Extraction of rare earth elements from aqueous solutions using the ionic liquid trihexyltetradecylphosphonium 3-hydroxy-2-naphthoate

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Supplementary material

S1: Remaining mean metal concentrations (± SD) after 1, 2, 4, 6 and 24 hours after extraction at room temperature from 10 mg/L feed solutions for La, Ce, Nd, Ho and Lu (n = 3) and mean extraction efficacies (e.e.) (± SD, n = 3).

	Lanthanum		Cerium		Neodymium	
time (h)	c (mg/L)	e.e. (%)	c (mg/L)	e.e. (%)	c (mg/L)	e.e. (%)
1	7.93 ± 0.18	21.32 ± 1.76	7.78 ± 0.33	16.41 ± 3.55	7.25 ± 0.34	22.61 ± 3.62
2	6.97 ± 0.16	23.55 ± 1.80	6.09 ± 0.38	33.91 ± 4.18	5.94 ± 0.48	38.10 ± 5.04
4	3.81 ± 0.41	60.22 ± 4.28	3.58 ± 0.22	61.67 ± 2.32	3.71 ± 0.21	61.82 ± 2.18
6	2.83 ± 0.36	69.63 ± 3.87	1.88 ± 0.87	79.51 ± 9.50	1.82 ± 0.84	85.63 ± 2.24
24	0.82 ± 0.04	88.80 ± 0.54	0.15 ± 0.02	98.39 ± 0.26	0.15 ± 0.04	98.32 ± 0.41

	Holmium		Lutetium	
time (h)	c (mg/L)	e.e. (%)	c (mg/L)	e.e. (%)
1	8.66 ± 0.25	16.28 ± 2.44	7.13 ± 0.65	25.76 ± 6.81
2	7.55 ± 0.27	27.54 ± 2.62	5.64 ± 0.04	40.91 ± 0.39
4	6.08 ± 0.37	48.69 ± 3.14	3.13 ± 0.08	67.65 ± 0.86
6	3.79 ± 0.39	64.21 ± 3.68	1.25 ± 0.22	87.05 ± 2.30
24	3.74 ± 0.47	62.29 ± 4.76	0.38 ± 0.08	96.17 ± 0.78

S2: Extraction efficacies of the TSIL $[P_{66614}][HNA]$ and of commonly used extractants. The exponents refer to the references in the publication.

Extractant	Type	REE	Efficiency	Reference
CA-12	Carboxylic acid	Y	> 95 %	Li *et al.* 2006[33]
Versatic 911	Carboxylic acid	Ce^{4+}	≤ 100 %	Ray *et al.* 1981[34]
D2EHPA	Organophosphorous acid	La, Ce, Pr, Nd	80 - 100 %	Basualto *et al.* 2013[35]
Cyanex 272	Organophosphorous acid	La, Ce, Pr, Nd	20 – 100%	Basualto *et al*. 2013[35]
TODGA	Glycol amic acid	Lanthanides	91 - 99%	Yuan *et al.* 2018[36]
DODGAA	Glycol amic acid	Lanthanides	≤ 100 %	Shimojo *et al.* 2016[37]
Primene JM-T	Primary amine	Y, Tb, Dy, Ho, Er	64 - 77%	Abreu *et al.* 2014[38]
N1923	Primary amine	REE	90 - 100%	Su *et al.* 2020[39]
$[P_{66614}][HNA]$	TSIL	Lanthanides	62% (Ho) – 98 % (Nd, Ce)	this work

S3: Remaining mean metal concentrations (± SD) after 1, 2 and 4 hours after extraction at 20°C and 30°C from 10 mg/L single element feed solutions for Ce and Nd (n = 3) and remaining mean metal concentrations (± SD) after extraction at 30°C from 10 mg/L double-element feed solutions for Ce and Nd (n = 3), including the respective mean extraction efficacies (e.e.) (± SD, n = 3).

	Cerium		Neodymium		Cerium & Neodymium	
time (h)	c (mg/L)	e.e. (%)	c (mg/L)	e.e. (%)	c (mg/L)	e.e. (%)
	Ce at 20°C		**Nd at 20°C**		**Ce at 30°**	
1	7.78 ± 0.33	16.41 ± 3.55	6.85 ± 0.80	19.87 ± 9.36	3.27 ± 0.45	47.36 ± 7.32
2	6.09 ± 0.38	33.91 ± 4.17	5.50 ± 0.19	35.57 ± 2.22	1.27 ± 0.05	85.92 ± 0.59
4	3.58 ± 0.22	61.67 ± 2.32	3.33 ± 0.19	60.81 ± 2.23	1.16 ± 0.19	86.74 ± 2.14
	Ce at 30°C		**Nd at 30°C**		**Nd at 30°C**	
1	6.98 ± 0.38	24.48 ± 4.07	4.26 ± 0.58	49.58 ± 6.81	3.32 ± 0.49	56.07 ± 6.54
2	5.57 ± 0.22	36.67 ± 2.52	1.68 ± 0.37	80.19 ± 4.39	1.12 ± 0.12	87.88 ± 1.27
4	2.22 ± 0.14	74.47 ± 3.81	0.94 ± 0.05	88.89 ± 0.63	0.85 ± 0.17	90.72 ± 1.83

S4: Mean metal concentrations (± SD) after 24 hours of extraction at room temperature from 10 mg/L double-element feed solutions of the elements La & Lu, La & Nd, Ce & Lu and Ce & Nd (n = 3), including the mean extraction efficacies (e.e.) (± SD, n = 3), and mean metal content (± SD) after back-extraction experiments and the corresponding mean back-extraction efficacy (b.e.e.) (± SD, n = 3).

	Extraction		Back-extraction	
element	c (mg/L)	e.e. (%)	c (mg/L)	b.e.e. (%)
La	0.28 ± 0.11	96.47 ± 1.33	7.35 ± 0.20	75.66 ± 2.03
Lu	0.08 ± 0.01	99.11 ± 0.07	6.79 ± 0.20	68.44 ± 2.09
La	0.16 ± 0.04	97.57 ± 0.67	5.46 ± 0.31	55.52 ± 3.34
Nd	0.04 ± 0.01	98.86 ± 0.01	3.18 ± 0.19	37.81 ± 7.45
Ce	0.10 ± 0.04	98.42 ± 0.65	4.87 ± 0.68	49.21 ± 7.07
Lu	0.10 ± 0.01	97.29 ± 0.40	4.62 ± 0.54	50.49 ± 1.22
Ce	0.15 ± 0.04	98.13 ± 0.44	3.27 ± 0.26	33.21 ± 2.67
Nd	0.07 ± 0.03	99.23 ± 0.30	3.52 ± 0.42	35.44 ± 4.23

S5: Mean (± SD) pH values in the aqueous phases after extraction for 1, 2 and 4 hours for Ce, Nd and Lu, initial pH = 2.5 (n = 3).

	Ce 20°C	Ce 30°C	Nd 20°C	Nd 30°C	Lu rt
time (h)	pH	pH	pH	pH	pH
1	3.06 ± 0.06	2.99 ± 0.04	3.12 ± 0.15	3.92 ± 0.18	2.95 ± 0.05
2	3.50 ± 0.06	3.39 ± 0.03	3.60 ± 0.06	4.18 ± 0.02	3.47 ± 0.02
4	4.42 ± 0.12	4.09 ± 0.04	4.36 ± 0.03	4.04 ± 0.02	4.24 ± 0.02

S6: Mean (± SD) leaching of $[P_{66614}][HNA]$ during extractions at room temperature (23 ± 1 °C) of La, Ce, Nd, Ho and Lu in % (n = 3).

	La	Ce	Nd	Ho	Lu
time (h)	leaching (%)	leaching (%)	leaching (%)	leaching (%)	leaching (%)
1	0.29 ± 0.04	0.54 ± 0.09	0.36 ± 0.05	0.20 ± 0.05	0.62 ± 0.04
2	0.38 ± 0.02	0.92 ± 0.03	0.47 ± 0.04	0.24 ± 0.04	0.94 ± 0.01
4	0.77 ± 0.03	0.96 ± 0.05	0.44 ± 0.08	0.38 ± 0.01	0.88 ± 0.01
6	0.73 ± 0.04	0.99 ± 0.03	0.94 ± 0.03	0.37 ± 0.05	0.51 ± 0.02
24	0.60 ± 0.02	0.94 ± 0.05	1.01 ± 0.04	0.29 ± 0.02	0.49 ± 0.01

S7: Mean (± SD) leaching of $[P_{66614}][HNA]$ during single- and double-element extractions at 20 and 30°C for Ce and Nd in % (n = 3).

time (h)	Ce 20°C leaching (%)	Ce 30°C leaching (%)	Nd 20°C leaching (%)	Nd 30°C leaching (%)	Ce&Nd 30°C leaching (%)
1	0.93 ± 0.03	0.93 ± 0.01	0.73 ± 0.07	0.65 ± 0.01	1.04 ± 0.12
2	1.07 ± 0.03	0.98 ± 0.02	0.88 ± 0.01	0.75 ± 0.02	0.80 ± 0.03
4	1.08 ± 0.08	0.74 ± 0.02	0.89 ± 0.02	0.71 ± 0.02	0.72 ± 0.04

S8: Mean (± SD) leaching of $[P_{66614}][HNA]$ during double-element extractions (e) at room temperature for 24 hours for La & Lu, La & Nd, Ce & Lu and Ce & Nd in % (n = 3) as well as mean leaching (± SD) during back-extraction experiments (b.e., n = 3).

time (h)	La & Lu leaching (%)	La & Nd leaching (%)	Ce & Lu leaching (%)	Ce & Nd leaching (%)
24 (e)	0.78 ± 0.03	0.78 ± 0.01	0.95 ± 0.02	0.70 ± 0.02
2 (b.e.)	0.13 ± 0.01	0.11 ± 0.03	0.09 ± 0.03	0.08 ± 0.01