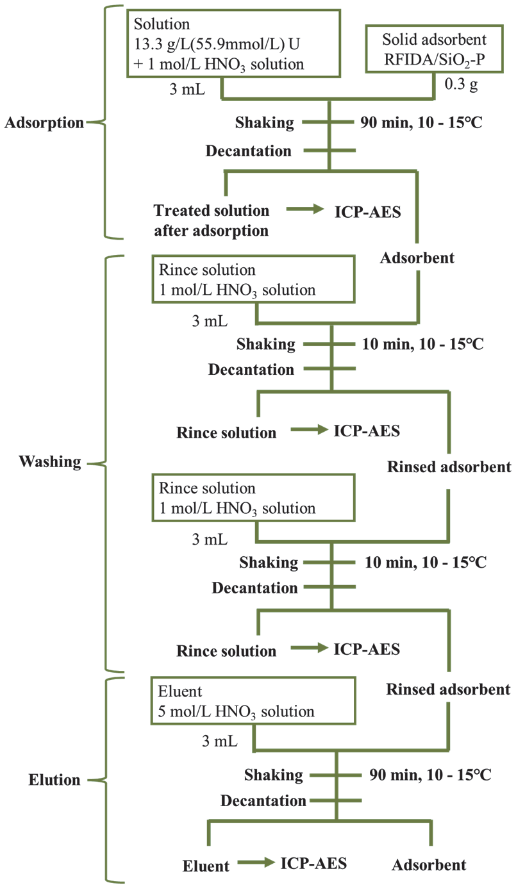


Fig. 5 Process flow of adsorption/elution tests

III. Results and Discussion

To clarify the extraction and adsorption behavior of U on RFIDA, the distribution coefficient (K_d) was calculated based on the results of U concentration analysis of the test solution before and after the tests. K_d was calculated as follows:

$$K_d = \left(\frac{(C_0 - C_1)}{M_1}\right)/(C_1/V_0) \tag{1}$$

K_d: Distribution coefficient [mL/g]
C_0: Initial concentration, before the adsorption test [mol/L]
C_1: Final concentration after the adsorption test [mol/L]
V_0: Volume of the test solution [mL]
M_1: Weight of adsorbent [g]

The K_d values determined in the U adsorption tests under each test condition are listed in **Table 2**. It is inferred that U forms complexes with RFIDA in this polymer layer coated on porous silica with a nitric acid solution. The K_d of the RFIDA/SiO_2 adsorbent ranged from approximately 1 to 3. It was confirmed that RFIDA-2 exhibited slightly higher adsorption performance for U.

Table 2 Calculated K_d values and concentration of U for adsorption tests

Adsorbent	U concentration in test solution [g/L] Initial	 After adsorption test	K_d [mL/g]
RFIDA-1	13.3	12.0	1.1
RFIDA-2		10.3	3.0

Table 3 Evaluation of U mass balance after adsorption/elution tests

Adsorbent	Adsorption amount of U [mg]	Amount of U recovered [mg]	Recovery ratio of U [%]
RFIDA-1	3.8	3.1	81
RFIDA-2	9.2	3.7	40

Moreover, the ratio of the amount of U adsorbed to the amount of U recovered gave the U recovery ratio (material balance). These results are shown in **Table 3**. Based on the results of the evaluation of the material balance, 80% of the uranium in RFIDA-1 was recovered by adsorption-elution, while the yield of RFIDA-2 was about 40%. Since the iminodiacetic acid group can be eluted in strong acid solution, it is considered that uranium complexed with the iminodiacetic acid group of RFIDA-1 and was eluted. Previous studies have revealed that the synthesized RFIDAs facilitate the adsorption reaction in strong acidic nitric acid solutions through the non-ionized iminodiacetic acid groups.[12,13] The extraction reaction of uranyl ions with a strong acid nitric solution by RFIDA is as follows:

$$\mathrm{UO_2^{2+}} + 2\mathrm{NO_3^-} + (\mathrm{R(COOH)_2})_2 \leftrightarrow \mathrm{UO_2(NO_3)_2(R(COOH)_2)_2} \tag{2}$$

Based on the adsorption reaction described in Equation (2), it is estimated that RFIDA-1 can adsorb a maximum of 0.06 mmol of uranyl ions, while RFIDA-2 can adsorb a maximum of 0.03 mmol. Under these conditions, the K_d values were 5.6 and 2.2, respectively. The experimentally determined K_d for RFIDA-1 was lower than the ideal K_d value. The portion of RFIDA-1 incorporated into the polymer layer through impregnation may not be contributing to the adsorption reaction.

In the elution reaction, since iminodiacetic acid was protonated by strong acid, recovery of adsorbed element (U) was achieved. For RFIDA-1, it can be concluded that the adsorbed uranium was sufficiently eluted, considering the losses and analytical errors in the test operation. The results of these studies suggest that REIDA-1 could be a viable candidate for the adsorption and elution of U.

On the other hand, assuming the binding of U to the iminodiacetic acid group of RFIDA-2, a lower K_d value is anticipated compared to RFIDA-1. Previous investigations into the adsorption behavior of Eu have not revealed any significant changes in adsorption behavior attributable to structural differences in RFIDAs.[12,13] The adsorption behavior of RFIDA-2 differs from that of RFIDA-1 depending on the cation valence, suggesting the possibility of adsorption to structural elements beyond the iminodiacetic acid group. It is possible that iminodiacetic acid and a part of the ether structure of RFIDA-2 contribute to the complexation with U. The adsorption/elution performance is influenced by the side chain structure of the ligand.

This experiment demonstrated that the synthesized RFIDAs adsorbed U even in nitric uranyl solutions with high nitric acid concentrations. However, the low K_d values preclude the use of batch processing for waste liquid treatment, suggesting that adsorption-elution techniques such as column chromatography are necessary. Furthermore, considering the interaction between iminodiacetic acid groups and cations, adsorption under more weakly acidic conditions is anticipated to be more effective. Therefore, optimization of adsorption conditions to enhance the adsorption performance is also necessary.

IV. Conclusion

Two RFIDA molecules were synthesized for the efficient treatment of spent radioactive liquid wastes. To understand the adsorption performance for U, adsorption and elution tests were conducted on the synthesized fluorous ligands. The synthesized RFIDAs exhibited adsorption performance for U in nitric acid solution through batch-wise experiments. Moreover, the adsorption/elution performance was found to depend on the side chain structure of the ligand. Further improvement of adsorption performance and examination of RFIDA structure are necessary for practical application to actual waste solutions. Investigation of the adsorption mechanism will be carried out, along with the structure and synthesis procedure of RFIDA suitable for reaction of the interaction with target elements.

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