Simultaneous Removal of Radioactive Nuclides with Nickel Alginate Microcapsules

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(Manuscript submitted January 27, 2003; accepted March 31, 2003)

Abstract
Nickel alginate microcapsules enclosing inorganic ion-exchangers (ferrocyanide and clinoptilolite) and organic extractant (DEHPA) were prepared by gelling the kneaded sols. The microcapsules with various shapes such as granule, column and film were easily obtained by changing the gelling methods. The metal ions of Cs\(^+\), Sr\(^{2+}\), Y\(^{3+}\), Eu\(^{3+}\) and Am\(^{3+}\) were readily adsorbed on the microcapsule within 6 h and relatively high uptake percentages above 90% were obtained. The uptake rate was independent of coexisting NaNO\(_3\) concentration up to 1 M and no appreciable swelling was observed. The uptake of metal ions followed a Langmuir-type adsorption equation and the uptake capacities of Cs\(^+\), Sr\(^{2+}\), Y\(^{3+}\) and Eu\(^{3+}\) were estimated to be 0.063, 0.011, 0.051 and 0.149 mmol/g, respectively. The microcapsules were thus effective for the simultaneous removal of radioactive nuclides from waste solutions.

1 Introduction
The rapid decontamination of accidental liquid wastes containing various radioactive nuclides is important from the standpoint of radiation exposure reduction and radiation protection. For this purpose, the development of “multi-functional” microcapsules with high uptake ability for different radioactive nuclides is required. In order to remove radioactive nuclides from the waste solutions, a large number of selective inorganic ion-exchangers and extractants have been developed.[1-4] Since most of these materials are very powdery or oily, some handling difficulties arise for the practical applications. The granulation of these materials with organic polymers seems to be very effective for the rapid decontamination and safety handling. The organic binding polymers for the encapsulation have a number of advantages such as simplicity of preparation procedure, high porosity, high content of active component and mechanical strength.[4] The gel network of the polymeric materials is further expected to prevent the escape of exchanger and extractant from the microcapsule. Alginic acid is a biopolymer,
which occurs in brown seaweeds and has carboxyl groups capable of forming complexes with divalent metal ions such as Ca^{2+}, Ba^{2+} and Ni^{2+}. Recently, the gel-forming property of this polymer has led to its extensive use in the biomedicine and biotechnology industries to immobilize or encapsulate enzymes, subcellular organelles and living cells. Thus, the prominent immobilizing ability of alginates seems to be applicable to the encapsulation of inorganic ion exchangers and organic extractants.

In this study, we have attempted to enclose and immobilize various inorganic ion-exchangers and organic extractants with alginate gel polymers to form microcapsules. The present study deals with the preparation procedure of microcapsules, their characterizations and the uptake properties of various radioactive nuclides.

2 Experimental

2.1 Materials and Preparation of Microcapsules

The inorganic ion-exchangers, Ni-ferrocyanide (NiFC) and clinoptilolite (CP), were used for the uptake of Cs^{+}, Sr^{2+} and Co^{2+} ions. The organic extractant, DEHPA (di-(2-ethylhexyl)phosphoric acid), was used for the uptake of Y^{3+}, Eu^{3+} and Am^{3+} ions. The preparation procedure for microcapsules is as follows. Viscous sodium alginate (NaALG) solutions were kneaded with both fine powders of inorganic ion-exchanger and oil drops of extractant. The content of each exchanger and extractant was 0.2 g in the NaALG solution (100 cm^3). The kneaded sol was then added dropwise to 0.5 M NiCl2 solution (gelling agent) with stirring at room temperature to form granular gel particles. After overnight standing, they were separated from the gelling solution and washed with deionized water. Air-drying at 40°C was performed to obtain the granular microcapsules. The microcapsules with various shapes such as granule, column and film were easily obtained by changing the gelling methods. The surface morphology and physicochemical property of microcapsules were examined by scanning electron microscopy (SEM, Hitachi 4100-L), electron probe microanalysis (EPMA, Hitachi X-650S).

2.2 Determination of Uptake

The uptake percentage and distribution coefficient of Cs^{+}, Sr^{2+}, Co^{2+}, Y^{3+}, Eu^{3+} and Am^{3+} ions were determined by the batch method. An aqueous solution (5 cm^3) containing 10 ppm metal ion in the presence of 10^{-1} ~ 10^{-4} M HNO3 was contacted with 50 mg of granular microcapsule at 25 ± 1°C for 1 d. After equilibration, the γ-activities of 137Cs, 85Sr, 60Co, 152Eu and 241Am ([Am^{3+}]: carrier free, 2.1 × 10^{-9} M) in the aqueous phase were measured by NaI(Tl) scintillation counter (OKEN, Model RC-101A) and pure Ge multichannel analyzer (CANBERRA, SERIES 35 PLUS). Here the radioisotopes of 85Sr and 88Y were produced on the reaction of 86Sr(γ, n)85Sr and 89Y(γ, n)88Y by bremsstrahlung from LINAC, Tohoku Univ., respectively. The uptake percentage, R (%), and the distribution coefficient, Kd (cm^3/g), are defined as

\[ R = \left( \frac{A_i - A_t}{A_i} \right) \times 100 \quad \text{(Eq. 1)} \]

\[ K_d = \left( \frac{A_i - A_f}{A_f} \right) \times \frac{V}{m} \quad \text{(cm^3/g),} \]

where \( A_i, A_t \) and \( A_e \) (cpm/cm^3) are the counting rates at the initial stage, at time \( t \), and at equilibrium, respectively; \( m \) (g) the weight of microcapsule; \( V \) (cm^3) the volume of aqueous phase.

3 Results and Discussion

3.1 Surface Morphology and Structure of Microcapsules

Figures 1 (a) and (b) show the SEM images of granular microcapsule (NiFC-CP-DEHPA-NiALG) prepared from the kneaded sol consisting of 0.2 g NiFC- 0.2 g CP- 0.2 g DEHPA and 100 cm^3 of NaALG solution.
The aggregates of inorganic exchangers (NiFC and CP) and oil drops of DEHPA are seen to be encapsulated in the NiALG gel matrices. Here the aggregates and oil drops are uniformly encapsulated in the alginate gel matrices crosslinked with Ni$^{2+}$ ions. The cross section of gel matrices has been reported to exhibit an “egg-box junction” which brings about the high porosity and mechanical strength of the microcapsule.\[^5\]

The moisture contents of gel particle and dried microcapsule were estimated to be about 90 and 2.0 wt\%, respectively.

### 3.2 Uptake Rate

The uptake percentage of Cs$^+$, Sr$^{2+}$, Co$^{2+}$, Y$^{3+}$, Eu$^{3+}$ and Am$^{3+}$ ions for the microcapsule was measured at regular time intervals. Figure 2 shows the effects of shaking time on the uptake percentage, $R$ (%), of the above metal ions in the presence of $10^{-3}$ M HNO$_3$. The uptake of Cs$^+$, Sr$^{2+}$, Y$^{3+}$, Eu$^{3+}$ and Am$^{3+}$ ions attained equilibrium within 6 h and relatively large $R$ values above 90 % were obtained. The uptake rate was enhanced with increasing reaction temperature up to 60°C. The relatively low $K_d$ value of Co$^{2+}$ may be due to the pH dependency of Co$^{2+}$ uptake and the presence of Ni$^{2+}$ eluted in the solution.

### 3.3 Effect of NaNO$_3$ Concentration on $K_d$

Figure 3 shows the effects of coexisting NaNO$_3$ concentration on $K_d$ values of various metal ions. The $K_d$ values for Cs$^+$, Sr$^{2+}$, Y$^{3+}$, Eu$^{3+}$ and Am$^{3+}$ ions were almost constant in the presence of NaNO$_3$ below 0.1 M and relatively high $K_d$ values above $10^3$ cm$^3$/g were obtained. The uptake rates of metal ions were independent of coexisting NaNO$_3$ concentration up to 1 M and no
appreciable swelling was observed.

3.4 Uptake Isotherm and Capacity

In order to estimate the uptake capacity, the uptake isotherms of various metal ions were obtained in a wide range of equilibrium concentration from $10^{-4} \sim 1.5 \times 10^{-1}$ mmol/dm$^3$. The equilibrium amount of metal ions tended to increase with equilibrium concentration, and then approached a constant value, indicating that the uptake of metal ions follows a Langmuir-type adsorption equation. For example, Fig. 4 shows the Langmuir plots for the uptake of Eu$^{3+}$ ions on the microcapsule. A fairly linear relation between $C_{eq}/Q_{eq}$ and $C_{eq}$ was obtained from Langmuir plots with correlation coefficient of 0.98. The maximum uptake capacity of Cs$^+$, Sr$^{2+}$, Y$^{3+}$ and Eu$^{3+}$ ions, $Q_{max}$, were estimated to be 0.063, 0.011, 0.051 and 0.149 mmol/g, respectively.

3.5 EPMA Observation of Various Metal ions in Microcapsules

The granule of microcapsule was contacted with a mixed solution containing Cs$^+$, Sr$^{2+}$, Co$^{2+}$, Y$^{3+}$ and Eu$^{3+}$ ions (each 200 ppm). The cross section of the microcapsule was then analyzed with EPMA. Figure 5 shows the SEM image of the cross section of the microcapsule. In the cross section, relatively large aggregates of NiFC crystals for size 50~200 μm, small aggregates of CP and oil drops of DEHPA below 10 μm are seen to be encapsulated in the granule. Figure 6 shows the energy dispersive spectra (EDS) of NiFC particle, indicating the incorporation of Cs$^+$ ions. The classification of the distribution of metal ions for each material enclosed in the microcapsule was as follows: NiFC: Cs$^+$; CP: Cs$^+$; DEHPA: Y$^{3+}$, Eu$^{3+}$; NiALG: Sr$^{2+}$, Y$^{3+}$, Eu$^{3+}$.

References