Article

Evaluation of the Scandium Affinity under the Iron Coexistence Using Radiation Grafted Adsorbents

Natsuki HAYASHI^{1*}, Hiroyuki HOSHINA², Haruyo AMADA², Takeshi YAMANOBE¹
and Noriaki SEKO^{1,2}

¹*Division of Molecular Science, Faculty of Science and Technology, Gunma University, Japan*

²*Environmental Polymer Group, Quantum Beam Science Center, Sector of Nuclear Science Research, Japan Atomic Energy Agency, Japan*

(Manuscript received May 30, 2014; Accepted August 11, 2014)

Abstract

Fibrous phosphoric acid adsorbents for scandium were synthesized using two methods; by radiation-induced graft polymerization of glycidyl methacrylate (GMA) with subsequent chemical modification (GMA-gP), and by direct radiation grafting with phosphoric monomer having both vinyl and phosphoric groups (HMP-g) onto a polypropylene coated by polyethylene nonwoven fabric. The resulting grafted fibrous adsorbent, HMP-g, having the grafted long side chain, has high affinity for scandium (Sc(III)) adsorption even under the coexistence with Fe(III) ion. The breakthrough capacity for 0.5 ppm Sc(III) solution with Fe(III) interference was 10.9 $\mu\text{mol-Sc(III)/g-adsorbent}$ for GMA-gP, and 17.8 $\mu\text{mol-Sc(III)/g-adsorbent}$ for HMP-g, respectively.

Keywords: Radiation Grafting, Scandium, Phosphoric adsorbent

1. Introduction

Rare metals are essential to modern life and are indispensable to industrial development in Japan. In particular, scandium, Sc, which is a kind of rare-earth element, is widely applied as an industrial key material in products such as battery separator or metal halide lamp¹⁾. Currently, most of the rare-earth elements are imported. From the view point of stockpiling, Japanese focused on recovering these elements from water streams, such as hot springs²⁾, and from urban mines which also contain different kinds of rare-earth metals. If we can successfully collect these metals, it will contribute to the security of metal resource supply. In order to collect such metals from urban mines, strong acids are commonly used to elute them in aqueous media. However, other heavy metals which are non-valuable such as ferric ion, Fe(III), are also eluted at the same time. It is desirable to establish a system for enhancing scandium uptake from hot spring waters which

contain iron as interfering element or to separate and purify neodymium or dysprosium from scandium and iron contaminated waters. Hence, it is important to develop an adsorbent with high resistance towards the acidic eluting solution and with high affinity for the target metal ion.

In order to overcome these demands, a fibrous phosphoric adsorbent was synthesized by radiation graft polymerization. The adsorbents prepared by this method are superior to those prepared in another way because new functions can be imparted to conventional polymer materials while maintaining its original properties. Specifically, hydrophilic trunk materials can be applied because the target ion is in aqueous media and the shape of material can be changed which prevents the deterioration of adsorption performance from increase in water pressure. Nonwoven fabric, a kind of fibrous material used as trunk polymer, provides rapid treatment performance of aqueous media due to high void fraction^{3,4)}. Irradiation of

* Corresponding author. Fax.: 81 27 346 9381

E-mail: seko.noriaki@jaea.go.jp (N. Seko).

nonwoven fabrics with electron beam creates active sites which can initiate graft polymerization when exposed to the monomer solution. This method is advantageous compared to other techniques because it can be performed at room temperature and without using chemical catalyst⁵.

The objective of this work is to synthesize two types of adsorbents containing phosphoric functional group, which has good affinity for Sc(III), by radiation graft polymerization to establish an environment friendly method for recovery of rare-earth metals, and to store the metals for the future supply.

2. Experimental

2.1 Preparation of Grafted Adsorbents

2.1.1 Preparation of GMA-gP

Polypropylene coated polyethylene nonwoven fabric (NF) obtained from Kurashiki Textile Manufacturing Co., Ltd. was used as trunk material for radiation graft polymerization. The NF with 0.1 mm apparent thickness was cut into 5×8 cm and sealed in polyethylene bag, purged with nitrogen gas, and irradiated with electron beam of 2 MeV energy and 3 mA current at dry ice temperature. The irradiated NF was put into a glass ampoule and the air inside the ampoule was immediately evacuated by a vacuum pump. In this work, we synthesized two types of phosphoric adsorbents. For the first one, the NF was irradiated to a total dose of 20 kGy and grafted in 5% glycidyl methacrylate (GMA) aqueous emulsion composed of 94.5% distilled water and 0.5% Tween20 for 1 h at 40 °C⁶. After grafting, the GMA-grafted NF was rinsed with methanol and distilled water to remove residual GMA monomer and homopolymer. After drying the GMA-grafted NF under reduced pressure, the amount of GMA grafted on trunk NF was calculated and expressed as degree of grafting (Dg). Dg was defined by the following equation:

$$Dg [\%] = 100 [(W_1 - W_0) / W_0] \quad (1)$$

where W_0 is weight of NF before grafting and W_1 that after grafting.

The GMA-grafted NF was reacted with 98% phosphoric acid for 2 h at 80 °C to introduce phosphoric group by ring opening reaction with the epoxy unit on the GMA-grafted NF. The phosphorylated of GMA-grafted NF is hereinafter referred to as GMA-gP adsorbent.

2.1.2 Preparation of HMP-g

The other type of adsorbent was prepared as follows. The NF irradiated to 20 kGy was grafted for 3 h at 60 °C in phosphoric monomer aqueous solution which contains vinyl bonds and pendant phosphoric group in the monomer (HMP) composed of 2-hydroxyl methacrylic phosphoric acid di-ester (50%) and mono-ester (50%) as shown in **Fig. 1**. It is well known that an ester compound undergoes hydrolysis in acidic medium. In this

Fig.1 Structure of phosphoric monomers.

experiment, HMP having both mono- and di-ester structure was selected to prevent the ester hydrolysis group⁷. By the introduction of mono-ester and di-ester, its acid resistance would be increased due to forming a network structure among intermolecular. The ester bond does not be decomposed under the acid condition, therefore. The HMP monomer solution was prepared by dilution with distilled water to make a 20 wt% solution. After grafting, the HMP-grafted NF (HMP-g) was rinsed similar to the GMA-gP treatment, and the Dg value was obtained from equation (1). Each monomer solution was emulsified with homogenizer and purged with N₂ gas⁸.

2.2 Adsorption Tests

The adsorption performances of both grafted phosphoric adsorbents in acidic media were evaluated by batch and column mode adsorption. In the batch adsorption test, 0.01 g adsorbent was put into a 50 ml of 0.5 ppm Sc(III) solution which also contains 0.5 ppm Fe(III) ion. The pH of solution was adjusted by adding nitric acid to mimic the urban mine solution, and the most suitable pH condition in acidic media to adsorb of Sc(III) was determined. After mixing in the metal solution for 2 h, the adsorbents were removed from the solution and the remaining metal concentration was measured by inductively coupled plasma atomic emission spectrometry (Perkin Elmer Co., Ltd., ICP-AES). Adsorption performance was expressed by the following equations;

$$Adsorption [\%] = 100 [(A_1 - A_0) / A_0] \quad (2)$$

Distribution coefficient

$$= (mg-metal \text{ per } g-adsorbent) / (mg-metal \text{ per } g-solution) \quad (3)$$

where A_0 and A_1 are the metal concentrations before and after batch adsorption, respectively.

To evaluate the adsorption capacity, a solution containing 0.5 ppm of each metal was pumped into a column with 7 mm inner diameter and packed with either 5 pieces of GMA-gP or 10 pieces of HMP-g. The total adsorbent volume was adjusted to 0.12 cm³. The column mode adsorption of Sc(III) at pH 2.9, which has the highest performance of pH dependency, were tested under the coexistence with Fe(III) ion at a space velocity (SV) 250 h⁻¹. The SV was calculated by dividing the flow rate of solution by the adsorbent volume in the column. The outflow

solution was fractionally collected by a fraction collector. The

breakthrough point was defined when the concentration at the outlet reached 5% of that at the inlet. The breakthrough capacity of the adsorbent for metal was calculated as the following equation;

$$\text{Breakthrough capacity [mol/kg]} = \int_0^{V_{0.05}} (C_0 - C) dV / W_g \quad (4)$$

where C_0 , C , V and $V_{0.05}$ are the metal concentrations of the feed and effluent, effluent volume and effluent volume when C/C_0 reaches 0.05, respectively. W_g is the weight of the phosphoric adsorbent.

2.3 Characterization of Phosphoric Adsorbent

The grafted NFs were characterized by using FTIR spectrometer (Perkin Elmer Co., Ltd., Spectrum One) with sapphire attenuated total reflectance (ATR) attachment.

The thermogravimetric analyses were performed using a TGA analyzer (SEIKO Instruments Inc., TG-TDA 6200). Thermogravimetric measurements were performed under dry state and nitrogen atmosphere with 10 °C/min heating rate.

The water content of the both phosphoric materials was determined as the following equation;

$$\text{Water content [\%]} = 100 [(W_w - W_d) / W_d] \quad (5)$$

where W_w and W_d are the weight of each phosphoric adsorbent in the wet and dry condition, respectively.

3. Result and Discussion

3.1 Fibrous Phosphoric Grafted Adsorbents

The conditions of grafting, chemical modification and resulting Dg were listed in **Table 1**. In the graft polymerization, both Dg's increased monotonously with grafting reaction time. The Dg's of the GMA-gP and HMP-g were 267% and 194% at reaction times of 1 h and 3 h, respectively. The epoxy groups were modified to phosphoric groups by reaction with phosphoric acid. The functional group density of the GMA-gP was 2.1 mmol/g-adsorbent while that of HMP-g was 1.2 mmol/g-adsorbent. The evidences for introduction of phosphoric group for GMA-gP and HMP-g was shown by IR spectroscopy. **Fig. 2** shows the FTIR spectra of trunk NF, GMA-gP and HMP-g. The trunk NF and the two adsorbents have a common absorption band around 3000 cm^{-1} . It is probably due to vibration of C-H bond in the trunk NF. The peaks at 1730, 1250 and 1150 cm^{-1} were corresponding to C=O, P=O and O-P-O bands appeared for both adsorbents⁷⁾.

3.2 Batch Adsorption of Sc(III) and Fe(III)

The effect of pH on Sc(III) adsorption in the acidic solution was studied by batch mode adsorption. The HMP-g adsorbent

Table 1 Grafting conditions for phosphoric adsorbents

	GMA-gP ⁶⁾	HMP-g
Concentration	GMA 5%	HMP 20%
Solvent	Tween20 0.5% distilled water 94.5%	distilled water 80%
Grafting Time	1 hour	3 hours
Grafting Temp.	40 °C	60 °C
Degree of Grafting	267%	194%

Fig.2 FTIR spectra of (A) trunk material, (B) GMA-gP, (C) HMP-g.

was mixed in a Sc(III)/Fe(III) solution with 0.5 ppm concentration from pH 1 to 3. Almost 90% of Sc(III) was removed by the adsorbent after 2 h. The selectivity of the adsorbent was evaluated by calculating the distribution coefficient given by equation (3).

Fig. 3 shows the effects of pH on the distribution coefficients for Sc(III) and Fe(III) of both phosphoric adsorbents. The highest distribution coefficient was attained at pH 3. Although the distribution coefficient values for GMA-gP were almost similar with very minimal differences, the values for HMP-g showed significant differences on the pH range studied. In the individual adsorption test that was carried out for each metal, the distribution coefficient value of HMP-g were 6.9×10^4 for Sc(III) and 3.4×10^3 for Fe(III), respectively. This result indicated that HMP-g adsorbent also has almost similar affinities towards Sc(III) and Fe(III). However, when Sc(III) and Fe(III) are both present in the solution, the obtained distribution coefficients were 1.9×10^6 and 2.2×10^4 for Sc(III) and Fe(III), respectively. The water contents of GMA-gP and HMP-g were 58% and 102%, respectively, showing almost 2 times difference. This indicated that the hydrophilicity of

HMP-g is higher than that of GMA-gP, then a surface diffusion on grafted side chain was also faster. This result implied that the grafted side chain of HMP-g could be longer than GMA-gP one. As a result, HMP-g adsorbent had higher affinity for Sc(III) than GMA-gP adsorbent.

3.3 Column Mode Adsorption

The column mode adsorption tests were performed by supplying a feed solution containing 0.5 ppm of Sc(III) and Fe(III) with pH 2.9 through an adsorbent packed column with continuous flow at $SV\ 250\ h^{-1}$. The result of the column mode adsorption tests were shown in Fig. 4 as breakthrough curves. Breakthrough curve is the relation of bed volume (BV) and C/C_0 which is the concentration ratio of the Sc(III) and Fe(III) solution before (C_0) and after (C) passing the column respectively. BV's at breakthrough point were 422 on Sc(III) and 524 on Fe(III) for GMA-gP and 655 on Sc(III) and 547 on Fe(III) for HMP-g. The calculated breakthrough capacities were $10.9\ \mu\text{mol-Sc(III)/g-adsorbent}$ and $10.2\ \mu\text{mol-Fe(III)/g-adsorbent}$ for GMA-gP, while for HMP-g, the breakthrough capacities were $17.8\ \mu\text{mol-Sc(III)/g-adsorbent}$, $10.2\ \mu\text{mol-Fe(III)/g-adsorbent}$. From this result, the adsorption rate of HMP-g was higher than that of GMA-gP. In addition, the adsorption saturated capacities of HMP-g were $90.0\ \mu\text{mol-Sc(III)/g-adsorbent}$, $51.0\ \mu\text{mol-Fe(III)/g-adsorbent}$, respectively. Although both adsorbents have phosphoric groups, the selectivity of HMP-g for Sc(III) has improved in comparison to GMA-gP. In the case of HMP-g, it has di-ester group in monomer so the resulting grafted adsorbent has become a network structure suitable for Sc(III) adsorption. The high durability under acidic solutions could be deduced from the TGA analysis. Degradation steps of the grafted materials normally have two steps, with the first stage corresponding to the degradation of the grafted side chain. The difference of degradation temperature between the two phosphoric adsorbents was $11\ ^\circ\text{C}$. Since the heat stability of HMP-g is higher than that of GMA-gP one, the adsorption performances in acidic solution could be expected.

References

- 1) T. Yoshida, Recycling of precious and rare metals, NTS, (2007) (in Japanese).
- 2) N. Seko, H. Hoshina, N. Kasai, Y. Ueki, M. Tamada, T. Kiryu, K. Tanaka and M. Takahashi, J. Ion Exchange, 21, 117-122 (2010).
- 3) N. Kubota, J. Membrane Sci., 22 (5), 271-277 (1997)
- 4) T. Shinohara, T. Fukuoka, T. Katoh and T. Mukaiyama, Basic knowledge for nonwoven fabric, Nikkan Kogyo Shinbun, (2012) (in Japanese).
- 5) K. Saito, M. Ito, H. Yamagishi, S. Furusaki, T. Sugo and J. Okamoto, Ind. Eng. Chem. Res., 28, 1808 (1989).
- 6) Y. Ueki, N. C. Dafader, H. Hoshina, N. Seko and M. Tamada, Radiat. Phys. Chem., 81, 890 (2012).
- 7) F. Basuki, N. Seko, M. Tamada, T. Sugo and T. Kume, J. Ion Exchange, 14 (Suppl.) 209 (2003).
- 8) N. Seko, N. T. Y. Ninh and M. Tamada, Radiat. Phys. Chem., 79, 22 (2010).

Fig. 3 Effect of pH on distribution coefficient for HMP-g adsorbent in 0.5 ppm Sc(III) solution under coexistence with Fe(III) (●: Sc(III), ▲: Fe(III)) and for GMA-gP adsorbent in 0.5 ppm Sc(III) solution under coexistence with Fe(III) (○: Sc(III), △: Fe(III)).

Fig.4 The adsorptive behavior of GMA-gP (●: Sc(III), ▲: Fe(III)) and HMP-g (○: Sc(III), △: Fe(III)) on 0.5 ppm Sc(III) solution under coexistence with Fe(III) at original pH.