



Adsorption characteristics of gadolinium and dysprosium with microcapsules containing an extractant



Kazuo Kondo*, Masashi Umetsu, Michiaki Matsumoto

Department of Chemical Engineering and Materials Science, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan

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ABSTRACT

The adsorption and separation of gadolinium and dysprosium from aqueous solution were conducted using microcapsules containing a metal extractant, dibenzoylmethane as an extractant. The spherical microcapsules with an average diameter of 196 μm were prepared through encapsulation of the extractant by *in situ* radical polymerization of divinylbenzene. The results for adsorption equilibrium of each metal were applied to the Langmuir adsorption isotherm model to explain the experimental results. The extent of metal adsorbed on the microcapsules increased as the pH of the metal solution increased. In a binary system of gadolinium and dysprosium, only dysprosium was adsorbed on the microcapsules at pH 6.0; this shows that the separation of these metals can be achieved at pH 6.0. The adsorption rate of the metals was also measured, which indicated that the metal complex formation reaction and the diffusion of the metal complex through the pores of the microcapsules contributed to the overall adsorption process of the metals.

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1. Introduction

In recent years, several metals have been in great demand for various fundamental materials. In particular, rare earth metals play very important roles as components in light emissive material, permanent magnets, and catalysts. Most demands for gadolinium and dysprosium are as contrast media for examinations of MRI and optical magnetic disks, respectively. However, rare earth metals and some other valuable metals can not be obtained as raw materials in Japan. Therefore, it has become more important to recover such valuable metals from waste materials.

The increase in the industrial demand for rare earth metals will result in an increased need for their recycling. Dilute aqueous solutions containing such metals can be obtained from industrial waste treatment processes. Therefore, it is important to develop technologies for the recovery and separation of rare earth metals from such dilute solutions.

Solvent extraction methods have generally been used for the recovery of metals from dilute solutions [1]. However, the separation of aqueous and organic phases after extraction is often difficult with this method. Moreover, the conventional solvent extraction technique has some disadvantages, such as the use of a large

amount of reagent [2], the formation of secondary phases, and the difficulty of back extraction.

For the last several decades, alternative solvent extraction techniques for the recovery of metals from dilute solutions have been developed. Supported liquid membranes [3], emulsion liquid membranes [4], solvent impregnated resins [5], and microcapsules (hereafter, MC) containing a metal extractant [6] are typical examples. Among these techniques, we have investigated microcapsules for the recovery and separation of rare metals and lanthanides [7,8]. The metals are extracted by the microcapsules to achieve quite high loadings and they can be easily back-extracted with an acidic solution.

We now propose the use of microcapsules as a new alternative technological method for the recovery and separation of rare earth metals. The use of polymeric materials that contain a selective extractant offers some advantage over the use of solvent extraction techniques [9–12]. In the work reported so far, the extractants impregnated in microcapsules are limited to acidic organophosphorus compounds or long-chain alkyl amines. The author previously carried out the extraction of copper with dibenzoylmethane as an extractant [13]. In this study, the adsorption equilibrium of gadolinium and dysprosium was measured using the microcapsules containing dibenzoylmethane and the adsorption rate of the metals was also measured to clarify the extraction mechanism as well as study this industrial application.

* Corresponding author.

E-mail address: kkondo@mail.doshisha.ac.jp (K. Kondo).

Nomenclature

A_{MC}	effective surface area
C_{eq}	metal concentration at equilibrium
D	distribution ratio of metal
E_a	apparent activation energy
K	extraction equilibrium constant or adsorption equilibrium constant
k	reaction rate constant
m, n	reaction order
q_{eq}	amount of metal adsorbed at equilibrium
q_{max}	maximum amount of metal adsorbed
$R_{0,MC}$	initial adsorption rate of metal
T	temperature
t	time
w	weight of microcapsule

2. Experimental

2.1. Reagents

Dibenzoylmethane (DBM) was purchased from Wako Pure Chemical Industry Co. Ltd. in Japan and used without further purification. For microencapsulation, divinylbenzene (DVB) was employed as a monomer to form the shell of the microcapsules. Toluene was used as the diluent for the extractant. 2,2-Azobis(2,4-dimethylvaleronitrile) (ADV N) was used as the polymerization initiator. ADV N is a special grade chemical and was used without further purification.

Aqueous solutions of the metals were prepared by dissolving $GdCl_3 \cdot 6H_2O$ and/or $DyCl_3 \cdot 6H_2O$ in a hydrochloric acid and sodium acetate mixture solution to produce a desired concentration. These reagents were analytical grade.

2.2. Preparation of the microcapsules

The reactor used for preparation of the microcapsules was a mixing vessel with four baffle plates and a capacity of 1 dm^3 . The continuous phase was 900 g of distilled water containing 2% w/w Arabic gum to act as a dispersion stabilizer. The continuous phase was stirred in the vessel using a flat paddle. After the temperature of the continuous phase reached 343 K, the dispersed phase consisting of DVB, ADV N, toluene, and the extractant was added to the continuous phase. The reactor was purged with nitrogen gas and the contents were agitated at 300 rpm for 3 h at 343 K under a nitrogen atmosphere to produce the MC through the *in situ* radical polymerization of DVB. The conditions used for the preparation of MC containing DBM are shown in Table 1. The obtained MC were collected by suction filtration, washed with distilled water, and then dried at room temperature. The MC was then screened using sieves with mesh sizes of 150–210 μm . The sizes of the resultant particles were then measured with a laser diffraction particle size analyzer (SALD-2000A, Shimadzu Co. Ltd., Japan).

Table 1
Conditions for the preparation of MC.

	Materials	Weight or volume
Continuous phase	Distilled water	882 g
	Arabic gum	18.0 g
Dispersed phase	DVB	15.0 g
	ADV N	3.6 g
	DBM	12.0 g
	Toluene	50.0 cm^3

The DBM content in the MC was measured as follows. Microcapsules of mass 0.1 g and 50 cm^3 of toluene were injected in a multiple-dose container and shaken for 48 h at 100 rpm and 303 K. After that, the mixture was filtered and the DBM concentration in the toluene solution was measured by ultra-violet and visible spectrophotometry (SHIMADZU UV-2500PC) from which the DBM content in the MC was calculated.

2.3. Solvent extraction

The aqueous solution was prepared by dissolving $GdCl_3 \cdot 6H_2O$ and/or $DyCl_3 \cdot 6H_2O$ in a hydrochloric acid and sodium acetate mixture solution to produce a concentration of 1.0 mmol/dm^3 . The pH of the solution was adjusted using 0.1 mol/dm^3 sodium chloride and sodium acetate mixture solution. The organic solution was prepared by dissolving DBM in heptane of analytical grade such that the DBM concentration was 30 mmol/dm^3 . Aqueous solution of 20 cm^3 and organic solution of 20 cm^3 were injected in an Erlenmeyer flask and shaken for 48 h at 100 rpm at 303 K. After that, the metal ion concentration in the aqueous phase was determined by inductively coupled plasma spectrometry (Shimadzu ICPS-8000, ICP-OES).

2.4. Metal adsorption equilibrium

2.4.1. Effect of pH

The adsorption behavior of Gd and Dy onto the MC containing DBM was examined batchwise. In a single metal system, the metal ion concentration was adjusted to 1.0 mmol/dm^3 for each metal ion. In a binary metal system, the metal ion concentration was adjusted to 0.5 mmol/dm^3 for each metal ion. Thus, the total metal concentration was 1.0 mmol/dm^3 . The pH of the aqueous solution was adjusted in a similar way to that described above. 10 mL of a metal solution and 0.1 g of MC were shaken together in a test tube at 303 K over 60 h at 100 rpm to attain adsorption equilibrium.

The metal concentrations in the aqueous solutions before and after adsorption were measured using ICP-OES. The metal adsorbed onto the MC was calculated from the mass balance difference before and after equilibrium.

2.4.2. Effect of metal concentration

In this experiment, the metal concentration was adjusted to $0.5\text{--}5.0 \text{ mmol/dm}^3$ for each metal ion. The pH of the aqueous solution was adjusted to 7.0 at equilibrium using a 0.1 mol/dm^3 sodium chloride – sodium acetate mixture solution. The other experimental procedure was the same as that mentioned above.

2.5. Metal adsorption rate

2.5.1. Effect of temperature

The adsorption rates of Gd and Dy onto the MC were measured varying the solution temperature (303–323 K). The metal solution was prepared in a similar way to that described in the metal equilibrium experiment.

The pH of the aqueous solution was adjusted to 7.0 using 0.1 mol/dm^3 sodium chloride – sodium acetate mixture solution. Ten milliliters of the aqueous solution and 0.1 g of MC were shaken together in a test tube at 150 rpm. After a periodical adsorption time, the aqueous solution was filtered and the metal concentration was determined. The same experiment as above was carried out under the condition of infinite agitation speed.

2.5.2. Effect of metal concentration

In this experiment, the metal adsorption rate was measured while varying the initial metal concentration ($1.0\text{--}5.0 \text{ mmol/dm}^3$).

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