Electronic supplementary information (ESI)

Adsorption and chromatographic separation of rare earths with EDTA- and DTPA-functionalized chitosan biopolymers

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Synthesis of EDTA bisanhydride

EDTA bisanhydride was synthesized according to a literature method described by Montembault *et al*.[1] EDTA (29.2 g, 0.1 mol), acetic anhydride (37.8 mL, 0.4 mol) and pyridine (48.4 mL, 0.6 mol) were combined in a 500 mL flask, equipped with a condenser and a magnetic stirrer. The reaction was carried out at reflux for 2 hours in an oil bath at 65 °C. Reflux was performed in an inert argon atmosphere, to prevent the reaction from contact with water, present in the air. The resulting brownish yellow bisanhydride was filtered off and washed thoroughly with acetic anhydride (three times) and dry diethyl ether (again three times) giving a creamy white powder, which was dried in a vacuum oven at 40 °C until it had a constant weight. Yield: 99% (25.48 g; 99 mmol). δ_H (300 MHz, DMSO-d_6): 2.67 (4H, m, CH_2-C**H**$_2$-N-CH_2-CO); 3.70 (8H, m, N-C**H**$_2$-CO). δ_C (75 MHz, DMSO-d_6): 51.15 (N-**C**H_2-**C**H_2-N); 52.21 (N-**C**H_2-CO); 165.77 (**C**O-O-**C**O). IR (ATR, cm^{-1}): 1806 (asymmetric C=O stretch anhydride), 1749 (symmetric C=O stretch anhydride), 1250 (C-O stretch), 1062 (C-N stretch), 926 (O-H bend).

Synthesis of DTPA bisanhydride

DTPA bisanhydride was synthesized in a similar way as described for EDTA bisanhydride.[1] DTPA (39.3 g, 0.1 mol) was used, along with acetic anhydride (37.7 mL, 0.4 mol) and pyridine (48.3 mL, 0.6 mol). Yield: 98% (35.01 g; 98 mmol). δ_H (300 MHz, DMSO-d_6): 2.59 (t, J = 6.15 Hz, 4H, CH_2-C**H**$_2$-N-CH_2-COOH); 2.75 (t, J = 6.15 Hz, 4H, C**H**$_2$-CH_2-N-CH_2-COOH); 3.30 (s, 2H, C**H**$_2$-COOH); 3.71 (s, 8H, C**H**$_2$-CO-O-CO). δ_C (75 MHz, DMSO-d_6): 49.85 (CH_2-**C**H_2-N-CH_2-COOH); 51.65 (**C**H_2-CH_2-N-CH_2-COOH); 54.86 (N-**C**H_2-CO); 169.19 (**C**O-O-**C**O); 172.54 (**C**OOH). IR (ATR, cm^{-1}): 1819 (asymmetric C=O stretch anhydride), 1771 (symmetric C=O stretch anhydride), 1683 (C=O stretch carboxylic acid), 1330 (C-O stretch), 1106 (C-N stretch), 943 (O-H bend).

Reference

[1] V. Montembault, J. C. Soutif and J. C. Brosse, *React. Funct. Polym.*, 1996, **29**, 29-39.

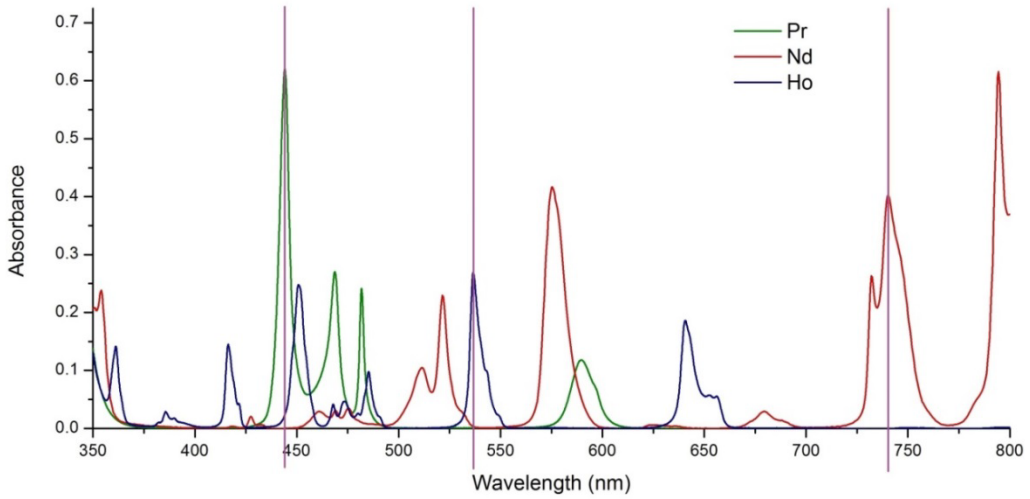

Figure S1: Optical absorption spectra of aqueous solutions (1000 ppm) of Pr^{3+}, Nd^{3+} and Ho^{3+}. The following wavelengths were used for determining the concentrations of the lanthanides: Pr^{3+} (444.0 nm), Nd^{3+} (740.5 nm) and Ho^{3+} (536.5 nm). These wavelengths are indicated by vertical lines in the spectra.

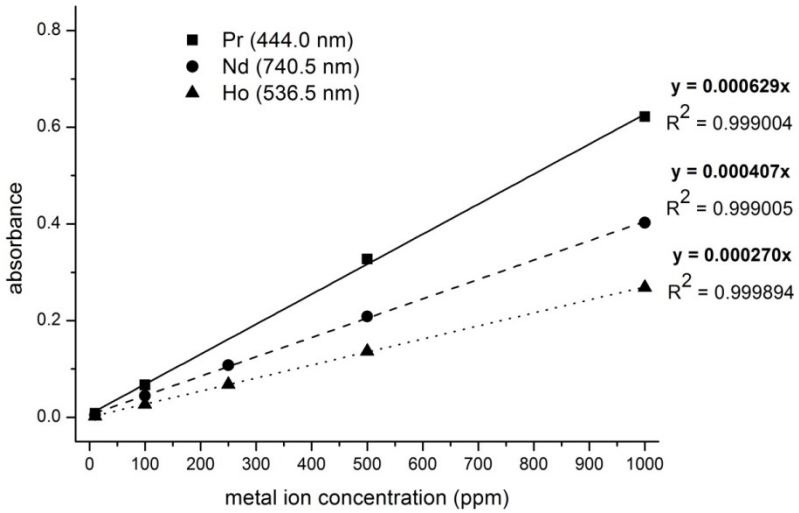

Figure S2: Calibration curves for Pr^{3+} (444.0 nm), Nd^{3+} (740.5 nm) and Ho^{3+} (536.5 nm).

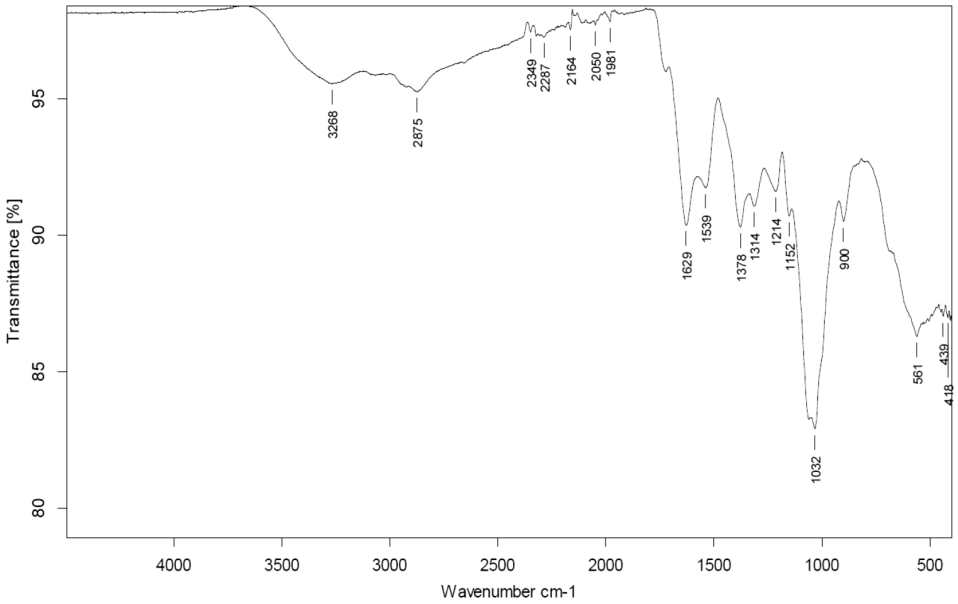

Figure S3: IR-spectrum EDTA-chitosan.

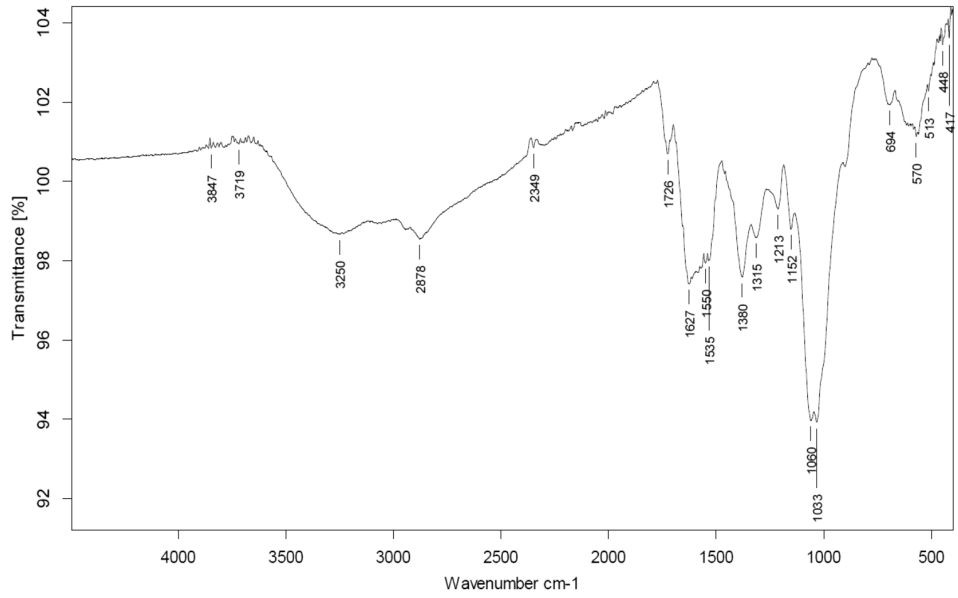

Figure S4: IR-spectrum DTPA-chitosan.

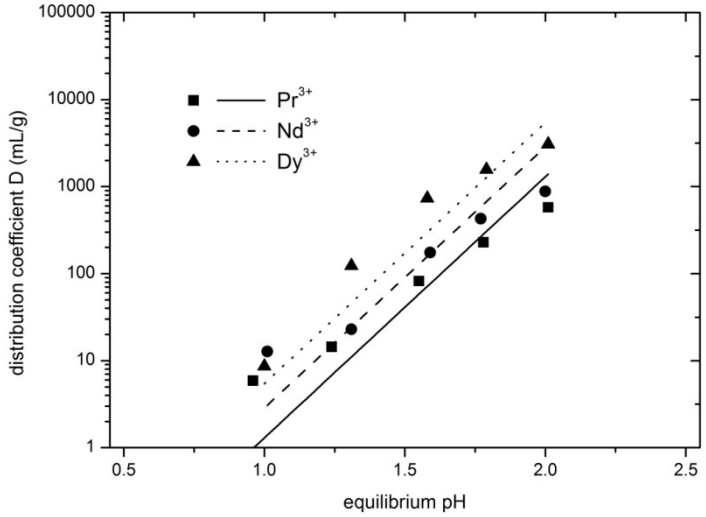

Figure S5: EDTA-chitosan distribution coefficient for some lanthanide ions as a function of equilibrium pH. The data points are linearly fitted with a fixed slope of 3.

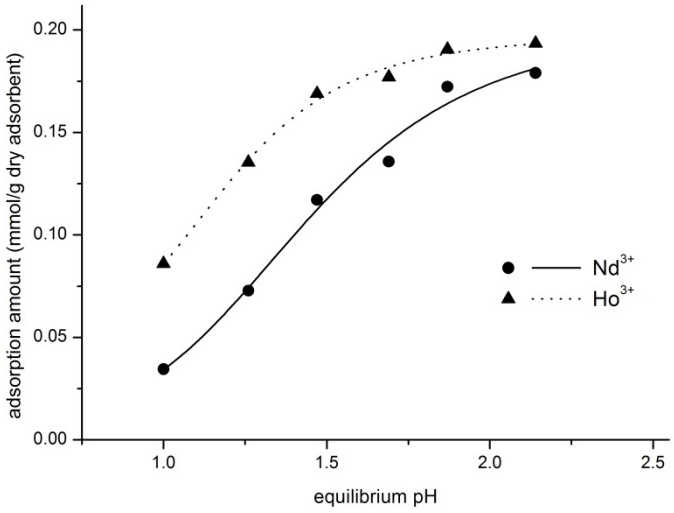

Figure S6: Selective adsorption amount for EDTA-chitosan as a function of equilibrium pH.

Table S1: Efficiency values of DTPA-chitosan for Nd^{3+} adsorption after consecutive regenerations (reuse of DTPA-chitosan).

Experiment	**Adsorption amount** mg Nd^{3+}/g DTPA-chitosan	**Efficiency** **%**
First use	78.6	100.0
First regeneration	77.2	98.2
Second regeneration	75.3	95.8
Third regeneration	74.2	94.4

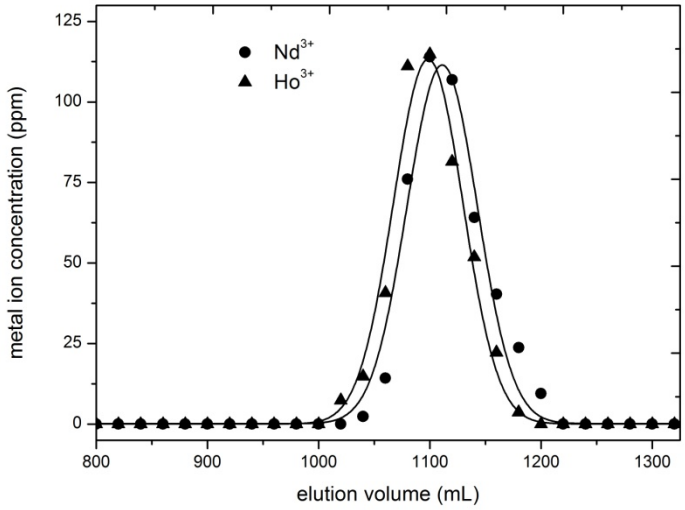

Figure S7: Chromatogram of Nd^{3+}/Ho^{3+} separation (ratio 1:1) with Chelex® 100 at pH 2.

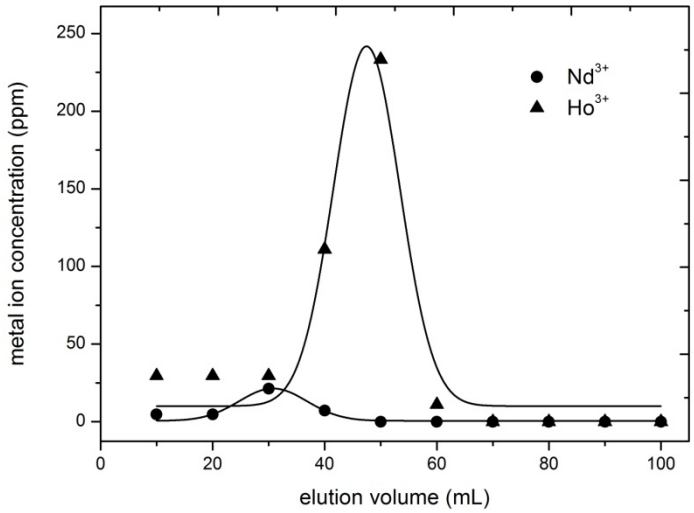

Figure S8: Elution curve for Nd^{3+}/Ho^{3+} separation (1:1 ratio) with DTPA-chitosan/silica at pH 1.25.

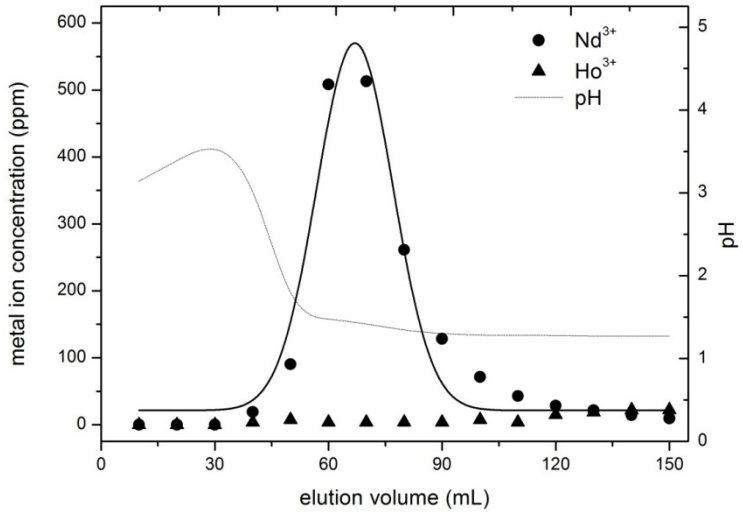

Figure S9: Breakthrough curve Nd^{3+}/Ho^{3+} separation (excess Nd^{3+}) with DTPA-chitosan/silica at pH 1.25.

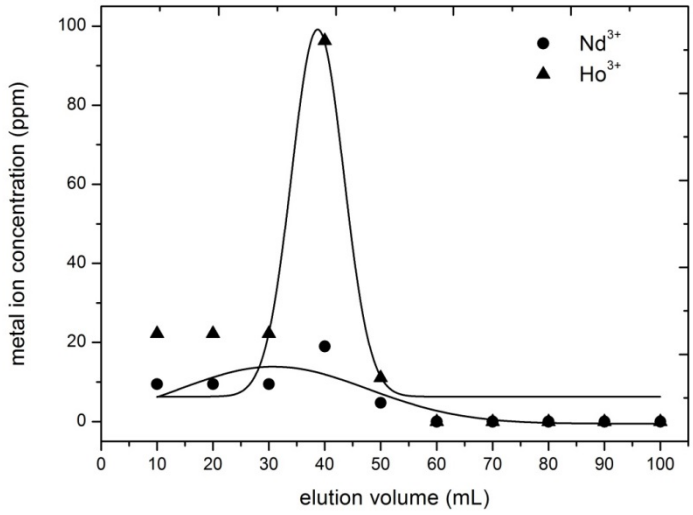

Figure S10: Elution curve Nd^{3+}/Ho^{3+} separation (excess Nd^{3+}) with DTPA-chitosan/silica.

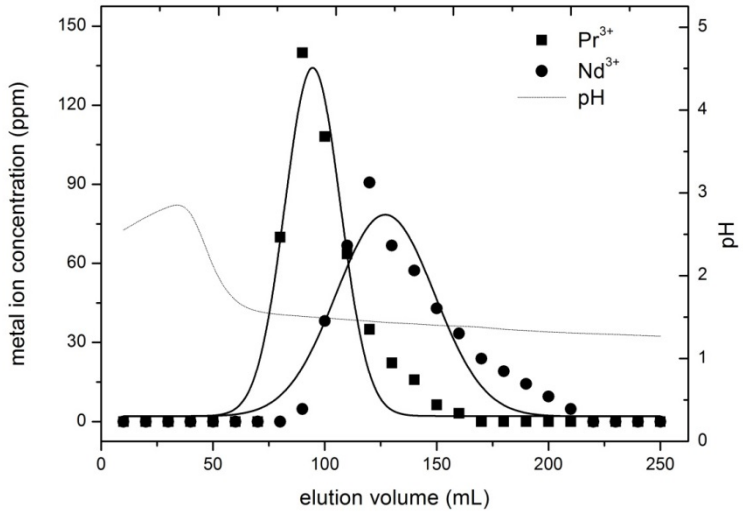

Figure S11: Chromatogram of Pr^{3+}/Nd^{3+} separation (1:1 ratio) with DTPA-chitosan at pH 1.50.