Acid-Stable Magnetic Core–Shell Nanoparticles for the Separation of Rare Earths

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ABSTRACT: Core–shell Fe3O4@SiO2 nanoparticles were prepared with a modified Stöber method and functionalized with N-[(3-trimethoxysilyl)propyl]ethylenediamine triacetic acid (TMS-EDTA). The synthesis was optimized to make core–shell nanoparticles with homogeneous and thin SiO2 shells (4.8 ± 0.5 nm) around highly superparamagnetic Fe3O4 cores (14.5 ± 3.0 nm). The core–shell Fe3O4@SiO2(TMS-EDTA) nanoparticles were then used for the extraction and separation of rare-earth ions. By comparing them with previously published results for Fe3O4(TMS-EDTA) and SiO2(TMS-EDTA) nanoparticles, it was clear that the core–shell nanoparticles combine the advantage of magnetic retrieval observed for Fe3O4(TMS-EDTA) nanoparticles with the higher selectivity observed for SiO2(TMS-EDTA). The advantages of the SiO2 shell include a lower specific weight and a larger grafted density compared to Fe3O4 surfaces, but also the improved resistance to acidic environments required for the stripping of rare-earth ions.

1. INTRODUCTION

Magnetic nanoparticles are very interesting materials that can be recovered from solution with the use of a magnet.1–3 Task-specific magnetic nanoparticles can be prepared by coating the surface with functional groups.2,3 Applications are found in targeted drug delivery, biosensors, dual imaging compounds, recoverable catalysts, and selective recovery of metal ions or molecules.3–15 Functionalized magnetic nanoparticles are well-suited for the selective extraction of metal traces from diluted wastewater streams or industrial effluents.7–20 This is done by capturing metal ions in solution, retrieving the loaded nanoparticles with a magnet, and then stripping the metal ions from the nanoparticles. This is a sustainable process since the nanoparticles are reusable and no hazardous chemicals are involved. Most examples report on the recovery of transition metals, heavy metals, or precious metals.7–25 On the other hand, the capture of rare-earth ions has been far less investigated.16,31,26

Core–shell nanoparticles are slightly more complex than conventional nanoparticles, but these hybrid materials can have significantly enhanced properties.27–29 The core is usually a magnetic and vulnerable material such as magnetite or cobalt that is prone to oxidation or dissolution in acidic environments. These cores are capped with an inert shell of, e.g., SiO2, TiO2, ZrO2, gold, graphene, or a polymer.3,30–32 The shell protects the core from oxidation or attack by chemicals, and it can be further functionalized by attaching functional groups to its surface.3,16,21–24 The advantage of layered materials can be the better stability or a synergy between different materials, which can result in unique chemical or physical properties.27–29

Functionalization of core–shell and regular nanoparticles can be achieved by covalent bonding, chemisorption, or electrostatic interactions of ligands onto their surface. Good results have been obtained with functionalized siloxanes, because these versatile compounds form strong covalent bonds with most oxide surfaces due to the presence of hydroxyl groups.33–37 The large number of commercially available trialkoxysilanes with various functional groups offers unique possibilities for the task-specific surface modification of oxide nanoparticles.16,35,38–41 The N-[(3-trimethoxysilyl)propyl]ethylenediamine triacetic acid (TMS-EDTA) used in this work is an EDTA derivative in which one of the carboxylate groups is replaced by an alkyl spacer with a reactive trialkoxysilane group for binding to the surface of the nanoparticle. EDTA has a good affinity for rare-earth ions and is also capable of separating them based on small differences in charge density.42–44 TMS-EDTA was therefore the preferred ligand to decorate the surface of the nanoparticles. The covalently bonded TMS-EDTA also provides nanoparticles with a good resistance against the strongly acidic environments required for the stripping of rare-earth ions after coordination (pH <2).26

Recently, our group compared the adsorption capacity and selectivity of TMS-EDTA-functionalized Fe3O4, TiO2, and SiO2 nanoparticles to gain a better understanding of the influence of the substrate on the behavior of the surface group.26 It was shown that TMS-EDTA-functionalized SiO2 nanoparticles performed better than the analogous Fe3O4 or TiO2 nanoparticles. This was attributed to the fact that SiO2 contains the highest density of hydroxyl groups on its surface, resulting in a large grafting density of TMS-EDTA functional groups. This dense layer of TMS-EDTA groups is capable of binding high quantities of rare-earth ions, but it also exhibits a significant size-based selectivity. It was shown that a denser layer of TMS-EDTA results in a better separation between small and large rare-earth ions. However, both SiO2 and TiO2 nanoparticles are
not magnetic, so their removal from solution is much more tedious than the fast magnetic retrieval that is possible for Fe$_3$O$_4$ nanoparticles. In this paper, core–shell nanoparticles were prepared consisting of magnetic Fe$_3$O$_4$ cores and a SiO$_2$ shell, which was subsequently functionalized with TMS-EDTA (Figure 1). The aim was to investigate whether these functionalized core–shell nanoparticles could combine the advantage of magnetic retrieval, with the enhanced selectivity that was observed for TMS-EDTA attached to SiO$_2$ nanoparticles. The chemical stability and loss of efficiency of these core–shell nanoparticles were also investigated to evaluate their potential as high-performance, reusable sorbents for rare-earth ions.

2. EXPERIMENTAL SECTION

Chemicals. N-[3-(3-Trimethoxysilyl)propyl]ethylenediamine (99%) was obtained from ABCR chemicals. Anhydrous FeCl$_3$ (97%) was purchased from Sigma-Aldrich. Ammonia (25 wt %) was obtained from Chem-Lab. Methanol (HPLC grade), absolute ethanol, glacial acetic acid, NaOH (97%), and HCl (37%) were purchased from VWR. Sm(NO$_3$)$_3$·6H$_2$O (99.9%), Gd(NO$_3$)$_3$·6H$_2$O (99.9%), Er(NO$_3$)$_3$·5H$_2$O (99.9%), n-octylamine (NOA) (99.9%), and tetraethyl orthosilicate (TEOS) (98%) were purchased from Acros Organics. La(NO$_3$)$_3$·6H$_2$O (99.9%) and Pr(NO$_3$)$_3$·6H$_2$O (99.9%) were supplied by Chempur. Nd(NO$_3$)$_3$·6H$_2$O (99.9%), Tb(NO$_3$)$_3$·5H$_2$O (99.9%), Dy(NO$_3$)$_3$·5H$_2$O (99.9%), and Ho(NO$_3$)$_3$·5H$_2$O (99.9%) were supplied by Alfa Aesar. All chemicals were used as received without further purification.

Equipment and Characterization. The nanoparticles were dispersed in a solvent using a Branson 5510 (10 L) and a Branson 2510 MTH (3 L) ultrasonic bath. The shaking during adsorption experiments was done with a mechanical shaker (IKA MS 3 basic). Particle imaging was done on a Jeol JEM2100 transmission electron microscope (TEM) using an acceleration voltage of 80 or 200 kV. ImageJ software was used for the size determination. The particles were dispersed in methanol (1 mg/mL) and deposited on a grid by solvent evaporation. Specific surface measurements were done by collecting nitrogen physisorption isotherms using a Micromeritics 3Flex surface characterization analyzer at 77 K. Prior to the measurement, the samples were outgassed at 353 K for 6 h under vacuum (Micromeritics VacPrep system). The BET method was applied in the 0.05–0.3 p/p$_0$ range using the 3Flex 3.00 software. Magnetization data were obtained with vibrating sample magnetometry (VSM) experiments performed on a VSM Maglab setup from Oxford Instruments at 300 K. Fourier transform infrared (FTIR) spectra were measured between 400 and 400 cm$^{-1}$ on a Bruker Vertex 70 spectrometer, with a platinum ATR module. Thermogravimetric analysis (TGA) was performed with a TA Instruments Q600 thermogravimeter, measuring from 25 to 1200 °C (10 °C/min, argon atmosphere). A CE Instruments EA-1110 elemental analyzer was used to measure the carbon, hydrogen, and nitrogen (CHN) content of the functionalized nanoparticles. The rare-earth concentrations were determined by total reflection X-ray fluorescence (TXRF) analysis on a benchtop Bruker S2 Picofox TXRF spectrometer equipped with a molybdenum X-ray source. This technique allows direct determination of the rare-earth content on the nanoparticles in dispersion. This is a major advantage of TXRF compared to inductively coupled plasma mass spectrometric (ICP-MS) analysis, where nanoparticles have to be digested in acid prior to analysis. For the sample preparation, Eppendorf microtubes were filled with an amount of sample solution (900 μL) and a similar concentration (10–100 ppm) of Ga$^{3+}$ as internal standard (1000 ppm gallium dissolved in 2–3% HNO$_3$). Gallium was chosen because this element has a high sensitivity and does not interfere with the lanthanide signals.

The microtubes were then vigorously shaken on a vibrating plate (IKA MS 3 basic). Finally, a 7 μL drop of this solution was put on a quartz plate, previously treated with a silicone/isopropanol alcohol solution (Serva) to avoid spreading of the sample droplet. The plates were then dried for 30 min at 60 °C prior to analysis. Each sample was measured for 30 min.

Synthesis of Fe$_3$O$_4$@SiO$_2$ Nanoparticles. An in-house synthesis procedure was followed to prepare precursor Fe$_3$O$_4$ nanoparticles coated with n-octylamine.$^{45}$ Ethylene glycol (37.5 mL) and n-octylamine (NOA; 25 mL) were combined into a flask and heated to 150 °C. Anhydrous FeCl$_3$ (2.4 g) was dissolved in a beaker containing ethylene glycol (10 mL) and Milli-Q water (3.0 mL). The iron(III) solution was slowly added to the flask containing ethylene glycol and n-octylamine, and further heated to reflux at 180 °C for 24 h. The particles were precipitated from the reaction mixture by a small magnet and washed three times with acetone. Finally, they were dried in vacuo at room temperature for 20 min to obtain a black powder of Fe$_3$O$_4$(NOA) nanoparticles with a typical yield of 1 g. The silica shell was grown on these seeds using a modified and optimized Stöber method.$^{22,31}$ Fe$_3$O$_4$(NOA) nanoparticles (50 mg) were dispersed in ethanol (40 mL) by placing them in an ultrasonic bath for 1 h. Without removing the solution from the sonicator bath, NH$_3$ (25%; 2 mL) was added to the nanoparticle dispersion and TEOS (0.8 mL) was added dropwise over an hour. The solution was then left in the sonicator bath for another 5 h. The nanoparticles were settled, and washed one time with water and two times with acetone. Finally, they were dried in vacuo (room temperature (RT)) for 30 min to obtain a grayish powder with a typical yield of 100 mg.

Functionalization Protocol. The Fe$_3$O$_4$@SiO$_2$ nanoparticles were functionalized with TMS-EDTA. The silanization procedure started by setting the pH at 4.5 with HCl (1 M) and then dispersing 100 mg of nanoparticles in MeOH/H$_2$O 85:15 (100 mL). The beaker was placed in an ultrasonic bath for 2 h.

TMS-EDTA (1 mmol) was then added together with a few drops of glacial acetic acid. The beaker was placed in an ultrasonic bath for 2 h. The nanoparticles have to be digested in acid prior to analysis. For the sample preparation, Eppendorf microtubes were filled with an amount of sample solution (900 μL) and a similar concentration (10–100 ppm) of Ga$^{3+}$ as internal standard (1000 ppm gallium dissolved in 2–3% HNO$_3$). Gallium was chosen because this element has a high sensitivity and does not interfere with the lanthanide signals.

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in vacuo at room temperature for 30 min, resulting in Fe₃O₄@SiO₂(TMS-EDTA) with a typical yield of 95–100 mg.

**Procedure for Adsorption and Stripping Experiments.** The TMS-EDTA functionalized core–shell nanoparticles were used to adsorb rare-earth ions from nitrate solutions and to separate rare-earth pairs. Adsorption and separation experiments started by dispersing 5 mg of nanoparticles in 5 mL of Milli-Q water using an ultrasonic bath (1 h). After a homogeneous dispersion of nanoparticles was obtained, single and binary rare-earth nitrate solutions were used to obtain the desired concentration of rare earths (1 mmol/L). This corresponds to 1 μmol of rare-earth ions per milligram of nanoparticles (an excess compared to the EDTA content). The pH was set using HCl (0.1 M) or NaOH (0.1 M), and the vials were placed on a mechanical shaker (240 rpm, 18 h). The particles were settled using a small NdFeB magnet. The solution was removed and the nanoparticles were washed two times with acetone to remove the remaining aqueous feed solution without influencing the adsorption equilibrium. The nanoparticles were then redispersed in 1 mL of Milli-Q water and the rare-earth content on the nanoparticles was analyzed with TXRF. The stripping of rare-earth ions from the nanoparticles was done by redispersing the washed nanoparticles in water (5 mL) and lowering the pH to 1.5 using an acidic HCl solution (1 M). The solution was then shaken for 2 h on a mechanical shaker (240 rpm).

### 3. RESULTS AND DISCUSSION

**Optimizing the Synthesis of Fe₃O₄@SiO₂(TMS-EDTA) Nanoparticles.** The magnetite nanoparticles were synthesized using a forced hydrolysis method. The Fe₃O₄ nanoparticles are capped with n-octylamine to protect their surface and can be stored for months. However, this weakly bound coating can be replaced by siloxane molecules in a later stage to allow further modification of the nanoparticle surface with functional groups or SiO₂ shells. The synthesis of the SiO₂ shell and the functionalization with TMS-EDTA was investigated in detail and optimized for its use as nanosorbent. A modified Stöber method was used to grow SiO₂ shells around the Fe₃O₄ seeds with an average yield of 100 mg per batch. The thickness of the SiO₂ shell around the magnetite core could be tuned by varying the NH₃/TEOS ratio but was also influenced by other parameters such as the solvent/reagent ratio. The thickness is related to the size of the Si−O−Si band in the infrared spectrum at 1091 cm⁻¹ (Figure 2). Methods A and B yielded poor nanoparticles, with insufficient covering of silica. Method C, D, and E were much more successful and ensured a reproducible covering of the nanoparticles with a thin but homogeneous layer of silica. The synthesis method that was retained used the following ratio of reagents: ethanol (40 mL), 25% NH₃ (2 mL), and TEOS (0.8 mL) (method E). This method yields nanoparticles with a homogeneous 4.8 ± 0.5 nm thick SiO₂ shell (TEM). This thickness is the right compromise between a good protection of the nanoparticle core, without losing too much surface area.

The functionalization parameters have great influence on the quality of the functional coating. The functionalization reaction of Fe₃O₄@SiO₂ nanoparticles with TMS-EDTA is pH-dependent because the hydrolysis rate of the alkoxysilanes is pH-controlled. Acidic conditions are required for the controlled silanization of the surface (pH 3–5) because an alkaline pH causes rapid polymerization of the silane chains. The solvent composition is also important. Water increases the hydrolysis rate while methanol slows it down. Different methanol/water ratios were tested to optimize the degree of functionalization (Figure 3) The success of the functionalization was monitored by FTIR spectroscopy by looking at the intensity of the carboxylate bands. The compiled FTIR spectra (Figure 3) show the intense asymmetrical stretch of the carboxylate groups at 1650 and 1400 cm⁻¹ is shown. This signal is related to the degree of TMS-EDTA functionalization.

![Figure 2. FTIR spectra of different Fe₃O₄@SiO₂(TMS-EDTA) samples from different synthesis methods. The influence of the reagent ratio on the Si−O peak at 1091 cm⁻¹ is shown. The ratio of reagents is given as ethanol (mL)/25% NH₃ (mL)/TEOS (mL).](image)

![Figure 3. FTIR spectra of different Fe₃O₄@SiO₂(TMS-EDTA) samples. The influence of the solvent (MeOH/H₂O ratio) on the carboxylate peaks at 1650 and 1400 cm⁻¹ is shown. This signal is related to the degree of TMS-EDTA functionalization.](image)
by FTIR, CHN, TGA, BET, and TEM analysis. All TGA curves for Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂(TMS-EDTA) can be found in the Supporting Information (Figure S2). The average TMS-EDTA content obtained from CHN analysis was 4.2 ± 0.3 wt %, compared to 3.0 wt % determined by TGA analysis. The average of both analytical techniques was used, which indicates that the nanoparticles contain 0.12 μmol/mg TMS-EDTA. This value is useful for comparison with the adsorption experiments. Vibrating sample magnetometry showed that the super-paramagnetic Fe₃O₄(NO) seeds had a saturation magnetization of 66 emu/g (Supporting Information, Figure S1). TEM images showed that the functionalized core−shell Fe₃O₄@SiO₂(TMS-EDTA) nanoparticles had a diameter of 24.1 ± 4.0 nm (Figure 4B). The Fe₃O₄(NO) seeds had a relatively well-defined spherical shape and an average diameter of 14.5 ± 3.0 nm (Figure 4A). The SiO₂ shell on the core−shell Fe₃O₄@SiO₂ nanoparticles had a thickness of 4.8 ± 0.5 nm (Figure 4B). The aggregation of the core−shell nanoparticles in Figure 4 is due to the TEM sample preparation. During the solvent evaporation the nanoparticles aggregate on the grid. Since the SiO₂ shell is thin and homogeneous, this results in a relatively high specific surface area. The specific surface area of the nanoparticles was 44.1 m²/g as determined by surface analysis using the BET method. This is an important characteristic for a sorbent nanoparticle. A thin SiO₂ shell is also important to maintain a high magnetic susceptibility, required for a fast magnetic removal of the nanoparticles from solution. The core−shell Fe₃O₄@SiO₂(TMS-EDTA) nanoparticles are quite hydrophilic due to the deprotonated carboxylate groups, thus forming very homogeneous and stable dispersions at pH 6 (used for adsorption experiments). Once they bind lanthanide ions, the surface charge diminishes and the nanoparticles can be removed from solution efficiently. Full retrieval (>99.9%) was possible within 10 s (Figure 5). Additionally, during stripping the carboxylate groups are protonated due to the acidic conditions (pH 1.5), making them less hydrophilic and therefore easy to retrieve. This greatly facilitates the adsorption/stripping process.

Adsorption and Stripping of Rare Earths. The adsorption of rare earths is pH-dependent because TMS-EDTA contains three carboxylic acid groups that are gradually deprotonated at increasing pH values. An excess of rare-earth ions was used and the samples were shaken for 18 h to ensure that a maximal adsorption was reached. Nd³⁺ was chosen as a model system because of its industrial relevance. Complex formation was observed between pH 3 and 6 (Figure 6). The excess of rare-earth ions helps to visualize the precipitation threshold. There is still complex formation at pH values higher than 6, but also hydrolysis and precipitation of the lanthanide ions. This pH range is therefore not convenient since the precipitation interferes with the complex formation. Below pH 2.5, the Nd³⁺ adsorption is quite low; therefore this lower pH range can be used to strip the lanthanide ions from the nanoparticles. Adsorption of rare-earth ions is best performed at pH 6, resulting in an adsorption of 0.118 μmol/mg (17.0 mg/g) for Nd³⁺. An excess of Nd³⁺ was used to obtain the maximal adsorption capacity. This value (0.118 μmol/mg) is in good agreement with the TMS-EDTA content on the surface of the nanoparticles (0.12 μmol/mg). If the adsorption capacity is compared with other nanoparticles described in the literature (Table 1), it is well within the range of most reported chelating nanoparticles. However, the main advantage of these nanoparticles is their high magnetic susceptibility, which allows for fast magnetic retrieval. Full retrieval (>99.9%) was possible within 10 s (Figure 5). Additionally, during stripping the carboxylate groups are protonated due to the acidic conditions (pH 1.5), making them less hydrophilic and therefore easy to retrieve. This greatly facilitates the adsorption/stripping process.

Figure 4. TEM images of (A) Fe₃O₄(NO) seeds and (B) Fe₃O₄@SiO₂(TMS-EDTA) nanoparticles. The magnetic core and the thin homogeneous SiO₂ shell are indicated on image B.

Figure 5. Magnetic retrieval of Fe₃O₄@SiO₂(TMS-EDTA) nanoparticles dispersed in water (1 mg/mL), before (left) and after 10 s (right).

Figure 6. Nd³⁺ removal from solution by Fe₃O₄@SiO₂(TMS-EDTA) nanoparticles as a function of pH. Depending on the pH, different domains were identified where the Nd³⁺ could be adsorbed by the nanoparticles, precipitated, or stripped back from the nanoparticles.
particles is not their adsorption capacity, but their selectivity and ability to separate rare-earth ions from each other. The adsorption kinetics were also investigated by contacting the nanoparticles with an excess of Nd\(^{3+}\) ions at pH 6.0 for increasing periods of time (mechanical shaker, 240 rpm). The results show a saturation of the nanoparticles with Nd\(^{3+}\) ions after 6 h (Figure 7). However, during most adsorption experiments the samples were shaken overnight (18 h) for convenience. The relatively long equilibrium times are attributed to the dense layer of EDTA on the surface, which is also responsible for the better than expected size-based selectivity that was observed (see Separation of Rare Earths).

The stripping efficiency as a function of pH was tested, together with the stability of the core−shell nanoparticles. After the nanoparticles were fully loaded with a solution containing an excess of Nd\(^{3+}\) ions, the nanoparticles were isolated. The nanoparticles were then contacted with an acidic solution to protonate the carboxylate groups and release the Nd\(^{3+}\) ions back in solution. For this stripping step, the pH was set using HCl (1 M) and the solutions were shaken for 2 h (same result as for 24 h). The damage to the nanoparticles was measured by analyzing the iron content in the stripping solution with TXRF, after 24 h of shaking. This iron content was then translated into a particle loss (percent). Stripping is best performed at pH 1.5 in order to have the right compromise between a high stripping efficiency (94%) and little damage to the nanoparticles (<0.5% particle loss) (Figure 8).

By comparing the stability of the core−shell nanoparticles with the simple (core) magnetite nanoparticles, it is clear that the SiO\(_2\) shell significantly increased the resistance of magnetite nanoparticles to acidic solutions (Figure 9). The SiO\(_2\) shell is only 4.8 nm thick, but it drastically increases the stability of the nanoparticles. SiO\(_2\) is much less sensitive to degradation by HCl than Fe\(_3\)O\(_4\) that is easily dissolved as FeCl\(_3\). The increased stability of core−shell nanoparticles in acidic solutions is particularly useful for metal binding surface groups that require harsher stripping conditions.

This increased stability is also translated into a good reusability. A sequence of five adsorption (pH 6.0) and stripping (pH 1.5) cycles with an excess of Nd\(^{3+}\) ions shows the evolution of the adsorption capacity of the core−shell nanoparticles (Figure 10). The experiments were done three times to reduce the experimental error. During the first cycle, a loss of adsorption capacity was observed from 0.118 to 0.092 μmol/mg. This is due to the release of some of the less well bonded TMS-EDTA groups or some irreversible adsorption. During the functionalization, some of the TMS-EDTA groups are weakly bound to other TMS-EDTA groups through one Si−O−Si linker. This partial oligomerization is an unavoidable phenomenon for trialkoxysilanes; however, most TMS-EDTA groups are firmly attached to the SiO\(_2\) surface with three Si−O−Si bonds. After this initial drop in adsorption capacity, the

<table>
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<th>Particle (ligand)</th>
<th>Particle size (nm)</th>
<th>Surf. group content (wt %)</th>
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<th>Ion uptake (mg/g)</th>
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\(^{a}\)This is the core−shell nanoparticle described in this paper.
adsorption capacity then stabilized and remained practically unchanged over the next four adsorption/stripping cycles. The initial drop in adsorption capacity can be avoided by washing the synthesized nanoparticles one time with a pH 1.5 HCl solution, before using them in adsorption experiments. The particle loss in each cycle increased slightly from 0.3% in cycle 1 to 1.6% in cycle 5, resulting in a cumulated particle loss of 4.7%. Furthermore, it should be mentioned that no particle degradation was observed visually. The supernatant remained completely colorless (Figure 5). This indicates that the particle loss is very limited and is most likely also due to process steps. The particles have to be transferred multiple times in different flasks, inevitably leading to some loss of particles along the way. Small quantities of nanoparticles were used (10 mg); therefore the percent particle loss seems higher even though only 0.47 mg of particles was lost after five adsorption/stripping cycles.

The separation of rare earths as a group from other elements is usually relatively efficient, and based on differences in oxidation state or chemical behavior.48 However, the mutual separation of a mixture of rare-earth ions is a challenge because of their common +III oxidation state and very similar chemical behavior. Most current techniques are based on the small differences in ionic radii.42 The selectivity of the functionalized core–shell nanoparticles was investigated and reported using enrichment factors (EFs). The enrichment factor compares the molar ratio of elements A and B before and after separation, according to eq 1. B was chosen to be the heavier (smaller) of the two rare-earth ions because this results in an enrichment factor of >1.

\[
EF = \frac{\left( \frac{B}{A} \right)_{\text{on nanoparticles}}}{\left( \frac{B}{A} \right)_{\text{feed solution}}} \quad (1)
\]

The separation of Er\textsuperscript{3+}/La\textsuperscript{3+} was chosen as a model to investigate the influence of the pH on the selectivity. The relatively large difference in ionic radius results in a high enrichment factor which helps to visualize a possible trend. An excess of rare-earth ions was used compared to the amount of TMS-EDTA groups and the rare-earth pairs were present in a 1:1 molar ratio. The core–shell \(\text{Fe}_3\text{O}_4@\text{SiO}_2\) (TMS-EDTA) nanoparticles display the highest selectivity around pH 6 (Figure 11). At this pH, TMS-EDTA also has a high adsorption capacity and selectivity. Higher pH values cause hydrolysis and precipitation of lanthanide ions (Figure 6).

Furthermore, the selectivity of the core–shell \(\text{Fe}_3\text{O}_4@\text{SiO}_2\) (TMS-EDTA) nanoparticles toward different pairs of lanthanide ions was investigated and compared with previously published results for \(\text{Fe}_3\text{O}_4\) (TMS-EDTA) and \(\text{SiO}_2\) (TMS-EDTA).26 \(\text{Ln}^{3+}/\text{La}^{3+}\) separations showed that the core–shell nanoparticles behaved similarly to \(\text{SiO}_2\) (TMS-EDTA) (Figure 12).

One can notice that the enhanced selectivity of TMS-EDTA on \(\text{SiO}_2\) substrates was also observed for the core–shell nanoparticles.26 This further supports the hypothesis that the higher density of TMS-EDTA groups on \(\text{SiO}_2\) surfaces is responsible for this enhanced size-based selectivity.26 It must be noted that the enrichment factor increases rapidly at the beginning of the \(\text{Ln}^{3+}/\text{La}^{3+}\) separation series and stagnates for the heaviest lanthanides. This is a well-known trend for solvent extraction and aminocarboxylate ligands.42,43 Another explanation for this can be that the heavier (smaller) lanthanide ions are able to penetrate the dense TMS-EDTA surface layer more easily, making the size-based selectivity less efficient.
4. CONCLUSIONS

Core–shell \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \) nanoparticles were synthesized and functionalized with metal-coordinating TMS-EDTA groups. The idea was that this type of hybrid nanoparticles could combine the advantage of magnetic retrieval (\( \text{Fe}_3\text{O}_4 \) core) with the higher selectivity that had been observed when TMS-EDTA was attached to \( \text{SiO}_2 \) compared to \( \text{Fe}_3\text{O}_4 \) nanoparticles.\(^{26}\) Thin and homogeneous \( \text{SiO}_2 \) shells (4.8 ± 0.5 nm thick) were grown around \( \text{Fe}_3\text{O}_4 \) cores (14.5 ± 3.0 nm diameter), using a modified and optimized Stöber method. This synthesis protocol allowed synthesizing high-quality \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \) (TMS-EDTA) nanoparticles. It was also shown that the functionalized \( \text{SiO}_2 \) shell offers a good size-based separation of rare-earth ions similar to the selectivity that had been previously observed for \( \text{SiO}_2 \) (TMS-EDTA) nanoparticles, but with the added advantage of magnetic retrieval.\(^{26}\) The fact that these core–shell nanoparticles combine the advantages of both the possibility of magnetic retrieval and a high selectivity for metal sorption makes this a very interesting sorbent for the selective recovery of rare-earth ions from dilute aqueous solutions. The nanoparticles showed a good chemical stability even in strongly acidic environments thanks to the \( \text{SiO}_2 \) shell. The reusability of the nanoparticles was also satisfactory with the adsorption capacity remaining stable after the first adsorption/stripping cycle.

ASSOCIATED CONTENT

Supporting Information

VSM measurement of the magnetite seed particles \( \text{Fe}_3\text{O}_4 \) (NOA) and TGA measurements for \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \) and \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \) (TMS-EDTA). Infrared spectra of \( \text{Fe}_3\text{O}_4 \), \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \), and \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \) (TMS-EDTA) nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the KU Leuven (Projects GOA/13/008 and IOF-KP RARE\(^3\)) and the FWO Flanders (Ph.D. fellowship to D.D.) for financial support. CHN analyses were performed by Dirk Henot, and TGA measurements were performed by Danny Winant and Dr. Stijn Schaltin. VSM was measured by Ward Brullot, and the BET surface analysis was performed by Ivo Stassen.

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