

Adsorption and Separation Behavior of Molybdenum from High-level Liquid Waste Using a Silica-based Hydroxyoxime Impregnated Adsorbent

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To separate Mo(VI) from high-level liquid waste, a silica-based (anti-DEHDO + Dodec)/SiO₂-P adsorbent was synthesized by impregnating anti-isomer of 5,8-diethyl-7-hydroxy-6-dodecanonoxime (DEHDO) as hydroxyoxime-type extractant and a molecule modifier 1-dodecanol into SiO₂-P support. Adsorption and separation behavior of Mo(VI) in HNO₃ solution onto the adsorbent were investigated by batch and column method, respectively. The adsorbent could effectively adsorb Mo(VI) in both methods.

I. INTRODUCTION

To minimize the radioactive waste accumulation and long-term radiological risk, the nuclide partitioning of high-level liquid waste (HLLW) emitted from the spent nuclear fuel PUREX reprocessing and the optimal dispersal and/or recycling of partitioned nuclide are thought to be a favorable way [1]. In the Japanese vitrification of HLLW, concentration of Mo in the vitrified HLLW was limited less than 3 wt% to prevent the glass from decreasing mechanical strength because concentrated Mo formed yellow solid (MoO₃) phases [2]. Therefore, selective separation of Mo from HLLW could contribute to reduction of high-level radioactive waste. In addition, handleability of HLLW was thought to be improved by the separation since a part of Mo(VI) in HLLW tends to precipitate.

For the purpose, to develop selective separation technique of Mo(VI) from HLLW based on extraction chromatography method, a silica-based (anti-DEHDO + Dodec)/SiO₂-P adsorbent was synthesized by immobilizing anti-isomer of 5,8-diethyl-7-hydroxy-6-dodecanonoxime (anti-DEHDO) as hydroxyoxime-type extractant and a molecule modifier 1-dodecanol (Dodec) into a macroporous silica/stylen-divinylbenzene copolymer composite support (SiO₂-P). In this study, adsorption and separation behavior of Mo(VI) in HNO₃ solution onto the adsorbent were investigated by batch and column method, respectively.

II. EXPERIMENTAL

The anti-DEHDO extractant was obtained from purchased LIX63 based on the literature [3]. A (anti-DEHDO + Dodec)/SiO₂-P was synthesized by impregnating 6 g of the purified anti-DEHDO and 4 g of the Dodec into 14 g of the SiO₂-P particles.

Adsorption behaviors, such as effect of HNO₃ concentration, contact time, metal ions concentrations on the adsorption of Mo(VI), were investigated by batch method. A weighed amount of the dry adsorbent as solid phase was mixed in a glass vial with 4 cm³ of HNO₃ solution containing 5 mM (M = mol·dm⁻³) simulated FPs ions using a thermostatic bath shaker. The concentration of metal ions in the liquid phase before and after the shaking were determined by ICP-AES. Distribution coefficient (K_d , cm³/g) was calculated as follows

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (1)$$

where, C_0 and C_e are the initial and equilibrium concentration (mM) of metal ions in solution, respectively. m and V are the weight of dry adsorbent in g and the volume of solution in cm³, respectively.

Separation behavior of metal ions by the adsorbent was examined by column method. 5 cm³ of simulated HLLW was fed into the adsorbent packed glass column by pump, and then the washing solution and eluent were also fed. The concentration

of metal ions in the effluent was also analyzed by ICP-AES. Temperature was controlled by circulating thermostatic water through the jacket of the column.

III. RESULTS AND DISCUSSION

Effect of HNO₃ concentration on adsorption behavior of Mo(VI), Zr(IV) and Re(VII), which was expected to represent Tc, towards (*anti*-DEHDO + Dodec)/SiO₂-P adsorbent was investigated. Fig. 1 presents K_d of the metal ions contained in HNO₃ solution onto the adsorbent as a function of initial HNO₃ concentration at 298 K. As can be seen, the adsorbent showed adsorption affinity for Mo(VI) and Zr(IV). In addition, there was little change in K_d value of Mo(VI) in this experimental condition but the adsorption of Zr(IV) decreased with increasing initial concentration of HNO₃. This indicated that the adsorbent could separate Mo(VI) from Zr(IV) and Re(VII) in HLLW condition, HNO₃ concentration of HLLW was 2 or 3 M.

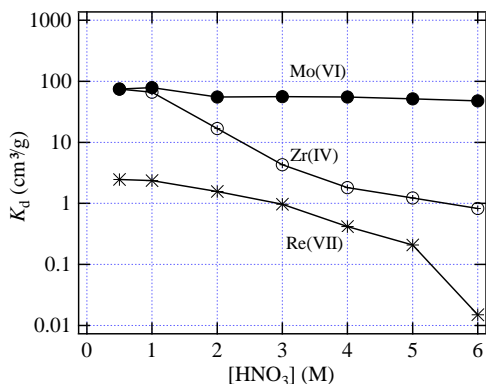


Fig.1. Effect of initial HNO₃ concentration on K_d of Mo(VI), Zr(IV) and Re(VII). ([HNO₃]:0.5 ~ 6 M; [Metal]: 5 mM; Time: 5 h; Phase ratio: 20 cm³/g; Temp.: 298 K)

Otherwise, the adsorption of Mo(VI) in 2 M HNO₃ solution onto the adsorbent reached equilibrium state within 30 min and the adsorption process could be expressed by Langmuir monomolecular layer adsorption mode.

Chromatographic separation of Mo(VI) by the adsorbent packed column was demonstrated using simulated HLLW containing 5 mM of Mo(VI), Zr(VI), Ru(III), Rh(III), Pd(II), Re(VII), La(III), Ce(III), Nd(III), Sm(III), Gd(III) and 2 M of HNO₃. Mo(VI), Zr(IV) and Pd(II) adsorbed onto the adsorbent and the other metal ions were washed out by 2 M HNO₃ solution. Zr(IV) and Pd(II) were successfully recovered by oxalic acid and thiourea, respectively. However, the adsorbed Mo(VI) could not be eluted by oxalic acid, thiourea and water-soluble hydroxyoximes. Further study on the elution of Mo(VI) is necessary to use the adsorbent repeatedly.

IV. CONCLUSIONS

To separate Mo(VI) from HLLW emitted from PUREX reprocessing, a silica-based (*anti*-DEHDO + Dodec)/SiO₂-P adsorbent was synthesized and investigated by batch and column methods. It was found that the adsorbent have good adsorption capabilities for Mo(VI). Zr(IV) and Pd(II) also adsorbed but the adsorbed Zr(IV) and Pd(II) were selectively eluted by oxalic acid and thiourea, respectively. Because the elution of Mo(VI) was difficult, further study is necessary to use the adsorbent repeatedly. However, the adsorbent was considered to be one of the good remover of Mo(VI) from HLLW.

ACKNOWLEDGMENTS

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