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Ion Imprinted Polymer Solid Phase Extraction (IIP-SPE) for Preconcentrative Separation of Erbium(III) From Adjacent Lanthanides and Yttrium

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Abstract: Erbium(III) ion imprinted polymer (IIP) materials were prepared by photochemical polymerization of the ternary complex, Erbium(III)—5,7-dichloroquinoline-8-ol-4-vinylpyridine, with methyl methacrylate (functional monomer) and ethylene glycol dimethacrylate (crosslinking monomer) in the presence of 2,2′-azobisisobutyronitrile (initiator). The synthesis was carried out in 2-methoxy ethanol (porogen) medium and the resultant material was filtered, dried and powdered to form unleached polymer particles. The imprint ion (erbium(III)) was removed by stirring the above particles with 6 mol/l HCl to obtain leached polymer particles. These leached particles are termed erbium(III) ion imprinted polymer (IIP) particles as it selectively rebind erbium(III) ions. Non-imprinted/control polymer (CP) particles were similarly prepared without the imprint ion. CP and unleached and leached IIP particles were characterized by XRD, microanalysis, and UV-visible spectrophotometric studies. Various parameters that influence ion imprinted polymer—solid phase extraction such as pH, weight of polymer particles, preconcentration time, elution time, eluent volume, and aqueous phase volume were varied and optimal conditions for each parameter for quantitative enrichment of erbium(III) were established. The selectivity coefficients of erbium(III) ion over Y, Dy, Ho and Tm were compared with separation factors reported for two of the best liquid—liquid extractants viz. di-2-ethylhexyl phosphoric acid and 2-ethylhexyl-ethylhexyl phosphate.

Keywords: Preconcentrative separation, ion imprinted polymer, erbium(III), synthesis, solid phase extraction

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INTRODUCTION

The separation of lanthanides is one of the challenging tasks for inorganic chemists as they possess identical chemical and physical properties. Ion exchange is the traditionally used method for the separation of individual lanthanides,but has many drawbacks such as tediousness, time consuming and frequent replacement of resins. Liquid-Liquid extraction is replacing other separation methods over the years during the preparation of high purity rare earth oxides as it is simple, rapid, reliable and easy to scale up. The preparation of high purity yttrium oxide (99.9–99.999%) in particular gains importance in view of its widespread use in the manufacture of lasers, superconducting materials and in colour television phosphor materials. The major impurities in 55% Y_2O_3 processed from monazite sand at Indian Rare Earths Limited (IRE), Alwaye are dysprosium and erbium. As the separation factors obtainable by the best liquid-liquid extractants viz. di-2-ethylhexyl phosphoric acid (D2EHPA) (1) and 2-ethylhexyl-2-ethylhexyl phosphonate (EHEHPA) (2) for erbium over yttrium are 1.37 and 1.40 respectively. Hence, it requires 30–40 stages of countercurrent extraction in order to separate erbium from yttrium. Furthermore, the separation factors for erbium over holmium, thulium and dysprosium are also in the range 2.10–5.40 (1, 2). In view of this, it is felt worth while to investigate the separation of erbium(III) from selected lanthanides using ion imprinting process as it offers wide ranging solutions to complex separation problems.

Ion imprinted polymers (IIP) were first introduced by Nishide and his colleagues way back in 1976 (3, 4) who showed for the first time ion templating effect in the synthesis of chelating polymers. They crosslinked a linear chain polymer, poly(4-vinylpyridine) with a bifunctional reagent (dibromoalkane) in the presence of metal ions. Rao et al. (5) reviewed various ion imprinted polymeric materials employed for the solid phase extraction of metal ions. Recently, Araki et al. (6), Vigneau et al. (7), and Gopikrishna et al. (8) have synthesized Gd and Nd IIPs with impressive separation factors over La. Biju et al. (9) have reported better selectivity coefficients for dysprosium ion compared to La, Eu, Nd and Y using Dy IIP particles synthesized by thermal polymerization in the presence of styrene and divinylbenzene as functional and crosslinking monomers respectively. Subsequently, the same authors (10) have reported improved selectivity coefficients by post γ-irradiation of Dy IIP particles. In our recent communications, we have reported the preparation of erbium(III) IIP particles by bulk polymerization via thermal (11) and radiochemical (12) means and have reported better selectivity coefficients compared to commercial liquid-liquid extractants such as D2EHPA and EHEHPA. This paper concerns with photochemical synthesis, enrichment studies and characterization of erbium(III) IIP and non-imprinted or control polymer (CP) particles. In addition to highlighting the imprinting effect, the selectivity coefficients of erbium(III) ion with respect to selected lanthanides were also determined and compared with the separation factors reported using liquid-liquid extraction.

EXPERIMENTAL

Materials

A stock solution of erbium(III) (1000 μg/ml) was prepared by dissolving 0.1144 g of erbium oxide (Rare Earth Products, Cheshire, UK, 99.9%) in 10 ml of hot 50% (v/v) HNO_3 and then diluting to 100 ml with deionized water. Arsenazo I (Aldrich, USA, 0.01%) solution was prepared by dissolving 0.01 g of the reagent in 100 ml of deionized water. A 0.1 mol/l ammonium acetate buffer was used to maintain the pH of the aqueous phase. 5,7-dichloroquinoline-8-ol (DCQ), 4-vinylpyridine (VP) (95%), methylmethacrylate (MMA), ethylene glycol dimethacrylate (EGDMA) and 2,2′-azobisisobutyronitrile (AIBN) were obtained from Aldrich (Milwauke, USA). Stock solutions of yttrium(III), dysprosium(III), holmium(III) and thulium(III) were prepared by dissolving 0.1270, 0.1148, 0.1145 and 0.1142 g of respective oxides (Rare Earth Products, Cheshire, UK, 99.9%) in 10 ml of hot 50% (v/v) HNO_3 and then diluting to 100 ml with deionized water to obtain 1000 μg/ml solutions. All other chemicals used were of analytical reagent grade.

Instrumentation

Absorbances were measured using Shimadzu-UV-2401 PC controlled double beam spectrophotometer (Shimadzu, Japan). A LI-120 digital pH meter (ELICO, India) was used for pH measurements. Rayonet photochemical reactor (The Southern New England Ultraviolet Company, UK) with UV source (300 nm) was used for photochemical polymerization. The X-ray diffraction patterns were obtained using CuKα X-ray source and Philips PW 1710 diffractometer (Holland). The CHN-analysis was carried out using Perkin-Elmer elemental analyzer (Perkin Elmer, USA).

Synthesis of Erbium(III) Ion Imprinted Polymer (IIP) Particles

The synthesis of erbium, yttrium, and holmium IIP particles was carried out by one pot synthesis via photochemical copolymerization of lanthanide-DCQ-VP ternary complex with MMA (functional monomer) and EGDMA (crosslinking monomer) in presence of AIBN as initiator (similar to synthesis procedure described elsewhere for erbium) (13). The imprint ion (1 mmol) (Er or Y or Ho) was complexed with 5,7-dichloroquinoline-8-ol (3 mmol) and 4-vinyl pyridine (2 mmol) in 10 ml of 2-methoxy ethanol by stirring for 2 h in 50 ml round bottom flask. To the above solution, MMA (8 mmol), EGDMA (32 mmol) and AIBN (0.05 g) were added and stirred for further 30 min so as to obtain a homogeneous solution. The pre-polymerization mixtures were then transferred into test tubes, cooled to 0°C, purged with N_2 for 10 min

and sealed with parafilm. This solution was polymerized by subjecting to UV radiation (300 nm) for 15 h to obtain unleached erbium(III) IIP materials ($\sim$6 g). The polymer materials thus formed were washed with water, dried in oven at 60°C and powdered. The synthesis of non-imprinted or control polymer particles (CP) was carried out as above in the absence of imprint ion. IIP and CP particles were synthesized thermally and radiochemically also as reported elsewhere (11–13).

The imprint ion, i.e. Erbium(III)/Yttrium(III)/Holmium(III) were leached from the respective ion imprinted polymer particles by stirring 1 g of the material with 50 ml of 6 mol/l HCl for 6 h. The resultant polymer particles obtained after filtration were dried in an oven at 60°C to obtain leached IIP particles.

General Procedure for Preconcentration of Erbium(III)

A portion of the solution containing <100 μg of erbium(III) was diluted to 200 ml in 500 ml beaker and the pH was adjusted to 8.0 ± 1.0 after the addition of 10 ml of 0.1 mol/l ammonium acetate buffer. 0.075 g of IIP particles were added to the above solution and stirred for 20 min using magnetic stirrer. The enriched erbium(III) ions were eluted from IIP particles using 20 ml of 1.0 mol/l of HCl by stirring for 20 min, filtered through a filter paper and the erbium(III) content in the eluent was determined spectrophotometrically using Arsenazo I procedure described elsewhere (14) by taking 10 ml of aliquots.

Selectivity Studies

100 μg of each lanthanide ion was subjected individually to preconcentration, elution and determination by Arsenazo I procedure by following the method described above.

Constants

The constants such as percent extraction, distribution ratio and selectivity coefficients were determined via triplicate measurements using Arsenazo-I spectrophotometric procedure.

$$\%E = \frac{C_{Ln}^{i} - C_{Ln}^{f}}{C_{Ln}^{i}} \times 100 \quad (1)$$

where C_{Ln}^{i} and C_{Ln}^{f} are the concentrations of lanthanides (mg/l) before and after extraction.

The distribution ratio (D_{Ln}) was determined using C^i_{Ln} and C^f_{Ln}

$$D_{Ln} = \frac{C^i_{Ln} - C^f_{Ln}}{C^f_{Ln}} \times \frac{v}{m} \quad (2)$$

where v is the volume of the solution and m is the mass of the polymer.

Selectivity ($S_{Er/Ln}$) is defined as

$$S_{Er/Ln} = \frac{D_{Er}}{D_{Ln}} \quad (3)$$

where D_{Er} = distribution ratio of erbium(III) ion with CP or IIP at equilibrium, D_{Ln} = distribution ratio of lanthanide(III) ion with CP or IIP at equilibrium.

RESULTS AND DISCUSSION

CP and unleached and leached erbium(III) IIP particles were characterized by X-ray diffraction, microanalysis and UV-visible spectrophotometric studies.

X-ray Diffraction

The peaks obtained at 2θ values of 22.28, 25.48, 26.32 and 28.41 in the XRD pattern of erbium(III)-DCQ-VP ternary complex (pattern A) were noticed in that of unleached erbium IIP particles alone (pattern C) and were absent in CP (pattern B) and leached IIP (pattern D) particles (See Fig. 1). These data indicate the complete removal of erbium(III) ions during leaching with 50 ml of 6 mol/l HCl for 6 h. This observation is analogous to the X-ray diffraction studies conducted on erbium(III) IIP particles obtained by thermal (11) and radiochemical methods (12).

UV-visible Spectrophotometry

UV-visible spectrophotometric determination of erbium(III) ions present in leached solutions of 1.0 g IIP particles with 50 ml of 6 mol l^{-1} HCl for 6 h gave 2 mg/l of erbium indicating the quantitative removal of erbium(III). Furthermore, the absence of 5,7-dichloroquinoline-8-ol in leachant solutions was confirmed by UV-visible absorption spectra of the above solution after raising the pH to $\sim$7.5. These observations confirm the above XRD studies. Again, the above findings are similar to the conclusions arrived in case of thermal (11) and radiochemical (12) methods.

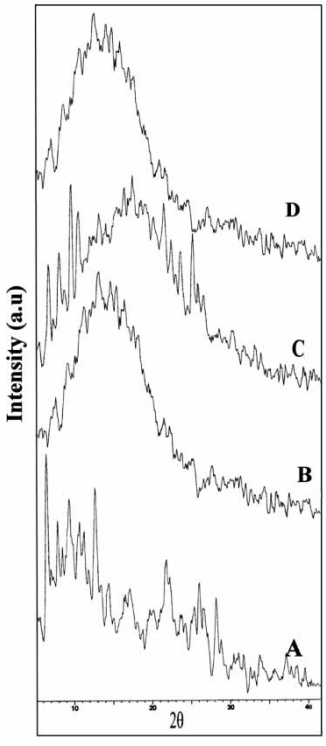

Figure 1. XRD patterns of erbium(III)-DCQ-VP ternary complex (pattern A), Control polymer (pattern B) and unleached (pattern C) and leached (pattern D) IIP particles.

Microanalysis Studies

The results of microanalysis studies of CP and unleached and leached IIP particles are given below:

i. CP, Calculated (%): C, 60.18; H, 6.73; N, 0.87
   Found (%): C, 59.12; H, 7.48; N, 1.04
ii. IIP, Unleached Calculated (%): C, 58.94; H, 6.59; N, 0.86; Er, 2.05
   Found (%): C, 56.42; H, 6.73; N, 1.00; Er, 2.02
iii. IIP, Leached Calculated (%): C, 60.18; H, 6.73; N, 0.87; Er, Absent
   Found(%): C, 60.09; H, 7.48; N, 0.66; Er, Not detectable by UV-visible spectrophotometry

The close similarity between calculated and experimentally found values of C, H and N particularly in the case of leached IIP particles indicate that 5,7-dichloroquinoline-8-ol is intact even after subjecting to acid leaching to remove erbium(III) ions. The CHN analysis data obtained in case of

photochemical polymerization method are analogous to the thermal (11) and radiochemical (12) methods.

Optimization of Enrichment and Elution Parameters of Erbium(III) Using CP and IIP Particles During Rebinding

A set of solutions (volume = 200 ml) containing 100 μg of erbium(III) was taken. The pH of the set of solutions was adjusted between 5.0–9.0 and the recommended procedure was applied using CP and leached IIP particles. The enrichment of erbium(III) by erbium IIP particles prepared by photochemical polymerization is constant and maximum in the pH range 7.0–9.0 (See Fig. 2) which is wider than those obtained by thermal (7.2–7.8) (11) and radiochemical (6.7–7.5) (12) methods. The decrease in percent enrichment of erbium at acidities higher than pH 7.0 is due to the competition between H^+ and erbium(III) during rebinding of erbium(III) ions. Again the lower enrichment values >9.0 is due to competition between the formation of erbium(III)—5,7-dichloroquinoline-8-ol-4-vinyl pyridine complex and erbium hydroxide during rebinding. Again the enrichment of erbium(III) is quantitative only with IIP particles. In all the subsequent work, the pH was adjusted to 8.0 ± 1.0 after the addition of 10 ml of 0.1 ml/l ammonium

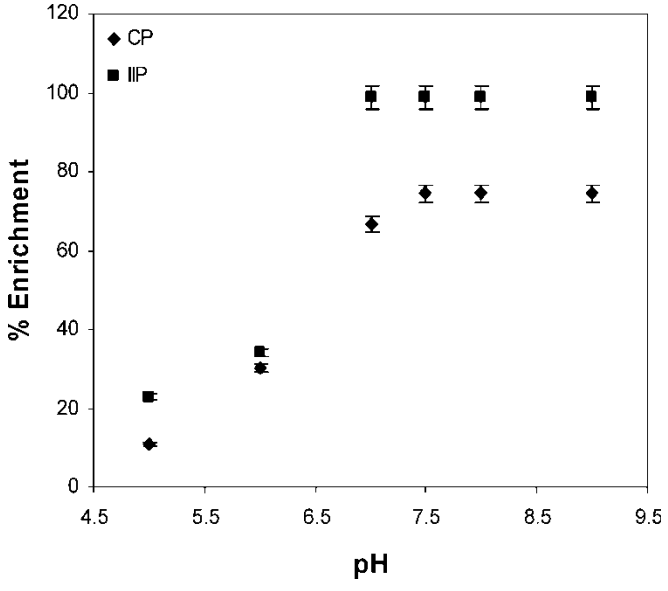

Figure 2. Effect of pH on the preconcentration of 25 μg of erbium(III) ions using leached CP and erbium IIP particles during rebinding (weight of polymer particles = 0.075 g, Aqueous phase volume = 200 ml, Elution time = 20 min, Eluent concentration = 1 mol/l HCl).

acetate buffer. Figure 3 shows the effect of weight of CP and leached IIP particles on the percent enrichment of erbium(III). As seen from Figs. 2 and 3, the imprinting effect is clearly seen at all pHs and weights of polymer particles. Moreover, a minimum of 0.075, 0.05 and 0.2 g of IIP particles obtained by photochemical, thermal (11) and radiochemical (12) polymerization respectively are necessary for quantitative enrichment of erbium(III) ions. Hence, the efficiency of percent enrichment is in the order of thermal > photochemical > radiochemical. This difference in behavior is attributed to the increase in interaction of ternary complex with functional monomer at 80°C compared to room temperature (30°C) synthesis via γ-irradiation. The synthesis due to photochemical irradiation falls between these two extremes as the raise in temperature due to photochemical irradiation is ~50°C (12). Swelling ratio studies carried out as on similar lines as described elsewhere (12) and rebinding studies (15) also explains the difference in behaviour of IIP particles synthesized by thermal, photochemical, and radiochemical means. As seen from Fig. 4, preconcentration and elution times of 20 min each were enough for preconcentration and elution of erbium(III) using leached IIP particles. Twenty minutes of preconcentration and elution times were employed in subsequent studies. Once again, the imprinting effect was noticed in all instances of preconcentration and elution times (See Fig. 4). Other parameters that influence the enrichment of erbium(III) ions viz aqueous phase volume, nature of eluent, eluent concentration and eluent volume with CP and leached IIP particles were systematically varied and

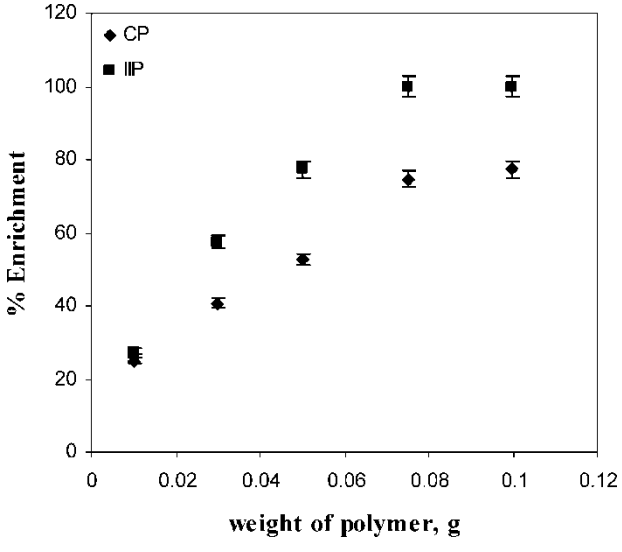

Figure 3. Effect of weight of polymer particles on the preconcentration of 25 μg of erbium(III) ions using CP and leached erbium IIP particles during rebinding (pH 7.5 ± 0.5, other conditions are same as in Fig. 2).

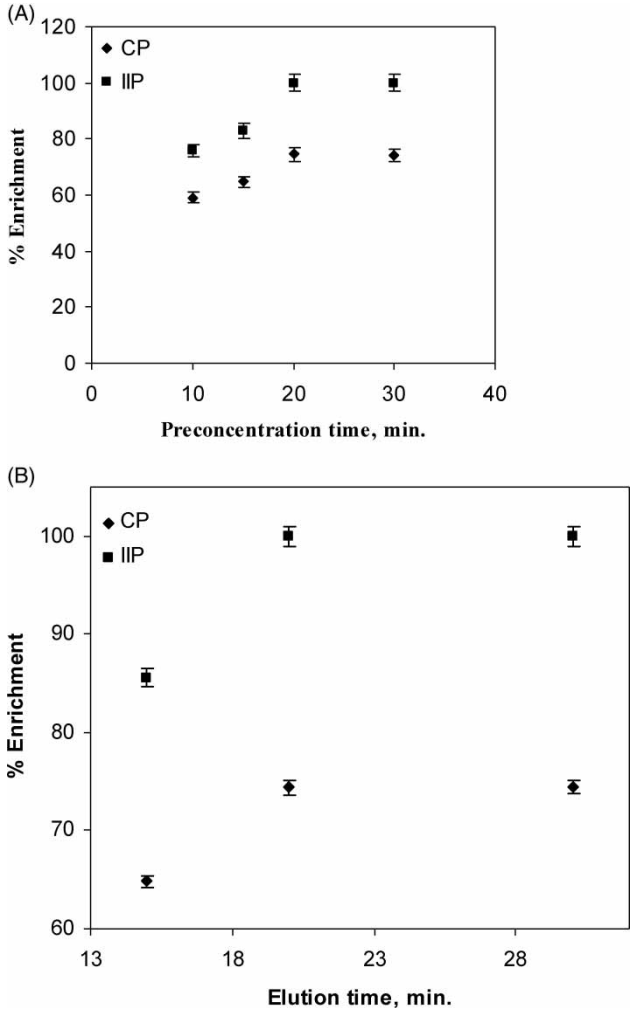

Figure 4. Effect of preconcentration (A) and elution (B) times on the preconcentration of 25 μg of erbium(III) ions using CP and leached erbium IIP particles during rebinding (pH 7.5 ± 0.5), other conditions are same as in Fig. 2.

the results obtained are shown in Table 1. As seen from Table 1, the change of aqueous phase volume from 20 to 200 ml did not affect the preconcentration efficiency of 25 μg of erbium(III) using 0.075 g of IIP particles. The enrichment factor and corresponding lowest concentration below which the recoveries become non-quantitative are 10 and 2 μg per 200 ml respectively. Similar observations were noticed with thermal (11) and radiochemical (12) polymerizations also in case of preconcentration and elution times, aqueous phase volume, enrichment factor and detection limits. Furthermore, it was

Table 1. Influence of various parameters on the percent extraction of 25 μg of erbium(III) with CP and erbium(III) IIP particles (0.075 g of IIP, pH 7.5 ± 0.5, preconcentration time = 20 min, elution time = 20 min, Aqueous phase volume = 200 ml, eluent volume = 25 ml)

S.No.	Parameter	Extraction (%)[a]		Chosen condition
		CP	IIP	
1	Aqueous phase volume (ml)			
	20	74.50	>99	200 ml
	50	74.50	>99	
	100	74.45	>99	
	200	74.42	>99	
	250	54.40	75.56	
2	Nature of eluent			
	1 mol/l HCl	74.50	>99	1 mol/l HCl
	1 mol/l H_2SO_4	68.86	91.49	
	1 mol/l HNO_3	74.50	98.50	
3	Eluent (HCl) concentration (mol/l)			
	0.1	58.63	82.15	1.0 mol/l
	0.5	74.15	>99	
	1.0	74.40	>99	
	2.0	74.45	>99	
4	Eluent volume (ml)			
	10	55.05	74.55	20 ml
	20	74.45	>99	
	25	74.45	>99	

[a]Average of triplicate measurements. The relative standard deviations are less than 5%.

observed that hydrochloric acid alone offers quantitative elution of previously preconcentrated erbium(III). Even though, 0.5 mol/l HCl is enough to elute preconcentrated erbium(III), 1.0 mol/l of HCl was employed in subsequent studies so as to ensure complete elution even at higher amounts of erbium(III). Again, a minimum of 20 ml of 1.0 mol/l of HCl is necessary for quantitative elution of erbium(III) (See Table 1). The examination of analytical data reported above was checked with 3 different batches of CP and leached IIP particles. The results obtained indicate the reproducibility of synthesis procedure.

Retention Capacity Studies

The retention capacity experiments were carried out by equilibrating 0.02 g of erbium(III) IIP or CP particles prepared by thermal, photochemical and radiochemical methods with 1 mg of erbium(III) ion in 25 ml of aqueous solution for 1 h (after

adjusting the pH of the solution to ~8.0) and subsequent elution with 25 ml of 1 mol/l of HCl for 20 min. The results obtained are shown in Table 2 from which it is clear that for erbium(III) IIPs and CPs the retention capacities are in the order thermal > photochemical > radiochemical, which can also be attributed to the reasons mentioned above in case of weight of IIP particles variation.

Statistical and Calibration Parameters

Under the optimal preconcentration conditions described above, the calibration curve was linear over 0 – 100 μg of erbium(III) present in 200 ml of sample solution. Five replicate determinations of 25 μg of erbium(III) present in 200 ml of sample gave mean absorbance of 0.129 with a relative standard deviation of 2.45%. The detection limit corresponding to three times the standard deviation of the blank was found to be 2 μg/200 ml. The linear equation with regression is as follows:

$$A = (0.005 \times C) + 0.004 \quad (4)$$

Correlation coefficient = 0.99984

where A is the absorbance and C is the amount of erbium(III) in μg per 200 ml of solution. All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

Selectivity Studies

The percent extraction and distribution ratios of selected lanthanides (one lanthanide at a time rather than a mixture of lanthanides as the spectrophotometric procedure do not permit) and selectivity coefficients of erbium(III) ion with respect to yttrium and other selected lanthanides using 0.05 g of CP and erbium, holmium and yttrium IIP particles are summarized in Table 3. (This weight was chosen to get reliable selectivity coefficients.) As seen from Table 3, erbium IIP particles alone resulted in significant imprinting effect. On the other hand, holmium and yttrium IIP particles

Table 2. Comparison of retention capacities of erbium(III) IIPs and CPs prepared by various polymerization methods

Nature of polymerization	Retention capacity [mg of erbium(III) per g of the polymer]	
	CP	IIP
Thermal (11)	7.06	11.44
Photochemical	4.89	6.01
Radiochemical (12)	4.77	5.59

Table 3. Percent extraction (%), distribution ratio (D) and selectivity coefficients of CP and yttrium, holmium and erbium IIP particles[a] (0.05 g of polymer, pH 7.5 ± 0.5)

	Percent extraction				Distribution ratio × 10^3 (ml g^{-1})				Selectivity coefficient ($S_{Er/Ln}$)			
		IIP				IIP				IIP		
Element	CP	Y	Ho	Er	CP	Y	Ho	Er	CP	Y	Ho	Er
Y	41.20	44.12	42.50	41.60	1.40	1.58	1.48	1.43	2.71	2.41	2.64	4.80
Dy	56.78	51.79	62.05	61.27	2.63	2.15	3.27	3.16	1.44	1.77	1.20	2.17
Ho	60.83	63.93	63.17	62.12	3.11	3.55	3.43	3.20	1.22	1.07	1.14	2.14
Er	65.45	65.50	66.14	77.42	3.79	3.80	3.91	6.86	—	—	—	—
Tm	69.23	67.41	67.54	68.85	4.5	4.1	4.16	4.42	0.84	0.92	0.94	1.55

[a]Average of triplicate measurements. The relative standard deviations are <5%.

show no imprinting effect, i.e., identical to CP particles, for respective lanthanides. Furthermore, the percent extraction of selected lanthanides viz dysprosium, holmium, erbium, and thulium increases with increasing atomic number or decrease in ionic radii on extraction with CP, Y and Ho imprinted polymers. A similar trend is observed in case of erbium(III) IIP particles also except that there is a significant imprinting effect during rebinding of erbium(III) ions as seen from Table 3. Again, the distribution ratios and $S_{Er/Ln}$ decrease with increase of atomic number or decrease in ionic radii. However, the percent extraction and distribution ratios are considerably less for yttrium and behaves like a lighter lanthanide ions on extraction with CP and Y, Ho and Er IIP particles. The distribution ratios, percent extraction and selectivity coefficients of erbium IIP particles obtained by photochemical polymerization are higher than those obtained by radiochemical polymerization (12). On the other hand, the selectivity coefficients obtained by photochemical polymerization are inferior to erbium(III) IIP particles obtained by thermal polymerization (11). Again, this observation is on similar lines to the trends observed in the optimization of experimental variable and retention capacity studies.

On comparison of selectivity data by control and ion imprinted polymers with the separation factors obtainable by the best liquid cation exchangers viz. D2EHPA and EHEHPA (1,2) reported elsewhere, the following observations can be made. $S_{Er/Ln}$ values determined with CP & Y and Ho IIP particles are lower compared to $\beta_{Er/Ln}$ values of D2EHPA and EHEHPA. On the other hand, erbium IIP particles gave significantly higher selectivity coefficients for erbium with respect to Y and comparable values in case of Ho when compared to D2EHPA and EHEHPA. These observations are attributed to imprinting effect noticed with erbium(III) IIP particles.

CONCLUSIONS

In this paper, we have adopted photochemical polymerization to obtain erbium(III) ion imprinted polymer particles via bulk polymerization using methyl methacrylate and ethylene glycol dimethacrylate as functional and crosslinking monomers. The percent extraction and distribution ratios either increase or decrease respectively with increasing atomic number or decreasing ionic size during rebinding with CP and Y, Ho and Er IIP particles. The only exception being the higher rebinding of erbium(III) with erbium IIP particles which is attributed to imprinting effect. Furthermore, erbium IIP partices gave significantly higher $S_{Er/Y}$ and comparable $S_{Er/Ho}$ values compared to $\beta_{Er/Y}$ and $\beta_{Er/Ho}$ values reported for D2EHPA and EHEHPA.

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REFERENCES

1. Pierce, T.B. and Peck, P.F. (1963) The extraction of lanthanide elements from perchloric acid by Di-(2-ethylhexyl)phosphate. *Analyst*, 88: 217.
2. Reddy, M.L.P., Rao, T.P., and Damodaran, A.D. (1995) Liquid-liquid extraction process for the separation and purification of Rare earths. *Metal Process Extract. Metall. Rev.*, 12: 91.
3. Nishide, H. and Tsuchida, E. (1976) Selective adsorption of metal ions on poly(4-vinylpyridine) resins in which the ligand chain is immobilized by crosslinking. *Makromol. Chem.*, 177: 2295.
4. Nishide, H., Deguchi, J., and Tsuchida, E. (1976) Selective adsorption of metal ions on crosslinked poly(4-vinylpyridine) resin prepared with a metal ion as template. *Chem. Lett.*, 169.
5. Rao, T.P., Sobhi, D., and Gladis, J.M. (2004) Tailored materials for preconcentration or separation of metals by ion-imprinted polymers for solid phase extraction (IIP-SPE). *Trends Anal. Chem.*, 23: 28.
6. Araki, K., Yoshida, M., Uezu, K., Goto, M., and Furusaki, S. (2000) Lanthanide-imprinted resins prepared by surface template polymerization. *J. Chem. Eng. Jpn.*, 33: 665.
7. Vigneau, O., Pinel, C., and Lemaire, M. (2001) Ionic imprinted resins based on EDTA and DTPA derivatives for lanthanides(III) separation. *Anal. Chim. Acta*, 435: 75.
8. Gopikrishna, P., Gladis, J.M., Rao, T.P., and Naidu, G.R.K. (2005) Selective recognition of neodymium(III) using ion imprinted polymer particles. *J. Mol. Recognition.*, 18: 109.
9. Biju, V.M., Gladis, J.M., and Rao, T.P. (2003) Ion imprinted polymer particles: synthesis, characterization and dysprosium ion uptake properties suitable for analytical applications. *Anal. Chim. Acta*, 478: 43.
10. Biju, V.M., Gladis, J.M., and Rao, T.P. (2003) Effect of γ-irradiation of ion imprinted polymer (IIP) particles of the preconcentrative separation of dysprosium from other selected lanthanides. *Talanta.*, 60: 747.
11. Kala, R., Gladis, J.M., and Rao, T.P. (2004) Preconcentrative separation of erbium from Y, Dy, Ho, Tb and Tm by using ion imprinted polymer particles via solid phase extraction. *Anal. Chim. Acta*, 518: 143.
12. Kala, R., Biju, V.M., and Rao, T.P. (2005) Synthesis, characterization and analytical applications of erbium ion imprinted polymer particles prepared via γ-irradiation with different functional and cross linking monomers. *Anal. Chim. Acta,*, 549: 51.
13. Kala, R., Gladis, J.M., and Rao, T.P. (2004) Synthesis of ion imprinted polymer particles for solid phase extractive preconcentration of erbium ions and a process thereof, IPA DEL (2004) dt.27-02-2004 W/O Int PA No.PCT/INO3/00427 dated 31.12.2003.
14. Snell, F.D. (1978) *Photometric and Fluorimetric Methods of Analysis—Metals*, Part 2; John-Wiley and Sons: New York.
15. Kala, R., Babu, P.E.J., and Rao, T.P. (to be communicated) Critical evaluation of binding parameters for erbium(III) ion imprinted polymer particles synthesized by thermal, photochemical and radiochemical polymerization methods.