

Magnetophoresis of Superparamagnetic Nanoparticles Applied to the Extraction of Lanthanide Ions in the Presence of Magnetic Field

Fernando Menegatti de Melo¹, Sabrina da Nobrega Almeida¹, Antonio Domingues dos Santos² and Henrique Eisi Toma^{1*}

¹Institute of Chemistry, University of São Paulo, São Paulo, SP, Brazil

²Institute of Physics, University of São Paulo, São Paulo, SP, Brazil

*Correspondence to:

Prof. Henrique E. Toma

Institute of Chemistry, University of São Paulo

São Paulo, SP, Brazil

Tel: + 55 11 3091 3887

E-mail: henetoma@iq.usp.br

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Abstract

Magnetic migration (magnetophoresis) and extraction of Dy^{3+} ions by magnetite (Fe_3O_4) nanoparticles functionalized with diethylenetriaminepentaacetic acid (MagNP@DTPA) were probed using an analytical balance and an external weighing device comprising a miniature neodymium ($\text{Nd}_2\text{Fe}_{14}\text{B}$) magnet and a Lego® system. Contrary to our expectation, when the paramagnetic Dy^{3+} ions were captured by the superparamagnetic nanoparticles, the overall magnetization decreased, due to the anti-ferromagnetic dipolar interactions between the lanthanide ion and the superparamagnetic core. This finding allowed to monitor, in real time, the lanthanide extraction process (nanohydrometallurgy) and the nanoparticles migration in the magnetic field.

Keywords

Magnetophoresis, Nanohydrometallurgy, Rare earth, Magnetic balance, Superparamagnetic nanoparticles

Introduction

Superparamagnetic nanoparticles (MagNP) are being extensively explored in nanotechnology, and one of the recent applications deals with magnetic separations at the nanoscale (magnetophoresis) [1-5] and elemental processing in the mineral area [6, 7] (magnetic nanohydrometallurgy) [8-10]. The understanding of such processes can lead to important technological advances in metal ion extraction, separation and recovery, as well as in electrowinning processes, including environmental remediation involving the capture and removal of heavy metal contaminants from industrial effluents [11, 12]. Because of the magnetic recycling capabilities, they provide a powerful strategy towards a green and sustainable chemistry [13-17].

In order to understand the features of this work, it is important to note that magnetic nanoparticles encompass many thousand paramagnetic atoms undergoing simultaneous magnetization, yielding a very strong response in the presence of the magnetic field. However, in the absence of the magnetic field, the spins keep randomly distributed, exhibiting no spontaneous magnetization. The magnetic response is similar to that observed for paramagnetic ions, but it can achieve several orders of magnitude higher intensities.

The nanoparticles magnetism is usually probed by means of expensive vibrating magnetometers and SQUID instruments, not available in most chemical laboratories. However, such facilities are also not suitable for real time monitoring the processes involving superparamagnetic nanoparticles in solution. For this reason, a simple and rapid way of performing magnetic measurements

in the laboratory is quite desirable. In this sense, one could try to use the classical Gouy [18] and the Faraday balances [19] which are widely employed for probing paramagnetic and diamagnetic substances, exhibiting typical magnetic susceptibilities around $+10^{-4}$ and -10^{-6} emu g $^{-1}$, respectively. However it should be noticed that in the case of Fe₃O₄ nanoparticles the magnetization intensity can reach 92 emu g $^{-1}$, reflecting an enhancement of 6 orders of magnitude in the magnetic behavior in relation to the paramagnetic ions. For this reason, if one tries to perform the measurements using the Faraday balance in a similar way as for conventional paramagnetic substances, instead of employing a typical 10 mg sample, the measurement would require 10^{-8} g of the superparamagnetic nanoparticles. This is clearly impossible to handle, even by using the best analytical or electronic balance available. Conversely, if one uses for instance, 10 mg of superparamagnetic nanoparticles in the Faraday balance, the magnetization becomes so high that the pending sample will jump towards the Faraday magnet pole, invalidating the measurement, independently of the experimental setup and precautions employed.

For this reason, in order to circumvent this limitation, we have improved on the external weighing technique previously developed in our laboratory [20], allowing to adapt the classical analytical balance for the Gouy method. Our device is set in a miniature scale, using a Lego® platform placed on the analytical balance plate, in addition to a small Nd₂Fe₁₄B magnet. The magnetic sample is introduced into an Eppendorf tube tightly inserted into a silver ring fixed at the end of an EPR or NMR tube used as a cantilever. By means of the Lego® platform, the cantilever provides efficient sample positioning, ensuring reproducibility and accuracy.

Our preference for Lego® toys to support the cantilever and magnet rail was due to their admirable micrometric precision and versatility. Such qualities have already been successfully explored by Quercioli et al. [21] in the design of versatile optomechanic systems. As a matter of fact, Lego® blocks can be conveniently assembled on the balance platform, allowing many distinct arrangements for supporting the cantilever, and also providing the necessary counterpoise for equilibrating the device when it is submitted to strong magnetic forces.

The Lego® design can be fitted into any analytical balance and can be easily removed, without compromising its normal function in the laboratory. Its greatest advantage is the possibility of probing directly the superparamagnetic nanoparticles in solution, as well as their magnetophoretic response, in a rather simple way. The application of this practical approach to the investigation of the magnetophoretic behavior of superparamagnetic nanoparticles in solution, and their performance in the capture of Dy³⁺ ions for hydrometallurgical applications, is reported in this paper.

Materials and Methods

Synthesis of MagNP@DTPA and their characterization

The engineered nanoparticles were synthesized and characterized as reported before [22]. The process employed

was based on the co-precipitation method [23], by reacting a mixture of FeCl₃·6H₂O and FeSO₄·7H₂O with ammonium hydroxide. After treating with tetramethylammonium hydroxide the nanoparticles were magnetically confined using an external Nd₂Fe₁₄B magnet, washed with water and kept under vacuum. In a second step, the MagNPs were coated with SiO₂ by the Stober [24] method, using tetraethylorthosilicate, in glycerol/water mixtures. In a third step, the particles were coated with ethylenediaminepropyltrimethoxysilane and finally, the amino-functionalized nanoparticles were treated with DTPA anhydride, in DMF, and isolated in solid form after washing with water and drying under vacuum. Characterization included elemental analysis, TEM, DLS, Zeta size, FTIR, Raman, EDX and vibrating magnetometer measurements [22].

Experimental Lego® setup

The Lego® setup is shown in Figure 1. It consists of a diamagnetic cantilever (EPR tube) with a silver ring tightly inserted into the open end. The cantilever is fixed at the base by means of three internal Lego® pieces (Figure 1 inset), allowing it to slide easily under application of a mild force. After attaching the cover, the cantilever keeps tightly fixed into the support. In order to accommodate the microtube (Eppendorf) sample, a silver ring was precisely hand moulded in order to prevent any displacement by the magnetic field. The magnet was supported on a mobile, vertical Lego® rail support, allowing movements along the z-axis, with its positioning controlled by a lateral ruler. A parallel projection of a laser pointer on a millimetric paper has also been used for improving the precision. By means of the adjustable vertical Lego® rail, the magnet was kept at a specific height (e. g. 0.40 cm to 2.00 cm) from the microtube sample, allowing to manage the influence of the magnet-sample distance in the measurements.

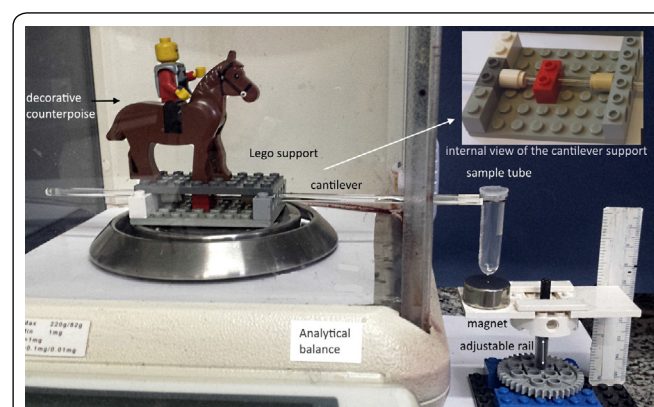


Figure 1: Lego® assembly for external weighing in an analytical balance, consisting of an adjustable diamagnetic cantilever with a tightly fixed silver ring for inserting the microtube sample. The miniature Nd₂Fe₁₄B cylindrical magnet (1.1 T, 2.0 cm x 1.0 cm), is placed on the mobile, vertical Lego® rail support. Inset: internal view of the cantilever base.

Magnetophoresis and capture of Dy³⁺ by the MagNP@DTPA nanoparticles

Magnetophoretic assays were carried out in three steps, as illustrated in Figure 2. First, 1 mL of 0.1 mol L⁻¹ Dy³⁺ solution was transferred to the microtube and its magnetic response evaluated using the Lego® assembly (Figure 2A).

Then, 8 mg of MagNP@DTPA was added and the weight precisely determined in the absence of the magnet, providing the exact mass of nanoparticles (Figure 2B). The sample was stirred for 300 min. in order to accomplish the capture of the Dy^{3+} ions by MagNP@DTPA. After applying a magnetic field (Figure 2C), there is a rapid magnetophoretic deposition of the nanoparticles, leading to a dramatic increase of the relative weight measured in the analytical balance.

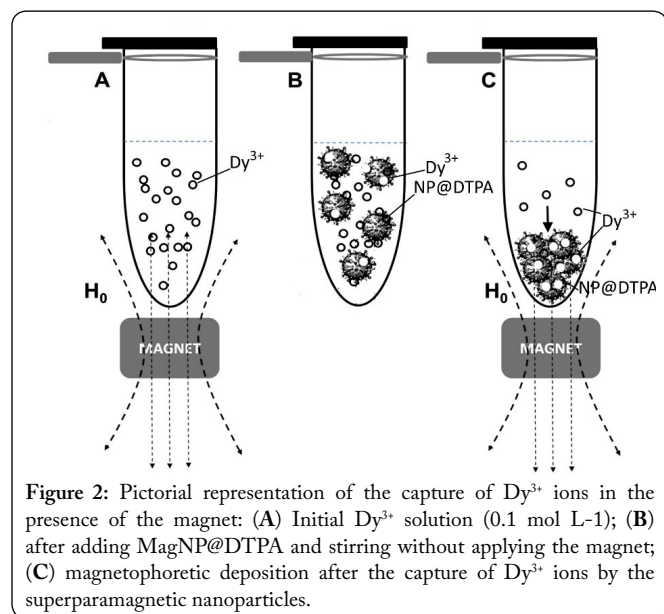
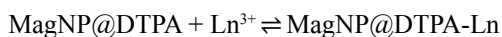


Figure 2: Pictorial representation of the capture of Dy^{3+} ions in the presence of the magnet: (A) Initial Dy^{3+} solution (0.1 mol L^{-1}); (B) after adding MagNP@DTPA and stirring without applying the magnet; (C) magnetophoretic deposition after the capture of Dy^{3+} ions by the superparamagnetic nanoparticles.

Results and Discussion

Magnetic nanohydrometallurgy [8–10] deals with the capture of metal ions by superparamagnetic nanoparticles and their magnetophoretic separation for processing the elements. The application of superparamagnetic nanoparticles (Fe_3O_4) coated with the diethylenetriaminepentaacetic (DTPA) complexing agent for the extraction and separation of lanthanide ions ($\text{Ln} = \text{La}^{3+}$ and Nd^{3+}) has already been successfully accomplished in our laboratory [22]. In this work we focused on Dy^{3+} ions, because their strongest magnetic properties in the lanthanide series were expected to be more interesting for magnetophoretic applications.



The engineered nanoparticles employed in the experiments exhibit a nanocrystalline magnetite core of about 15 nm determined by TEM, coated with an about 7 nm SiO_2 protecting shell estimated from the difference to the hydrodynamic radius. This shell also encompasses the salinization with triethoxibis (ethylenediamine)propylsilane (EAPS), followed by the covalent binding of DTPA. It can be represented as MagNP@ SiO_2 (EAPS)DTPA, or simply MagNP@DTPA, as illustrated in Figure 3.

In solution, the average nanoparticle hydrodynamic radius was 22 nm, and their zeta potentials were pH dependent, starting from 20 mV at pH 3, reflecting the positive charge from the protonated amino groups, and the presence of neutral carboxylic acid groups. Above pH 5, the carboxylic groups are deprotonated, and the nanoparticles become electrostatically

stabilized by a negative charge, yielding -30 mV zeta potential. Considering the zeta potentials and the pK_a of the Dy^{3+} ions, the capture experiments with the MagNP@DTPA nanoparticles were carried out at pH 6, using MES buffer. At this pH most of the carboxylic groups are deprotonated, with no risk of precipitating the metal ion hydroxides.

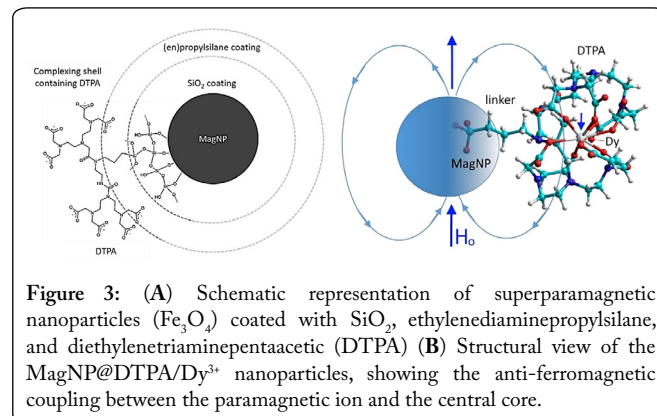


Figure 3: (A) Schematic representation of superparamagnetic nanoparticles (Fe_3O_4) coated with SiO_2 , ethylenediaminepropylsilane, and diethylenetriaminepentaacetic (DTPA) (B) Structural view of the MagNP@DTPA/ Dy^{3+} nanoparticles, showing the anti-ferromagnetic coupling between the paramagnetic ion and the central core.

The capture of the lanthanide ions (La^{3+} and Nd^{3+}) has already been investigated in our laboratory [22] using expensive energy dispersive X-ray fluorescence equipments. The procedure requires collecting, periodically, suitable samples for the analysis. Real time monitoring is not possible using such instrumentation. For comparison purposes, the same methodology has been applied for the capture of Dy^{3+} ions by MagNP@DTPA, yielding an adsorption equilibrium constant of $2.57 \times 10^{-3} \text{ g(MagNP)} \text{ L}^{-1}$ in comparison with 2.92×10^{-4} and $4.22 \times 10^{-4} \text{ g(MagNP)} \text{ L}^{-1}$ for the La^{3+} and Nd^{3+} ions, respectively. The maximum amount of captured Dy^{3+} ions corresponded to 63.2 mg(Dy)/g(MagNP).

Probing magnetophoresis

Magnetophoresis deals with the nanoparticles migration in the presence of an applied magnetic field. Its understanding is essential for the application of nanoparticles in magnetic separation processes, however, the theory involved is yet under development and has been the subject of many recent discussions [1–5]. In addition the advances in the experimental procedures remain yet quite limited.

There are lots of benefits associated with the use of magnetic nanoparticles in separation processes [25]. However, since magnetic nanoparticles are very small, their magnetophoretic pathway can be perturbed by the thermal energy and the viscous drag forces [26]. For this reason, a strong magnetic force is necessary to overcome the thermal randomization. Because of the high complexity of the analytical solutions dealing with inhomogeneous magnetic fields, no attempt will be made to discuss the theoretical formalisms and approximations involved. Instead, we will concentrate on the experimental procedure employed, using the basic theory just as a guide.

The simplest theoretical approach considers the magnetophoretic displacement of the isolated nanoparticles of radius R and magnetic moment m as a function of the applied field H , under the attractive force of the magnetic field gradient,

$$F_{mag} = m(H)\mu_0 \left[\frac{\partial H}{\partial r} \right] \quad \dots\dots\dots(1)$$

Where μ_0 is the magnetic constant (equal 1 in cgs unit).

In this work, it should be noted that the major measurements were carried out under the so called low field magnetophoretic regime [27, 28] where magnetic particles are distant from the magnet and the gradients are smaller than 100 T/m. In this case the moment is proportional to H , ($m = \chi H$), and equation 10 becomes

$$F_{mag} = \chi\mu_0 H \left[\frac{\partial H}{\partial r} \right] \quad \dots\dots\dots(2)$$

The opposite viscous drag force exerted by the solvent, is given by

$$F_{vis} = 6\pi\eta Rv \quad \dots\dots\dots(3)$$

Where η is the viscosity, and v = velocity. The balance of such forces allows to evaluate the magnetophoretic velocity v , as

$$v = \frac{1}{6\pi\eta R} \chi\mu_0 H \left[\frac{\partial H}{\partial r} \right] \quad \dots\dots\dots(4)$$

Under this condition, the migration of the isolated nanoparticles should be directly proportional to the magnetic field H and to the magnetic field gradient ($\partial H/\partial r$).

It should be noticed that at the high field limit, — a situation where the particles are very close to the magnet, — the magnetic moment (m) approaches saturation, becoming almost insensitive to changes in the field [3]. However, its contribution to our measurements is completely negligible, since the nanoparticles close to the bottom of the microtubes should undergo instantaneous deposition, without contributing to the measured magnetophoretic rates.

By using a simple analytical balance arrangement, the magnetophoretic migration can be easily monitored by the relative weight increase as long as magnetic nanoparticles reach the bottom, attracted by the magnet (Figure 4). The contribution of gravity and of the magnetic attraction on the paramagnetic ions in solution is completely negligible with respect to the relative weight increase observed experimentally. In this way, from the successive weighing measurements as a function of time one can obtain the magnetophoretic deposition rates, from which it is possible to evaluate the corresponding kinetics, and to extract the velocity constants (Figure 4).

As one can see in Figure 4A, it is easy to follow the magnetophoretic decantation process, employing a simple weighing procedure in real time. The response monitored in this way actually reflects an average profile, because of the convective fluid motion induced by the different

magnetophoretic velocities that the particles can have at the top and at the bottom of the system [1].

By changing the distance from the magnet, the kinetics and the relative weight at the equilibration point are strongly affected by the magnetic field as shown in Figure 4B and 4C. As predicted by eq. 13, the magnetophoretic rates decrease at longer distances from the magnet (Figure 4D and 4E).

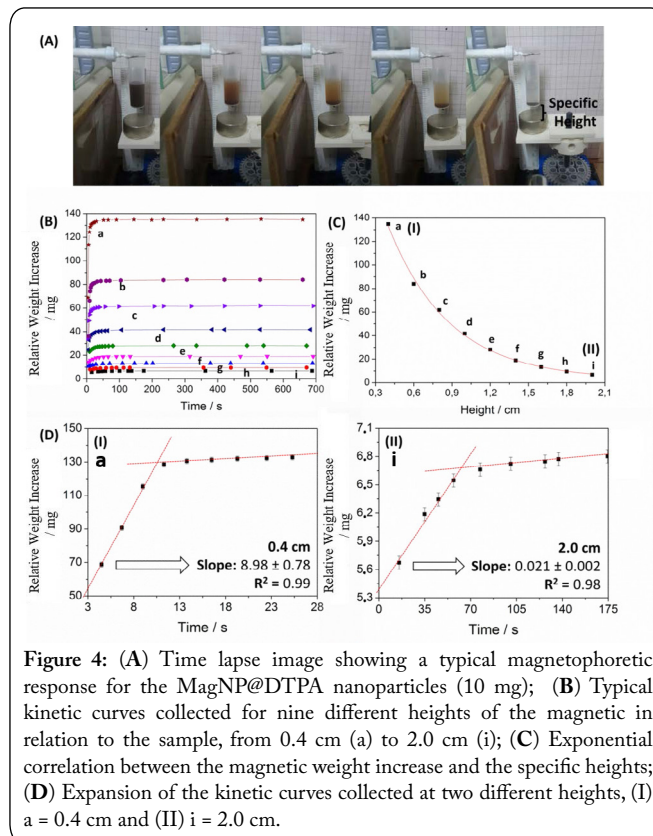
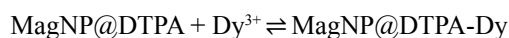


Figure 4: (A) Time lapse image showing a typical magnetophoretic response for the MagNP@DTPA nanoparticles (10 mg); (B) Typical kinetic curves collected for nine different heights of the magnetic in relation to the sample, from 0.4 cm (a) to 2.0 cm (i); (C) Exponential correlation between the magnetic weight increase and the specific heights; (D) Expansion of the kinetic curves collected at two different heights, (I) a = 0.4 cm and (II) i = 2.0 cm.

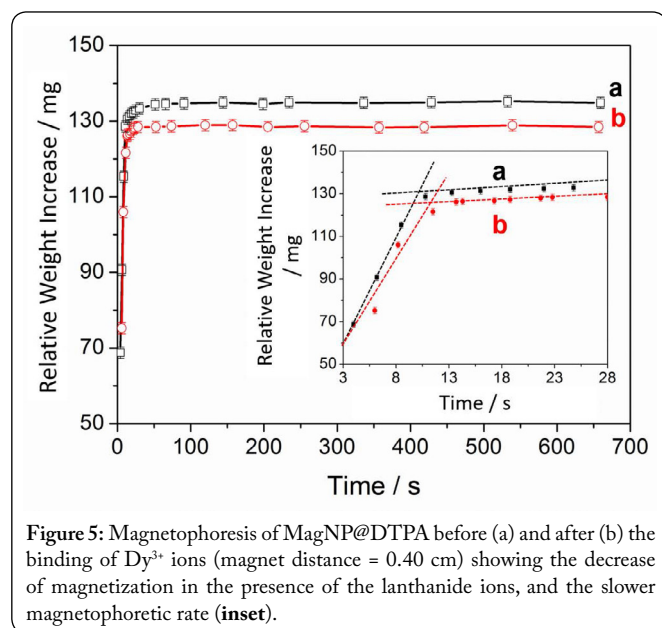
Monitoring the Dy³⁺ capture by magnetophoresis

The capture of Dy³⁺ ions by the MagNP@DTPA nanoparticles and the analysis was carried out under rigorous conditions, as reported in the experimental section. The reaction can be represented as



In order to monitor the capture of Dy³⁺ ions, the magnetophoretic experiments were carried out according to the three steps previously described in Figure 2. In this case, the application of magnetic field to 1 mL of the starting 0.1 mol L⁻¹ Dy³⁺ solution produced practically no change in the apparent weight, indicating a negligible contribution of the paramagnetism of the Dy³⁺ ions. Then, 8 mg of MagNP@DTPA was added to the Dy³⁺ solution, in the absence of the magnet, and the mixture was kept under stirring for 300 min. After this, the corresponding magnetophoretic curve was obtained, as shown in Figure 5. A similar experiment was repeated in the absence of Dy³⁺ ions. The comparison, shown in Figure 5 revealed that a systematic decrease of magnetism, by 5.9 ± 1 % results after the binding of the Dy³⁺ ions. This result is consistent with the occurrence of an anti-ferromagnetic coupling between the paramagnetic Dy³⁺

ions and the superparamagnetic core. This can be better seen in Figure 3B, where the Dy^{3+} ions are shown in a region of negative magnetic field gradients in relation to the applied field.



The magnetophoretic velocity is also slightly reduced after the binding of Dy^{3+} ions, with the curve slopes decreasing from 8.98 to 8.52. This is consistent with the decrease of the magnetization of the nanoparticles and with the increase of the hydrodynamic radii due to the presence of the Dy^{3+} ions.

We have demonstrated that the decrease of magnetization can be precisely probed with the external weighing device. Actually, this property provides an effective way of monitoring the binding of the Dy^{3+} ions to the magnetic nanoparticles. In order to explore this feature, the experiments of the

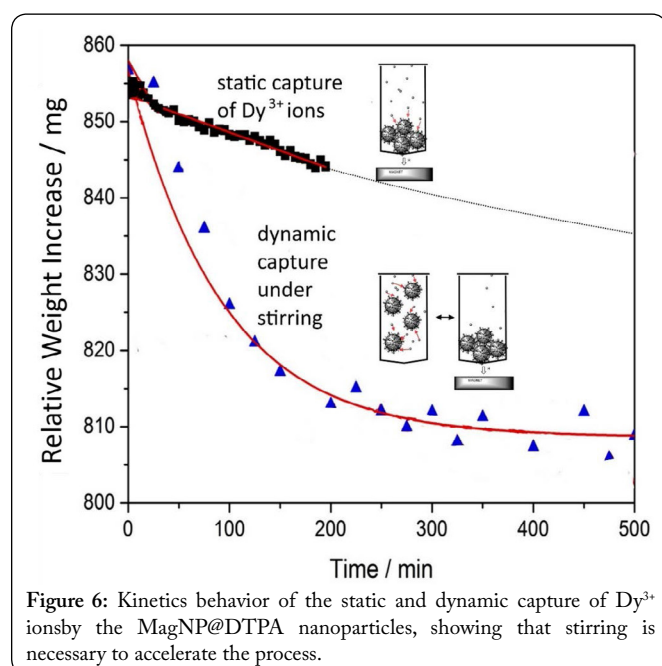


Figure 6: Kinetics behavior of the static and dynamic capture of Dy^{3+} ions by the MagNP@DTPA nanoparticles, showing that stirring is necessary to accelerate the process.

capture of Dy^{3+} ions by MagNP@DTPA nanoparticles were conducted under static and dynamic regimes. In the first case, the nanoparticles were added to the Dy^{3+} solutions without stirring, and the weight monitored after the magnetophoretic deposition. In this regime, the weight started to decrease very slowly, commanded by the diffusional capture of Dy^{3+} ions, as shown in Figure 6. The process proceeds rather slowly, requiring several days to be complete.

The experiment was repeated under the stirring regime. In this case the relative weights were monitored intermittently, after 25 min stirring showing an exponential decrease until achieving stabilization, because of the saturation of MagNP@DTPA with the Dy^{3+} ions. These results are shown in Figure 6.

The magnetophoretic results revealed that the capture of the Dy^{3+} ions by the MagNP@DTPA nanoparticles involves a slow Dy^{3+} diffusion controlled adsorption kinetics, calling the attention for the time required for equilibration (> 200 min), and for the importance of stirring in the absence of magnetic field.

Conclusions

The reported magnetic weighing device allowed to convert a classical analytical balance into a practical magnetometer which can be used in many laboratory experiments. By keeping the same experimental arrangement and a constant distance from the magnet, an excellent reproducibility can be obtained for the measurements. On the other hand, by using a standard material (e. g. high quality $\text{Fe}_3\text{O}_4 = 92 \text{ emu g}^{-1}$) for calibration, one can evaluate the saturation magnetization of the samples, in a rather simple way.

The possibility of evaluating the magnetic behavior of the nanoparticles in the presence of solvent is another particularly relevant aspect. In most typical magnetic experiments, the necessity of previous isolation of the solid materials and their drying can have strong influence on the results, considering the interactions occurring in the aggregation of the nanoparticles.

The comparison of the magnetophoretic behavior of MagNP@DTPA and MagNP@DTPA-Dy revealed a 5.9% decrease of magnetization after the binding of the paramagnetic Dy^{3+} ions. This result was ascribed to antiferromagnetic dipolar interaction between dysprosium ions and the magnetic nanoparticles. The observed decrease of magnetization correlates with the captured amount (6% w/w) of the Dy^{3+} ions, allowing to probe the metal ion extraction from the changes in the magnetophoresis response.

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