



Neodymium(III) and lanthanum(III) separation by magnetic nanohydrometallurgy using DTPA functionalized magnetite nanoparticles

Sabrina da N. Almeida, Henrique E. Toma *

Instituto de Química, Universidade de São Paulo, São Paulo, SP, Brazil



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ABSTRACT

A successful nanohydrometallurgical separation of neodymium and lanthanum ions has been demonstrated by using superparamagnetic nanoparticles functionalized with ethylenediaminepropylsilane/diethylenetriaminepentaacetic acid, as complexing agents. Neodymium is preferentially captured in relation to lanthanum, reflecting the trends of the stability constants dictated by the lanthanide contraction. A high separation efficiency (>99%) has been achieved after three successive complexation and releasing stages. The overall process can be performed under green and sustainable conditions, e.g., at room temperature, in aqueous solution and mild pHs, allowing the nanoparticles recycling, and dispensing the use of more time/energy consuming physical separation processes.

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1. Introduction

Rare earths (REE) are very important elements in modern technology because of their applications in catalysis (Edelmann, 2009), metallurgy, ceramics, medicine (Hanninen and Harma, 2011; Kodaiara et al., 2011) and electronics (Blasse and Grabmaier, 1994; Brito et al., 2009; Carlos et al., 2009; Harma et al., 2001; Quirino et al., 2008). They are usually found in the trivalent state, although bivalent and tetravalent states can also be observed in the case of elements such as europium and cerium, respectively. The most important sources are represented by the monazite, bastnäsite and xenotime minerals. Monazite is a phosphate mineral of thorium and light REE, containing typically 45% Ce, 23% La and 17% Nd and minor amounts of Pr, Sm, Gd and Y. Such light elements are actually the most relevant ones, accounting for about 95% world consumption of REE. Bastnäsite, a fluorocarbonate mineral, is another important source of light REE, while xenotime, is a phosphate mineral containing mainly heavy REE.

Brazil and India were the first REE producers about five decades ago, but at the present time, China is the absolute world producer, also exhibiting the largest reserve of the elements. Recent discoveries in the central region of Brazil have ranked the country in the second position after China (Andrade, 2013), and there are some expectations to be confirmed, which can place the country even in the first rank. However, at the present time, the Brazilian production is yet quite modest. A

national initiative is being started, demanding major investments in this area.

Nowadays, the interest on neodymium is particularly large because of its use in commercial supermagnets, such as those based on Nd₂Fe₁₄B alloys. One of the most important sources of neodymium is the monazite ore, which is particularly abundant in Brazil. In the mineral processing of monazite, after the removal of thorium phosphate and insoluble CeO₂ products, a concentrate is generated containing mainly La³⁺ and Nd³⁺ ions, with smaller amounts of the other elements. Such concentrates are usually processed by rather elaborate solvent extraction methods, including ionic exchange and other procedures, in order to fractionate the elements, and to achieve their separation at several purity grades (De Jong et al., 2005; Takahashi et al., 2014). As a matter of fact, REE separation is far from trivial, since the elements exhibit very similar chemical properties, and the only possibility of success relies on the exploitation of the so called lanthanide contraction effect accompanying the increase of the atomic number. Such radial contraction determines the trends in the stability constants of the complexes, allowing some discrimination between the elements, which can be employed for separation purposes.

In this work we are applying the magnetic nanohydrometallurgy (MNHM) method (Condomitti et al., 2011a, 2011b, 2012, 2014) originally described in this journal for the production of copper, to the separation of the lanthanide elements, particularly La³⁺ and Nd³⁺. This technology is based on the use of functionalized superparamagnetic nanoparticles composed by magnetite, for capturing and processing metal ions in solutions by means of complexation reactions. For this

* Corresponding author.

E-mail address: henetoma@iq.usp.br (H.E. Toma).

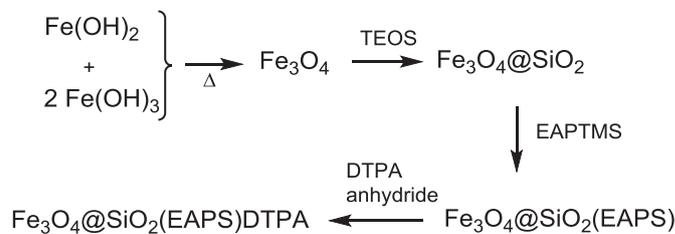
purpose, highly magnetic nanoparticles are required, exhibiting superparamagnetic behavior and a large surface area. The particles should be protected by a silica coating for improving its chemical resistance. In addition, their external surface should be further functionalized in order to achieve the highest density of the complexing agents as possible, for maximizing the uptake of the metal ions of interest. After complexation, the superparamagnetic nanoparticles charged with the complexed metal ions can be captured and confined magnetically, such that their metal content can be easily released from the particles by a simple acid–base treatment, or by performing in situ electrochemical deposition. Then, the particles can return to the process, providing a sustainable, recyclable strategy, capable of dealing with the elements without using any solvent, resin, filtration or precipitation procedure. Therefore, in MNHM the logistic relies on the direct use of superparamagnetic nanoparticles coupled with an external magnet in order to confine, transport and release the nanoparticles during the processing of the elements. It can be an important strategy, considering the current efforts for achieving elemental sustainability (Hunt et al., 2015; Toma, 2013, 2015).

In the case of the lanthanide elements, we have chosen one of the best classical complexing agents available, which is DTPA, the diethylenetriaminepentaacetic acid. In order to improve the ion sequestering capability, this agent was covalently linked to the nanoparticle by means of a previously anchored (ethylenediamine)propylsilane (EAPS) group, via the formation of amide bonds, as illustrated in Fig. 1.

2. Methodology

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and other basic reagents were of analytical grade and employed as supplied. Tetraethylorthosilicate (TEOS), ethylenediaminepropyltrimethoxysilane (EAPTMS) and diethylenetriaminepentaacetic anhydride (DTPA) were obtained from Sigma/Aldrich.

Fe_3O_4 @DTPA superparamagnetic nanoparticles (NPs) of about 30–40 nm were obtained by the co-precipitation method (Ahn et al., 2012), starting from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.088 mol) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.043 mol) and reacting with ammonium hydroxide (0.425 mol). After 1 h, the suspension of magnetic nanoparticles (MagNPs) was treated with tetramethylammonium hydroxide, TMAOH. The suspension was separated with an external $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnet, washed with water and kept under a vacuum. In a second step, the MagNPs were coated with SiO_2 using tetraethylorthosilicate, TEOS, (Stober et al., 1968) and then functionalized with ethylenediaminepropyltrimethoxysilane, EAPTMS. Typically, 1 g of magnetic nanoparticles was dispersed in 100 mL of glycerol and 40 mL of water, and after 10 min of sonication, 4 mL of TEOS was added dropwise at 80 °C (Mashhadizadeh and



Scheme 1.

Amoli-Diva, 2013; Gao et al., 2011). The reaction mixture was stirred for 4 h and the nanoparticles were magnetically confined and washed with water. After that, 133 mL of ethanol and 1 mL of water were added followed by 1.9 mL of EAPTMS (Bruce and Sen, 2005). The system was stirred for 1 day and the material was magnetically isolated, washed with water and dried under a vacuum. In a third step, the amino functionalized NPs were treated with 0.5073 g of DTPA anhydride, in DMF, and kept under stirring at 70 °C, for 14 h. Then, the particles were magnetically confined, washed with water, and dried under a vacuum (Yua et al., 2013; Zhu et al., 2014). Energy dispersive X-ray fluorescence (EDXRF) measurements were carried out using an EDX720 instrument from Shimadzu, equipped with a X-ray tube with Rh target and a Si(Li) detector. The adsorption isotherms were obtained by mixing 0.0100 g of NP@DTPA with 10 mL aqueous solutions containing different concentrations of the lanthanide nitrate (Synth Co.). The suspensions were left in a thermostated shaker at 25 °C for 90 min, in order to ensure equilibrium conditions. After that, the magnetic nanoparticles containing the lanthanide ions were separated magnetically, with the aid of an external magnet and analyzed with the EDXRF instrument. All the tests were made at pH 6 using 2-(4-morpholine) ethanesulfonic buffer, in order to prevent the lanthanide hydrolysis.

A Lakshare VSM 7410 vibrating sample magnetometer was employed for the magnetization measurements of the particles. The FTIR spectra were recorded on a Bruker alpha model ATR equipment, with the samples carefully prepared as disk pellets containing precisely 200 mg KBr, and 0.5% of nanoparticles, and working at a spectral resolution of 0.5 cm^{-1} .

Dynamic light scattering and zeta potential experiments were carried out using a Zetasizer Nano S (Malvern, UK) at 25 °C. The colloids were placed in standard 10.0 mm quartz cuvettes and illuminated with a He-Ne laser at $\lambda = 633 \text{ nm}$. The scattered light was collected at 173° to the laser beam. The average hydrodynamic size was determined with an accuracy of 4–5%.

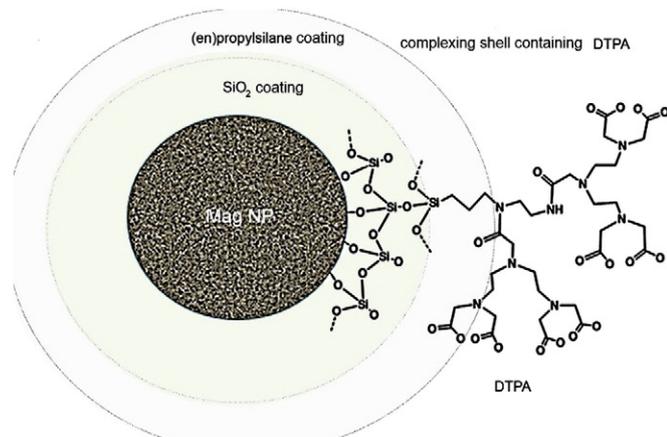


Fig. 1. Magnetic nanoparticles protected by a SiO_2 coating, containing an (ethylenediamine)propylsilane shell for supporting the covalently bound DTPA molecules, NP@ SiO_2 (EAPS)DTPA, or simply NP@DTPA.

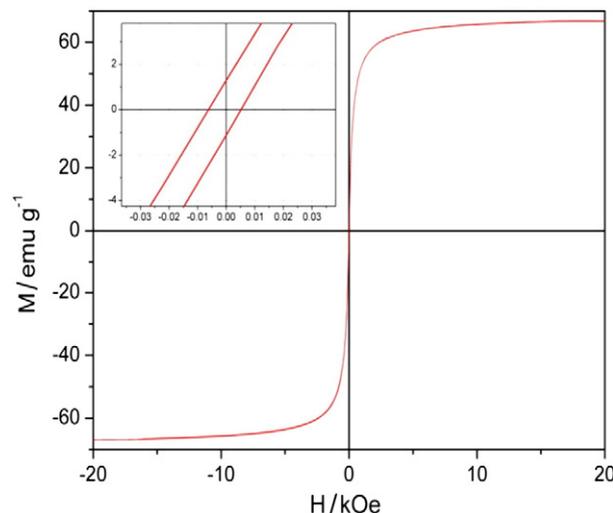


Fig. 2. Magnetization curve for Fe_3O_4 @ SiO_2 nanoparticles, at room temperature, showing a negligible hysteresis effect in the expanded scale (inset) around $H = 0$.

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