Supporting Information

Selective Extraction of Heavy and Light Lanthanides from Aqueous Solution by Advanced Magnetic Nanosorbents

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Characterization of dMNP-DTPA nanosorbents:

Vibrating Sample Magnetometer (VSM): Magentic properties were characterized using a DMS 1660 VSM where each pre-weighted sample is placed inside an external magnetic field to get magnetized at room temperature. A hysteresis loop was acquired by applying a scanning magnetic field of 13500 Oe to -13500 Oe.

Elemental analysis: Dry samples were sent to Midwest Microlabs, LLC (Indianapolis, IN) for determination of carbon (C), hydrogen (H), and nitrogen (N) content. In this CHN analysis, a sample is burned in an excess of oxygen at 990 ^{o}C, and the combustion products (carbon dioxide, water, and nitric oxide) are collected by various traps. The masses of these combustion products can be used to calculate the C, H, N composition of the sample. The results of the elemental analysis were used to determine the loading density of DTPA onto the surface of dMNPs.

Fourier Transform Infrared Spectroscopy (FTIR): IR spectra of vacuum dry samples were obtained and analyzed on a Thermo-Nicolet Avatar 370 FTIR spectrometer (SmartPerformer, ZnSe crystal) operating in attenuated total reflectance (ATR) mode. A background scan of the ZnSe crystal was performed prior to measuring each sample. Each spectrum was taken as an average of 64 sample scans at a resolution of 4 cm^{-1}. Moderate pressure was applied to the samples to ensure the good contact between samples and ZnSe crystal. The resultant spectra were baseline corrected. Special interest was focused on the signals assigned to the carboxylate group as well as the primary and secondary amine groups.

Transmission Electron Microscopy (TEM): Particle size and chemical composition was confirmed using TEM (Tecnai TF30-FEG STwin). The samples were prepared by drying the solvent of the MNPs' dispersion onto a 200 mesh copper grid with a carbon coated Formvar film.

*Inductively coupled plasma mass spectrometry (ICP-MS):*Lanthanide concentrations in aqueous solutions were characterized using an ELAN 6000 ICP-MS (Perkin Elmer) before and after contact with the magnetic nanosorbents following the procedure described in the ref.[1]. The concentration of lanthanides in the sorbent phase was determined by the material balance equation.

Properties of dMNP-DTPA:
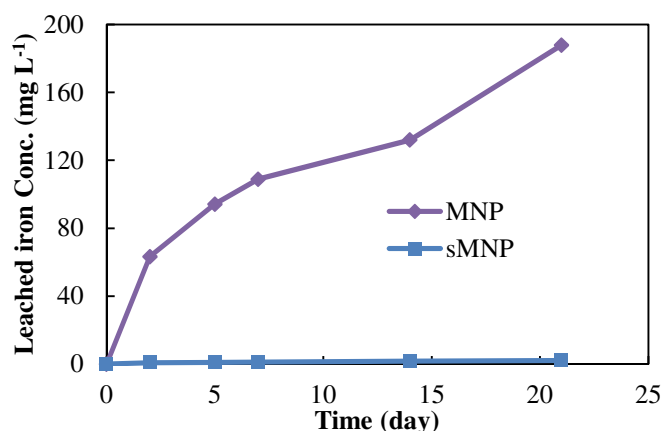
Figure S1. Time dependence of iron leaching from MNP and sMNP in 0.1M HNO_3.

Zeta potential data of dMNP and dMNP-DTPA as a function of pH are shown in Figure S2. The standard method used to transfer mobility data to zeta potential data assumes smooth hard particles. Therefore, the polymer surface structure of dMNP and dMNP-DTPA gives rise to a large uncertainty to the absolute zeta potential data. However, the sign of the zeta potential and the position of the point of zero charge (PZC) should be correct. In both cases, the data had positive values at low pH, passed through a PZC, and then turned to negative at high pH. The zeta potential data suggested the surface charge of dMNP and dMNP-DTPA, which was highly related to their sorption power.
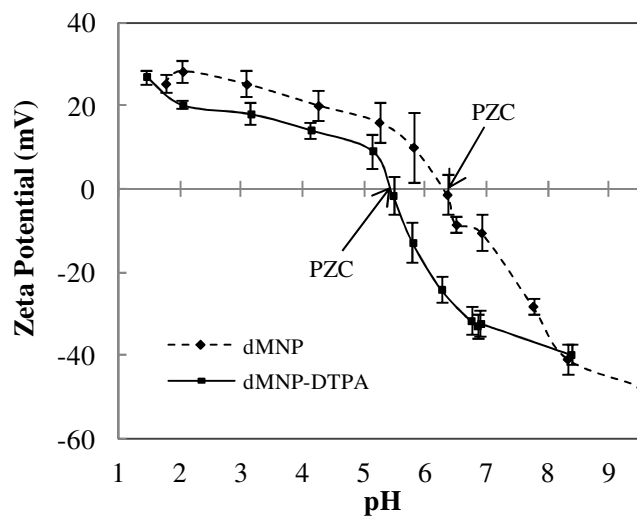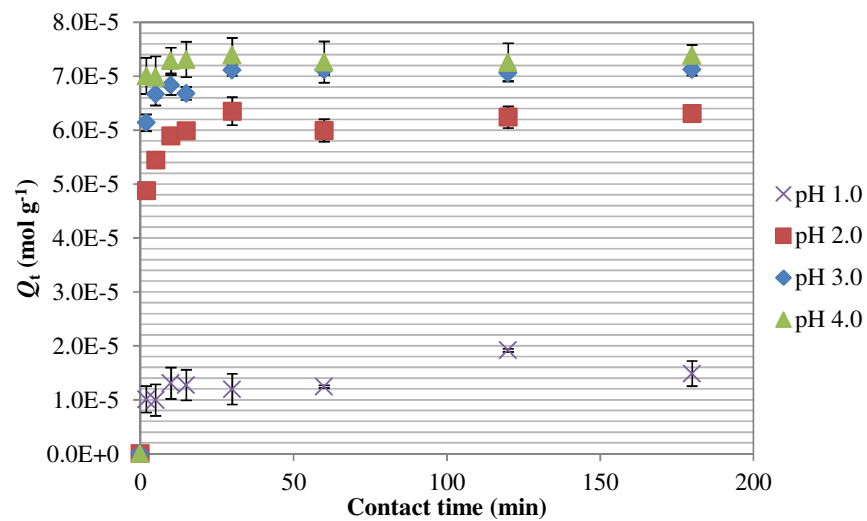
**Figure S2.** Zeta potential vs. pH for dMNP and dMNP-DTPA at a particle concentration of 30 μg/mL.

Ln(III) Sorption:
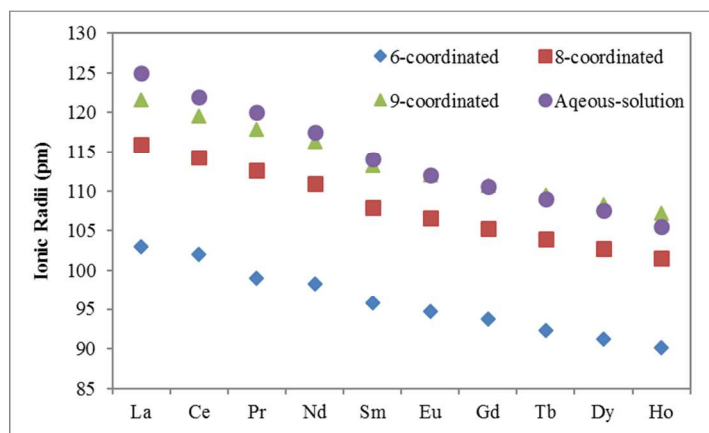
Figure S3. Crystal ionic radii (pm) of Ln(III) for 6-fold, 8-fold and 9-fold coordination and ionic radii of Ln(III) in aqueous solution (data from ref.[2,3]).

Figure S4. pH effect on the total adsorbed amount (in mol g^{-1}) of all Ln(III) on dMNP-DTPA conjugates at different time (room temperature).
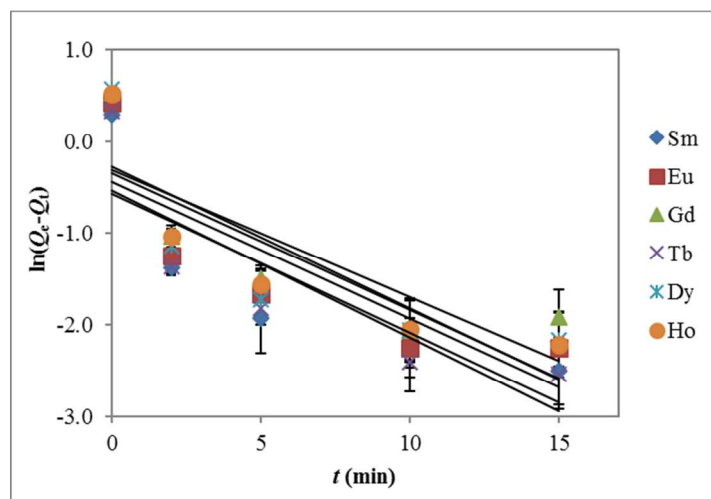
Figure S5. Lagergren plots for sorption of Ln(III) ions on dMNP-DTPA (pH 3.0 acetate buffer, room temperature).

Table S1. Pseudo-first-order kinetic parameters for Ln(III) sorption on dMNP-DTPA.

Element	Q_e (exp.) (mg L^{-1})	Q_e (calc.) (mg L^{-1})	k_1 (min^{-1})	R^2
La	0.091	NA	NA	NA
Ce	0.234	NA	NA	NA
Pr	0.502	NA	NA	NA
Nd	0.748	NA	NA	NA
Sm	1.346	0.564	0.152	0.6966
Eu	1.533	0.645	0.150	0.6867
Gd	1.721	0.737	0.139	0.6544
Tb	1.402	0.589	0.161	0.7195
Dy	1.787	0.708	0.149	0.6580
Ho	1.692	0.759	0.155	0.7327
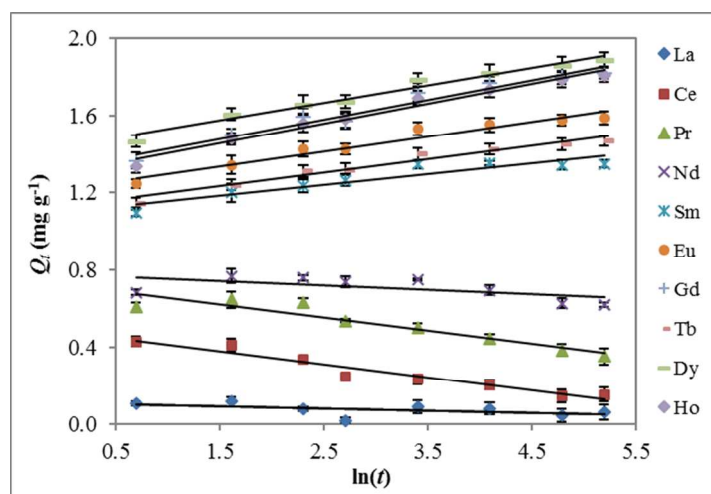
Figure S6. Elovich plots for sorption of Ln(III) ions on dMNP-DTPA (pH 3.0 acetate buffer, room temperature).

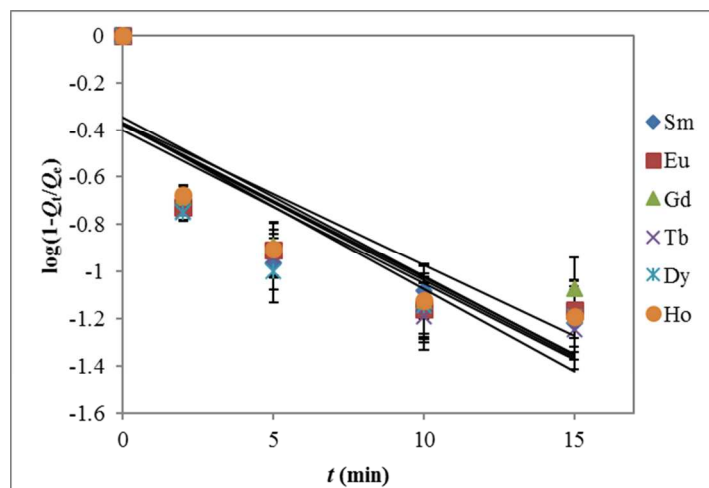**Table S2.** Elovich kinetic parameters for Ln(III) sorption on dMNP-DTPA.

Element	Q_e (exp.) (mg L^{-1})	Q_e (calc.) (mg L^{-1})	α (g mg^{-1} min^{-2})	β (mg g^{-1} min^{-1})	R^2
La	0.091	0.072	-3.90E-03	-0.011	0.2718
Ce	0.234	0.250	-1.25E-02	-0.068	0.9361
Pr	0.502	0.492	-3.18E-04	-0.067	0.8787
Nd	0.748	0.696	-1.16E-13	-0.023	0.395
Sm	1.346	1.291	6.63E+09	0.056	0.8665
Eu	1.533	1.486	1.09E+08	0.077	0.9486
Gd	1.721	1.673	4.97E+06	0.101	0.9607
Tb	1.402	1.368	1.34E+08	0.070	0.9622
Dy	1.787	1.748	9.60E+07	0.090	0.9691
Ho	1.692	1.655	2.96E+06	0.103	0.9749
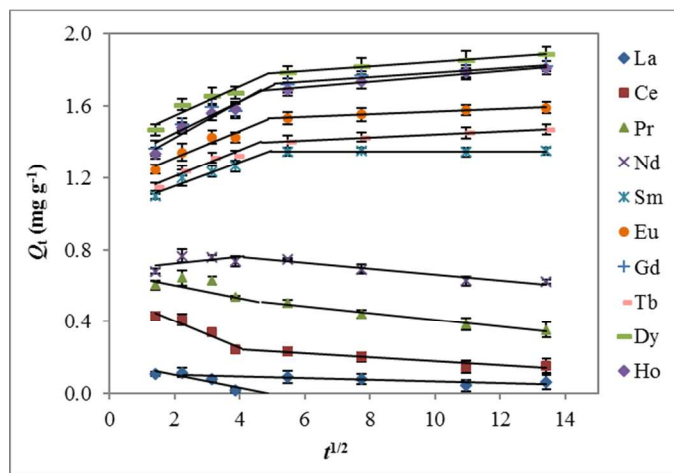
Figure S7. Intra-particle diffusion plots for sorption of Ln(III) ions on dMNP-DTPA (pH 3.0 acetate buffer, room temperature).

Table S3. Intra-particle diffusion kinetic parameters for Ln(III) sorption on dMNP-DTPA.

Time Range	0-15 min			30-180 min		
Element	k_{id}	C	R^2	k_{id}	C	R^2
La	-0.036	0.177	0.7736	-0.005	0.113	0.5929
Ce	-0.075	0.556	0.9183	-0.011	0.289	0.8820
Pr	-0.026	0.671	0.3221	-0.019	0.595	0.9810
Nd	0.019	0.684	0.2871	-0.017	0.828	0.9296
Sm	0.066	1.023	0.9061	0.000	1.349	0.0011
Eu	0.077	1.157	0.9073	0.007	1.496	0.9840
Gd	0.088	1.272	0.8409	0.012	1.663	0.9615
Tb	0.072	1.064	0.9296	0.008	1.359	0.9929
Dy	0.080	1.387	0.8537	0.012	1.722	0.9957
Ho	0.100	1.224	0.9107	0.015	1.615	0.9859

Figure S8. Liquid film diffusion plots for sorption of Ln(III) ions on dMNP-DTPA (pH 3.0 acetate buffer, room temperature).

Table S4. Liquid film diffusion kinetic parameters for Ln(III) sorption on dMNP-DTPA.

Element	Qe (exp.) (mg L^{-1})	Qe (calc.) (mg L^{-1})	K$_{fd}$ (min^{-1})	R^2
La	0.091	NA	NA	NA
Ce	0.234	NA	NA	NA
Pr	0.502	NA	NA	NA
Nd	0.748	NA	NA	NA
Sm	1.346	1.332	0.152	0.6966
Eu	1.533	1.516	0.150	0.6867
Gd	1.721	1.695	0.139	0.6544
Tb	1.402	1.391	0.161	0.7195
Dy	1.787	1.767	0.149	0.6580
Ho	1.692	1.676	0.155	0.7327

References:

(1) Turanov, A. N.; Karandashev, V. K.; Baulin, V. E. Extraction of Metal Chloride Complexes by Phosphoryl-Containing Podands. *Solvent Extr. Ion Exch.* **1996**, *14* (2), 227–245.

(2) Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr., Sect. A* **1976**, *32* (5), 751–767.

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