

Selective Separation and Recovery of Mo(VI) by Hybrid Microcapsules Containing Organic Extractants-10179

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ABSTRACT

The content of molybdenum in high level vitrified waste is limited. The selective separation and recovery of Mo(VI) from HLLWs containing highly concentrated HNO₃ are very important in relation to the volume reduction of radioactive wastes, partitioning of nuclides and to make efficient use of resources. The organic extractant LIX63 (5,8-diethyl-7-hydroxy-6-dodecanone oxime) is effective for the extraction of Mo(VI). The selective uptake of Mo(VI) from nitric acid solution was studied by using microcapsules (MCs), LIX63HALG and LIX63Ca-HALG. The characterization of LIX63HALG and LIX63Ca-HALG was examined by a scanning electron microscope (SEM), and the uptake and recovery of Mo(VI) were investigated by batch and column methods, respectively. The particle sizes of LIX63HALG and LIX63Ca-HALG were about 1.2 mm and 0.9 mm in diameter. Fine droplets of LIX63 were uniformly encapsulated in the matrices. The uptake rate of Mo(VI) for both MCs was fairly fast and the uptake attained equilibrium within 5 h; the uptake percentage was above 99% within 3 h in the presence of 1 M HNO₃. The order of the K_d value for different metal ions at 1 M HNO₃ was Mo(VI) >> W(VI) > Cr(VI) > Re(VII) >> Se(IV). The uptake of Mo(VI) was followed by a Langmuir adsorption isotherm, and the maximum uptake capacity of Mo(VI) for LIX63HALG was estimated to be 0.54 mmol/g. In a similar way, the maximum uptake capacity of Mo(VI) for LIX63Ca-HALG was estimated to be 0.73 mmol/g. The breakthrough curve of Mo(VI) for the column packed with LIX63HALG had S-shaped profiles, and 5% breakpoint and breakthrough capacity were estimated to be 24 cm³ and 0.11 mmol/g, respectively. The 5% breakpoint and breakthrough capacity of Mo(VI) for the column packed with LIX63Ca-HALG were estimated to be 15 cm³ and 0.19 mmol/g, respectively. The adsorbed Mo(VI) was effectively eluted with 5 M HNO₃. LIX63CaALG exhibited a relatively high uptake percentage of 99.9% for Mo(VI). Thus, the LIX63-MCs were effective for the separation and recovery of Mo(VI) from HLLWs containing highly concentrated HNO₃.

INTRODUCTION

Large amounts of Mo(VI) (~4 kg/1tHU, 43 GWd/t) exist in high-level liquid wastes (HLLWs). A part of Mo(VI) in HLLWs tends to precipitate, and the content of Mo is restricted to less than 3 wt% for the vitrification process in order to avoid the formation of yellow solid (MoO_3) phases and the lowering of mechanical strength of glass products[1]. The selective separation and recovery of Mo(VI) from HLLWs containing highly concentrated HNO_3 are very important in relation to the volume reduction of radioactive wastes, partitioning of nuclides and utilization of rare metal resources.

Various methods such as solvent extraction and ion exchange on polymeric materials have been suggested for the separation of oxoanions[2],[3]. Various oxime-based chelating extractants such as LIX 63 and LIX 84 have also been proposed as suitable reagents for the extraction of oxoanions[4]. In order to utilize these extractants having high affinity for oxoanions, the microencapsulation with alginate gel polymers seems to be one of the most promising techniques for the practical column operation[5]-[9]. Alginate, a natural polysaccharide extracted from brown seaweed, is a promising matrix for the immobilization of extractants; it was preferred over other materials because of its various advantages such as biodegradability, hydrophilic properties, natural origin, abundance and presence of binding site due to its carboxylate functions[10]. In the environmental field, alginate beads are widely used for the removal of heavy metals from wastewater[11]. Alginate is the salt of alginic acid having carboxyl groups capable of forming gels by crosslinking with multivalent metal ions. This immobilizing property of alginate has led to its extensive applications to the microencapsulation of enzymes, subcellular organelles, and living cells[12][13]. In this study, we have attempted to encapsulate LIX63 extractant into the porous alginate gel polymers for the selective separation of Mo(VI).

This paper deals with the preparation of different MCs enclosing this extractant, characterization, uptake properties, and breakthrough and elution properties of Mo(VI) for the column packed with MCs.

EXPERIMENTAL

Materials

The organic extractant, LIX63 (5, 8-diethyl-7-hydroxy-6-dodecanone oxime with kerosene) was ordered from Cognis Corporation. Sodium alginate (NaALG, 500-600 cP) was purchased from Wako Pure Chemical Ind. The MoO_4^{2-} solutions were obtained by dissolving Na_2MoO_4 (Wako Pure Chemical Ind.) and diluting the standard solutions (10^3 ppm, Wako Pure Chemical Ind.). The metal solutions of WO_4^{2-} , CrO_4^{2-} , ReO_4^- and SeO_3^{2-} were obtained by diluting the standard solutions (10^3 ppm, Wako Pure Chemical Ind.).

Preparation of MCs

In this experiment, the MCs were prepared by the following two methods shown in **Fig. 1**; the first one called LIX63HALG and the other called LIX63Ca-HALG. LIX63HALG was prepared as follows. The NaALG solution (50 cm^3 , 1.5 wt%) was kneaded with 2.0 g of LIX63 and fully dispersed. The well-kneaded sol was injected dropwise into 0.1 M HNO_3 solution using a medical needle under constant stirring at room temperature to form flaky MCs. The MCs were

stirred gently for one night to enhance the aging. The MCs were then separated from the solution, washed with distilled water and finally air-dried at 30°C for 2 d.

The procedure for the preparation of LIX63Ca-HALG is similar to that for LIX63HALG. LIX63Ca-HALG was prepared as follows. The NaALG solution (50 cm³, 1.5 wt%) was kneaded with 2.0 g of LIX63 and fully dispersed. The well-kneaded sol was added dropwise to a 0.5 M Ca(NO₃)₂ solution using a medical needle with stirring at room temperature to form spherical MCs(LIX63CaALG). Washed and dried MCs were shaken with 0.1 M HNO₃ for 12 h. These MCs treated with HNO₃ finally converted to LIX63Ca-HALG.

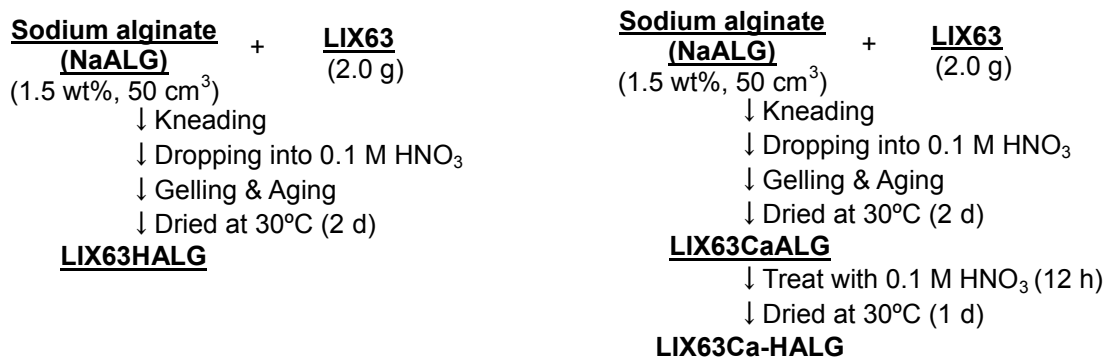


Fig. 1 Preparation of MCs.

Characterization

The surface and cross section morphology of MCs were observed by a scanning electron microscope (SEM, Hitachi TM-1000). The incorporation of Mo(VI) ions into MCs was confirmed by electron probe microanalysis (EPMA, JEOL, JXA-8200WD/ED).

Determination of Distribution Coefficient (K_d)

The distribution of Mo(VI), W(VI), Cr(VI), Re(VII), and Se(IV) ions for MCs was estimated by the batch method. An aqueous solution (5 cm³) of 10 ppm of each metal ion solution was contacted with 50 or 25 mg of different MCs at 25±1°C up to 5 h, which was found to be sufficient for attaining equilibrium. The concentrations of these metal ions were measured by ICP-AES (SII, SPS 7800). The uptake percentage (R , %) of metal ions removed from the solution and the distribution coefficient (K_d , cm³/g) are defined as:

$$R = (C_0 - C_t)/C_0 \times 100, (\%) \quad (\text{Eq. 1})$$

$$K_d = ((C_0 - C_f)/C_f) \times V/m, (\text{cm}^3/\text{g}) \quad (\text{Eq. 2})$$

Where C_0 , C_t , and C_f are the concentration of metal ions initially, at time t , and at equilibrium, respectively; m (g) the weight of MC; V (cm³) the volume of the aqueous phase.

Breakthrough and Elution

The column was prepared by packing 0.5 or 1.0 g of the MC in a glass column (5 mm in diameter and 200 mm in length) with a thermostatic water jacket. The column experiment was

conducted at constant temperature ($25 \pm 1^\circ\text{C}$). Every 1.4 or 3.0 cm^3 of the effluent was fractionated, and the concentration was determined by ICP-AES. A breakthrough curve was obtained by plotting the breakthrough ratio (C/C_0) against the effluent volume, where C_0 and C (ppm) are the concentration of the initial solution and the effluent, respectively.

For the elution experiments, 0.5 or 1.0 g of the MC was packed into the glass column. The Mo(VI) ions (0.35 mg or 0.2 mg) were previously loaded on the upper part of the column. The eluent used in this study was 5 M HNO_3 . The effluent was collected by a fraction collector, and the concentration was determined by ICP-AES. The elution chromatogram was obtained by plotting the elution percentage (Elution, %) against the elution volume. The elution percentage is defined as the ratio of the eluted amount of Mo(VI) in each fraction to the initial amount loaded on the column. The retention volume (V_R) and number of theoretical plates (N) are defined as:

$$V_R = V_m + \rho K_d V_a, \text{ (cm}^3\text{)} \quad (\text{Eq. 3})$$

$$N = 16(V_R/W)^2 \quad (\text{Eq. 4})$$

Where V_m , ρ , V_a , and W are void volume, density of MCs, volume of MCs and peak width, respectively.

Real HLLW

The preparation procedure for real HLLW (JAEA, FBR-JOYO) is shown in **Fig. 2**; the spent MOX fuel (Pu content: 30%, burnup fraction: 119 GWd/t) was dissolved by nitric acid, and after the removal of U and Pu, the real HLLW was used for the Mo(VI) uptake experiments. The uptake property for the real HLLW was examined as follows: 500 mg of LIX63CaALG was added to 5 cm^3 of real HLLW in the beaker. After immersion, the beaker was shaken gently every 30 min for 5 h. The concentration of metal ions in supernatant was measured by ICP-AES.

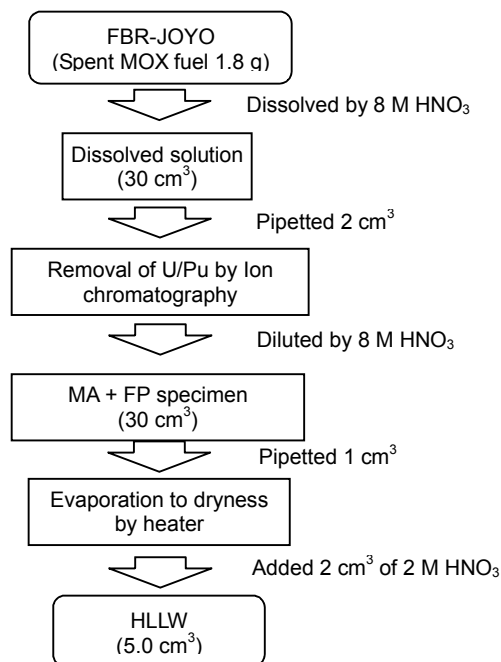


Fig. 2 Preparation procedure for real HLLW.

RESULTS AND DISCUSSION

Surface Morphology

The SEM images of representative LIX63HALG are shown in **Figs. 3(a)** and (b). Obvious flaky granules were obtained, and a number of fine drops of LIX63 were enclosed in the alginate matrices. On the surface of LIX63HALG, fine droplets ($\sim 20 \mu\text{m}$ in diameter) are seen to be encapsulated. Some creases are also observed on the surface of LIX63HALG. The particle sizes of MCs were estimated to be 1.2 mm in diameter from SEM images. **Figs. 3(c)** and (d) show the SEM images of LIX63Ca-HALG. LIX63Ca-HALG is obtained as a spherical shape. On the surface of LIX63Ca-HALG, fine droplets ($\sim 1 \mu\text{m}$ in diameter) are seen to be encapsulated. The particle size of MC was estimated to be 0.9 mm in diameter from SEM images.

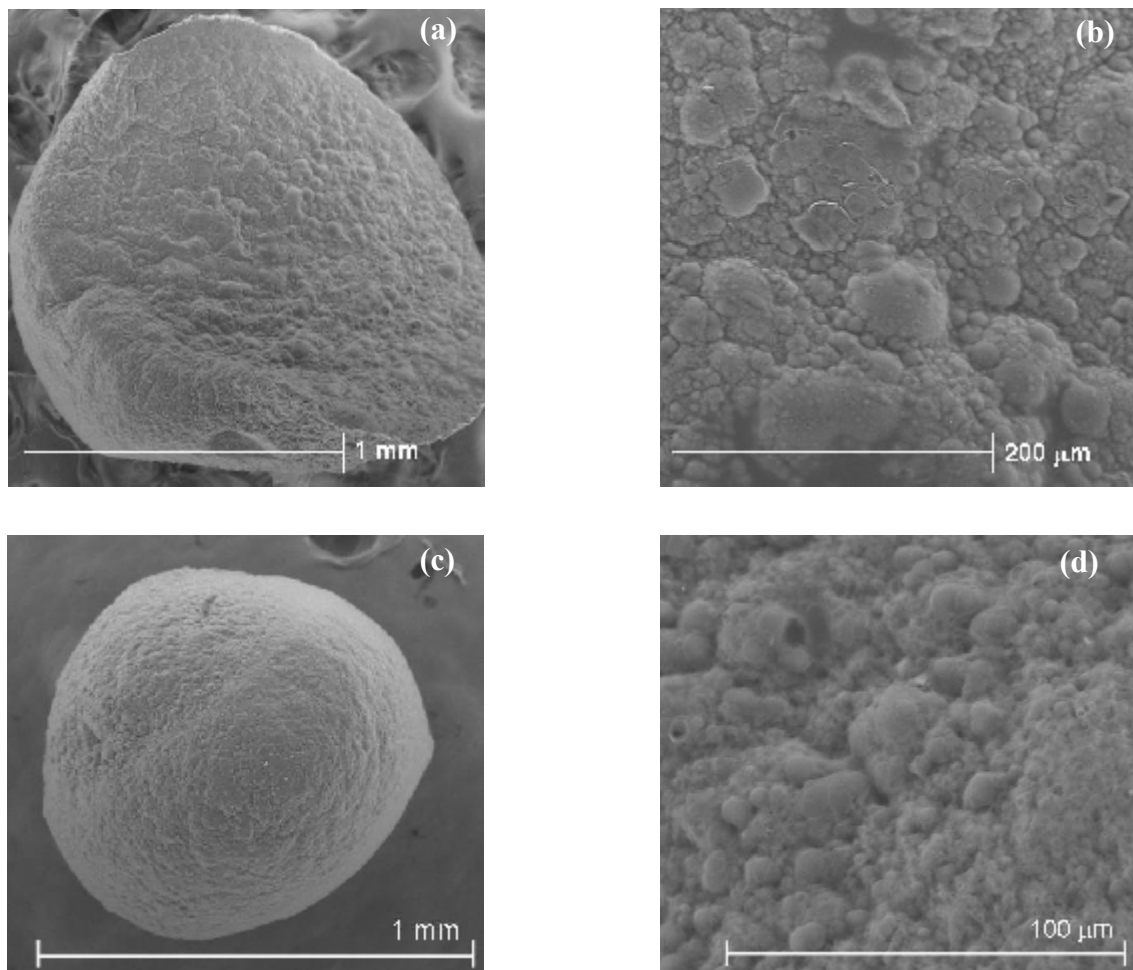


Fig. 3 SEM images of the surface of LIX63HALG and LIX63Ca-HALG.

(a): LIX63HALG, (b): Magnified LIX63HALG, (c): LIX63Ca-HALG, (d): Magnified LIX63Ca-HALG

Uptake Rate

The uptake properties of Mo(VI) were examined by the batch method. **Figs. 4 and 5** show the effects of shaking time on the uptake percentage, R (%), of Mo(VI) for LIX63HALG and LIX63Ca-HALG. The uptake of Mo(VI) for both MCs was fairly fast in the initial stage within 0.5 h and the uptake equilibrium was attained within 5 h.

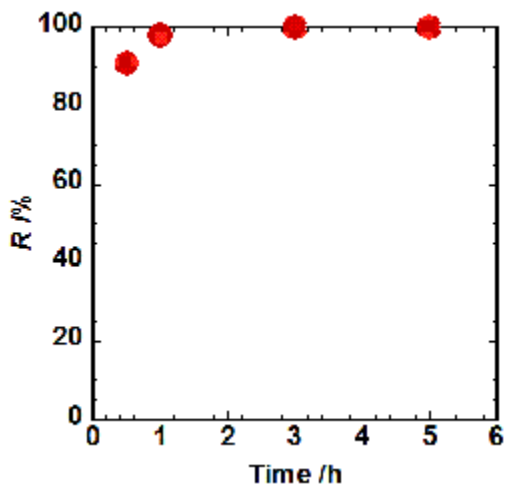


Fig. 4 Uptake rate of Mo(VI) for LIX63HALG. V/m : $100 \text{ cm}^3/\text{g}$; 10 ppm Mo(VI); 3 M HNO_3 ; 25°C .

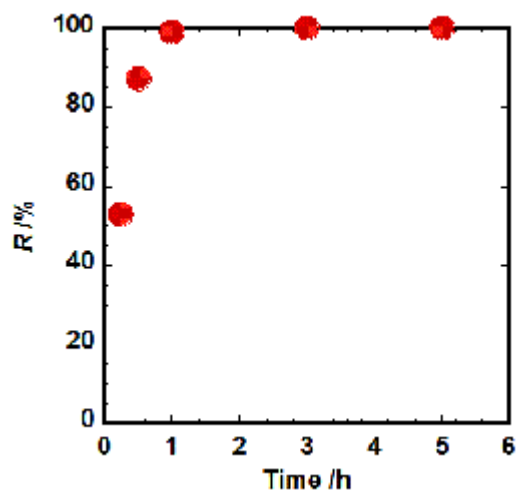


Fig. 5 Uptake rate of Mo(VI) for LIX63Ca-HALG. V/m : $200 \text{ cm}^3/\text{g}$; 10 ppm Mo(VI); 1 M HNO_3 ; 25°C .

Effect of HNO_3 concentration on K_d of Mo(VI)

The uptake ability of Mo(VI) for LIX63HALG from various nitric acid concentrations is shown in **Fig. 6**. As for the uptake on LIX63HALG, a relatively large K_d value of about $10^5 \text{ cm}^3/\text{g}$ was obtained around 10^{-1} to 1 M HNO_3 , and then decreased above 3 M HNO_3 . It is known that Mo(VI) exists as MoO_4^{2-} in weakly acidic, neutral and alkaline media predominantly in the pH region above 2. At lower pH ($\text{pH} < 2$), the chemical species of Mo(VI) may be shifted to the MoO_2^{2+} form, and then extracted with LIX63; it is assumed that the extraction of Mo(VI) with LIX63 is expressed by the following chemical equations[4]:



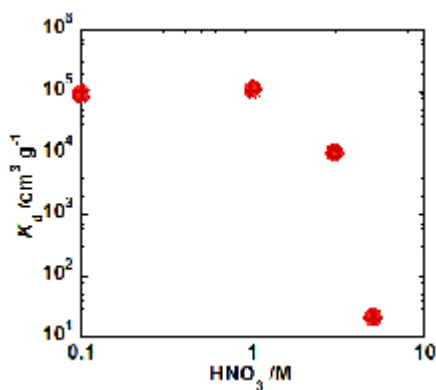


Fig. 6 Effect of HNO₃ concentration on K_d of Mo(VI) for LIX63HALG. 10 ppm Mo(VI); V/m: 100 cm³/g; 25°C.

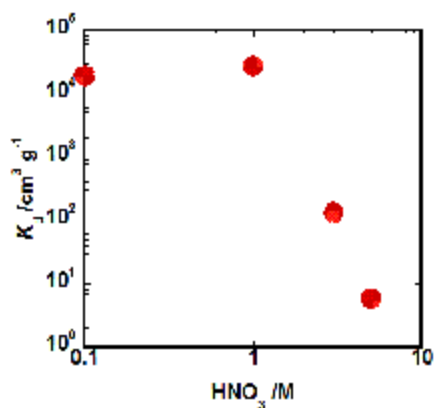


Fig. 7 Effect of HNO₃ concentration on K_d of Mo(VI) for LIX63Ca-HALG. 10 ppm Mo(VI); V/m: 200 cm³/g; 25°C.

Thus, the K_d value of Mo(VI) tended to decrease with increasing nitric acid concentration. This result was similar to that in a previous report for the LIX 63/Mo(VI) extraction system[4]. **Fig. 7** shows the K_d value of Mo(VI) for LIX63Ca-HALG. A similar tendency was observed compared to the result in **Fig. 6**. However, the K_d value decreased rapidly when 3 M or higher concentration of HNO₃ was present. The reason for the considerable lowering was probably due to the elution of calcium ions in the presence of highly concentrated HNO₃.

Distribution of Various Oxoanions

The uptake affinity for various oxoanions, Mo(VI), W(VI), Cr(VI), Re(VII) and Se(IV), on LIX63HALG was examined at different concentrations of HNO₃ up to 5 M by the batch method (**Fig. 8**). A large K_d value of Mo(VI) around 10⁶ cm³/g was obtained in the presence of 0.1 to 1 M HNO₃. K_d values of other oxoanions were below 10³ cm³/g. The order of the K_d value at 1 M HNO₃ was Mo(VI) >> W(VI) > Cr(VI) > Re(VII) >> Se(IV). These results indicate that the chromatographic separation of Mo(VI) from the mixed solution of oxoanions can be achieved by controlling the concentration of nitric acid. LIX63Ca-HALG shows a similar tendency (**Fig. 9**), however, the uptake of W(VI) for LIX63Ca-HALG was larger than that for LIX63HALG.

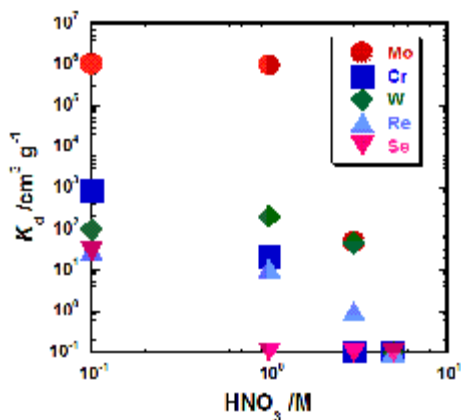


Fig. 8 K_d values of various oxoanions for LIX63HALG. [Oxoanion]: 10 ppm; V/m: 100 cm³/g; 25°C.

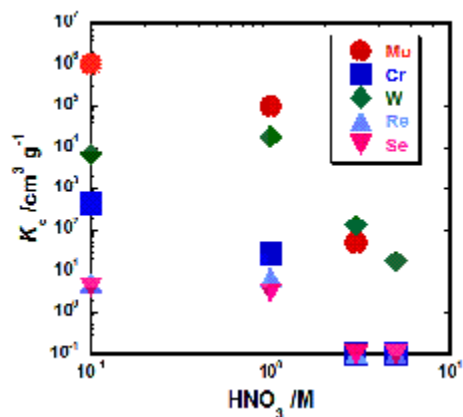


Fig. 9 K_d values of various oxoanions for LIX63Ca-HALG. [Oxoanion]: 10 ppm; V/m: 100 cm³/g; 25°C.

Uptake Isotherm of Mo(VI)

The uptake isotherm of Mo(VI) for LIX63HALG was obtained in a wide range of initial Mo(VI) concentrations from 50 to 2×10^3 ppm. The equilibrium amount of Mo(VI) adsorbed on LIX63HALG approached a constant value by the increasing of Mo(VI) concentration, suggesting that the uptake of Mo(VI) follows a Langmuir-type adsorption equation [14]. The Langmuir equation can be rewritten as follows:

$$C_{\text{eq}}/Q_{\text{eq}} = 1/KQ_{\text{max}} + (1/Q_{\text{max}})C_{\text{eq}} \quad (\text{g/dm}^3), \quad (8)$$

where C_{eq} (mol/dm^3) and Q_{eq} (mol/g) are the equilibrium concentrations of Mo(VI) in the aqueous and solid phases, respectively; Q_{max} (mol/g) is the maximum amount of Mo(VI) taken up; K (dm^3/mol) is the Langmuir constant. As shown in **Fig. 10**, a fairly linear relation between $C_{\text{eq}}/Q_{\text{eq}}$ and C_{eq} was obtained from Langmuir-plots for LIX63HALG. The result shows that the Q_{max} value for LIX63HALG was estimated to be 0.54 mmol/g. The uptake of Mo(VI) for LIX63Ca-HALG also followed a Langmuir adsorption isotherm, and the maximum uptake capacity of Mo(VI) was estimated to be 0.73 mmol/g (**Fig. 11**).

Incorporation of MCs

The incorporation of Mo(VI) ions into MCs was confirmed by EPMA. **Fig. 12** shows color mapping of a cross section of LIX63HALG contacted with a 700 ppm Mo(VI) – 3 M HNO_3 solution at $V/m = 100 \text{ cm}^3/\text{g}$ for 5 h at 25°C . The unreacted area for Mo(VI) is seen in the center of the cross section because of insufficient shaking time. In order to accomplish the sufficient incorporation, LIX63Ca-HALG was contacted with a 2,000 ppm Mo(VI) – 1 M HNO_3 solution at a V/m ratio of $100 \text{ cm}^3/\text{g}$ for 24 h. Mo(VI) was uniformly incorporated into the LIX63Ca-HALG (**Fig. 13**).

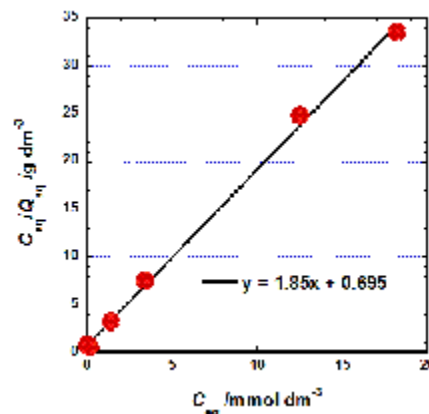


Fig. 10. Langmuir-plot of Mo(VI) uptake for LIX63HALG. 25°C .

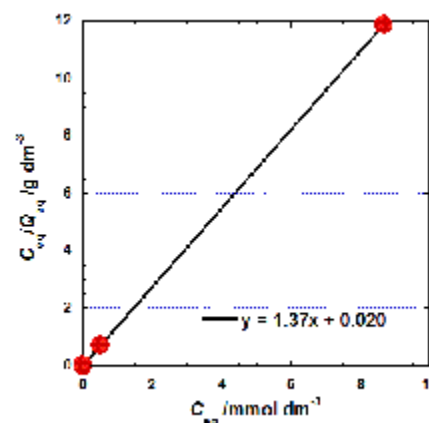


Fig. 11. Langmuir-plot of Mo(VI) uptake for LIX63Ca-HALG. 25°C .

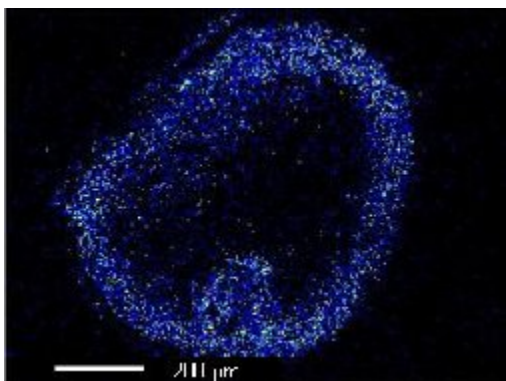


Fig. 12 EPMA color mapping of cross section of LIX63HALG. 700 ppm Mo(VI); 3 M HNO₃; *V/m*: 100 cm³/g; Shaking time: 5 h; 25°C.

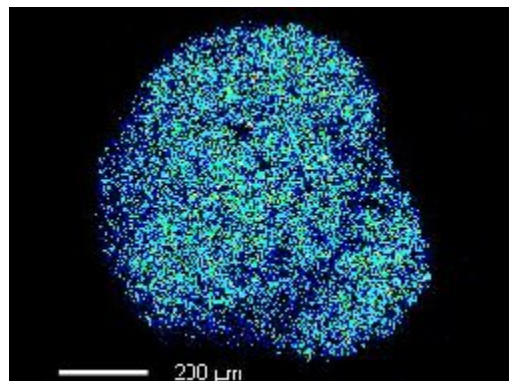


Fig. 13 EPMA color mapping of cross section of LIX63Ca-HALG. 1000 ppm Mo(VI); 1 M HNO₃; *V/m*: 100 cm³/g; Shaking time: 24 h; 25°C.

Breakthrough Properties of Mo(VI)

The breakthrough properties of Mo(VI) from nitric acid solution were examined using the column packed with LIX63HALG and LIX63Ca-HALG. **Fig. 14** shows the breakthrough curve of Mo(VI) for the column packed with LIX63HALG. The breakthrough curve had a symmetrical S-shaped profile, indicating no dislodgment of LIX63 from the matrix of HALG. The breakpoint of 5% breakthrough and breakthrough capacity (*B.T.Cap.*) for LIX63HALG were 24 cm³ and 0.11 mmol/g, respectively. The breakthrough curve of Mo(VI) for the LIX63Ca-HALG column is shown in **Fig. 15**. The breakpoint of 5% breakthrough and breakthrough capacity (*B.T.Cap.*) for LIX63HALG were 15 cm³ and 0.19 mmol/g, respectively.

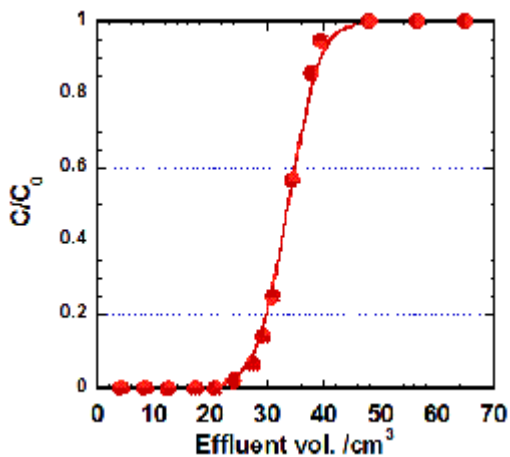


Fig. 14 Breakthrough curves of Mo(VI). LIX63HALG: 0.5g; Flow rate: 1.8 cm³/min; Feed: 500 ppm Mo(VI) – 3 M HNO₃; 25°C.

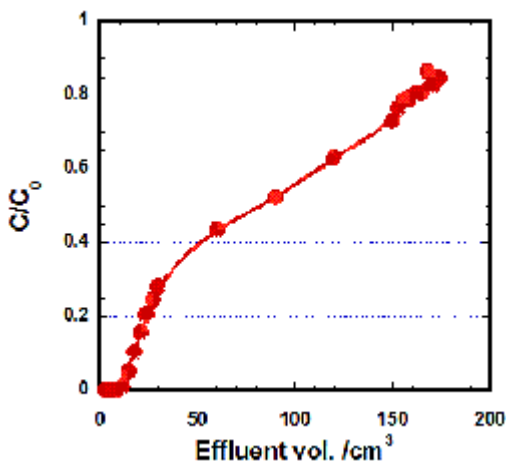


Fig. 15 Breakthrough curves of Mo(VI). LIX63Ca-HALG: 1.0g; Flow rate: 2.0 cm³/min; feed: 1000 ppm Mo(VI) – 1 M HNO₃; 25°C.

Elution Properties of Mo(VI)

The elution properties of Mo(VI) were examined by using a 5 M HNO₃ eluent. **Fig. 13** shows the elution chromatogram of Mo(VI) for the column packed with LIX63HALG. An elution curve having $N=14.4$ was obtained, yielding the V_R value of 38 cm³ which was close to the calculated one. About 99% of the adsorbed Mo(VI) can be successfully eluted. The elution chromatogram of Mo(VI) for the LIX63Ca-HALG column is shown in **Fig.14**. An elution curve having $N=13.9$ was obtained, yielding the V_R value of 27.5 cm³. Over 99% of the adsorbed Mo(VI) could be successfully eluted. The 5 M HNO₃ eluent was thus effective for the elution of Mo(VI).

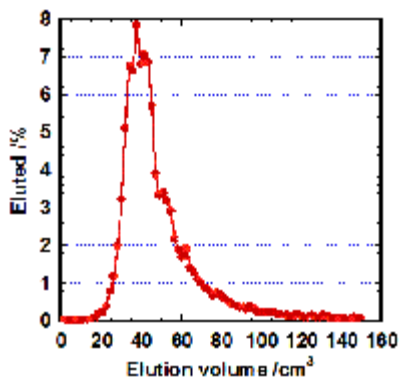


Fig. 16 Elution curves of Mo(VI) from LIX63HALG column. LIX63HALG: 0.5g; Mo(VI): 300mg; Eluent: 5 M HNO₃; Flow rate: 0.2 cm³/min; 25°C.

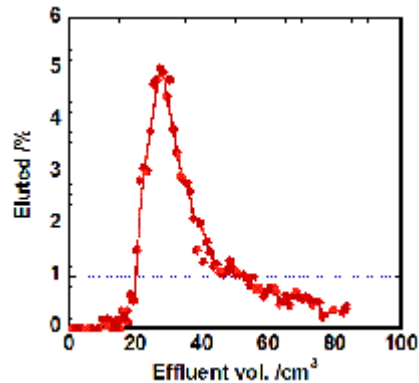


Fig. 17 Elution curves of Mo(VI) from LIX63Ca-HALG column. LIX63Ca-HALG: 1.0g; Mo(VI): 200mg; Eluent: 5 M HNO₃; Flow rate: 0.2 cm³/min; 25°C.

Uptake from real HLLW

The uptake of metal ions on LIX63CaALG is listed in **Table I**. LIX63CaALG exhibited a relatively high uptake percentage of 99.9% for Mo(VI). The other metal ions of Ln, Ag, Sn, and Zr also had adsorbability to the microcapsules. These metal ions were probably adsorbed on the CaALG matrices by the ion-exchange reaction.

Table I. Comparison of uptake (%) for various metal ions.

Metal ions	Uptake /%	Metal ions	Uptake /%
Y	-	Al	-
La	8.3	Ba	-
Ce	14.8	Cd	-
Pr	44.2	Cr	-
Nd	10.7	Fe	-
Sm	4.9	Mo	99.9
Eu	-	Ni	-
Gd	-	Pb	-
Sr	-	Sn	98.9
Ba	-	Zn	-
Ag	96.3	Zr	80.2

CONCLUSIONS

The uptake properties of Mo(VI), characterization and dynamic adsorption properties were investigated by using LIX63-MCs. The uptake of Mo(VI) for LIX63HALG and LIX63Ca-HALG was fairly fast in the initial stage within 0.5 h and uptake equilibrium was attained within 5 h. The K_d value of Mo(VI) for LIX63HALG was almost constant ($10^5 \text{ cm}^3/\text{g}$) up to 1 M HNO_3 , while the K_d value decreased with a HNO_3 concentration of about 3 M. The K_d value of Mo(VI) for LIX63Ca-HALG was similar to that for LIX63HALG. However, the decrease rate of the K_d value at 3 M or higher HNO_3 concentration was larger than that of LIX63HALG. A comparison of K_d values for various oxoanions in different HNO_3 concentrations indicates that the chromatographic separation of Mo(VI) from mixed oxoanion solution can be achieved by controlling the concentration of nitric acid. The uptake isotherm Mo(VI) followed a Langmuir-type adsorption equation. The breakthrough capacity of Mo(VI) for LIX63Ca-HALG was larger than that for LIX63HALG. The adsorbed Mo(VI) was effectively eluted with a 5 M HNO_3 solution. A high uptake percentage of 99.9% for Mo(VI) was obtained by using the dissolved solutions of spent fuel from FBR-JOYO. Thus, the LIX63-MCs were effective for the separation and recovery of Mo(VI) from HLLWs containing highly concentrated HNO_3 .

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