



Selective separation of rare earth ions from aqueous solution using functionalized magnetite nanoparticles: kinetic and thermodynamic studies



Radwa M. Ashour^{a,b}, Ramy El-sayed^c, Ahmed F. Abdel-Magied^b, Ahmed A. Abdel-khalek^d, M.M. Ali^b, Kerstin Forsberg^e, A. Uheida^a, Mamoun Muhammed^f, Joydeep Dutta^{a,*}

^a Functional Materials, Applied Physics Department, SCI School, Isafjordsgatan 22, SE-164 40 Kista Stockholm, Sweden

^b Nuclear Materials Authority, P.O. Box 530, El Maadi, Cairo, Egypt

^c Experimental Cancer Medicine, KFC, Novum, Department of Laboratory Medicine, Karolinska Institute, 141 86 Stockholm, Sweden

^d Department of Chemistry, Faculty of Science, Beni-Suef University, Beni-Suef, Egypt

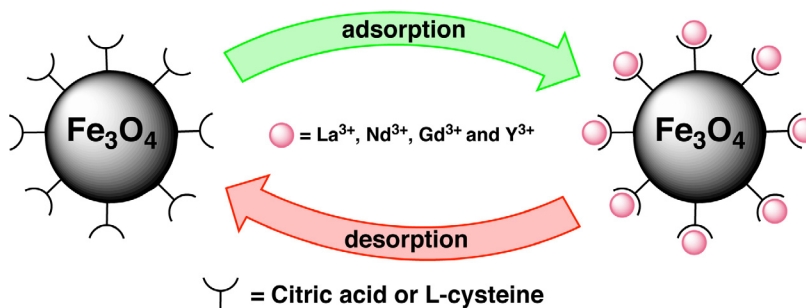
^e Department of Chemical Engineering, KTH Royal Institute of Technology, 100 44 Stockholm, Sweden

^f Institute of Graduate Studies and Research, Alexandria University, Alexandria, Egypt

HIGHLIGHTS

- Functionalized Fe₃O₄ NPs with citric acid and L-cysteine were prepared.
- Selective separation of La³⁺, Nd³⁺, Gd³⁺ and Y³⁺ by the functionalized Fe₃O₄ NPs.
- Cys@Fe₃O₄ NPs showed high La³⁺, Nd³⁺, Gd³⁺ and Y³⁺ adsorption capacity.
- The adsorption process followed a pseudo-second order rate law.

GRAPHICAL ABSTRACT



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ABSTRACT

Separation of rare earth ions (RE³⁺) from aqueous solution is a tricky problem due to their physico-chemical similarities of properties. In this study, we investigate the influence of the functionalized ligands on the adsorption efficiency and selective adsorption of La³⁺, Nd³⁺, Gd³⁺ and Y³⁺ from aqueous solution using Magnetite (Fe₃O₄) nanoparticles (NPs) functionalized with citric acid (CA@Fe₃O₄ NPs) or L-cysteine (Cys@Fe₃O₄ NPs). The microstructure, thermal behavior and surface functionalization of the synthesized nanoparticles were studied. The general adsorption capacity of Cys@Fe₃O₄ NPs was found to be high (98 mg g⁻¹) in comparison to CA@Fe₃O₄ NPs (52 mg g⁻¹) at neutral pH 7.0. The adsorption kinetic studies revealed that the adsorption of RE³⁺ ions follows a pseudo second-order model and the adsorption equilibrium data fits well to the Langmuir isotherm. Thermodynamic studies imply that the adsorption process was endothermic and spontaneous in nature. Controlled desorption within 30 min of the adsorbed RE³⁺ ions from both Cys@Fe₃O₄ NPs and CA@Fe₃O₄ NPs was achieved with 0.5 M HNO₃. Furthermore, Cys@Fe₃O₄ NPs exhibited a higher separation factor (SF) in the separation of Gd³⁺/La³⁺, Gd³⁺/Nd³⁺, Gd³⁺/Y³⁺ ions compared to CA@Fe₃O₄ NPs.

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* Corresponding author.

E-mail address: joydeep@kth.se (J. Dutta).

1. Introduction

Rare earth elements (REEs) have received attention due to their use in different applications such as in superconductors, telecommunications, nuclear and solar energy conversion, photocatalysis, and biosciences [1,2]. In recent years, REEs separation chemistry has gained a great attention not only for their industrial applications, but also their environmental mitigation. Gadolinium (Gd) is useful in ceramic industries, metallurgy, nuclear techniques in fuel element fabrications and heavy water reactors as neutron poison. Aqueous Gd^{3+} ion, even at trace level, considered as hazardous material [3,4]. In view of all the above-mentioned uses and its high toxicity, selective separation of Gd^{3+} from aqueous solutions is of extreme importance. Due to the similar chemical and physical properties of REEs, separating them from a mixture is still a challenging task [5,6]. The most commonly used techniques for the separation and recovery of REEs are precipitation [7], liquid-liquid extraction [8], ion exchange [9] and adsorption [10]. Amongst these, solid-phase extraction (SPE) is proven to be an effective and convenient method for REEs recovery. SPE has been proven to be an easy operation offering high adsorption capacities, rapid phase separation and economical cost effectiveness [11]. Various types of adsorbents (organic, inorganic, carbon based material and bio-sorbents) have been developed for SPE recovery of REEs [12–17]. Magnetic nanoparticles have been found increased attention as nanoadsorbents for environmental decontamination due to the possibilities of using external magnetic field to guide the process of separation [18]. Furthermore, upon desorption of the adsorbed ions, the magnetic nanoparticles can be reused, making them promising sustainable adsorbents. Functionalized magnetic nanoparticles using inorganic materials have been demonstrated to be excellent candidates for selective adsorption of RE^{3+} ions and metal traces from aqueous solution [19–23]. Dupont et al. reported the functionalization of magnetite (Fe_3O_4) and nonmagnetic (silica and titanium dioxide) nanoparticles with *N*-[(3-trimethoxysilyl)propyl]ethylenediamine triacetic acid (TMS-EDTA) and their behavior towards the adsorption and separation of RE^{3+} ions in aqueous media [24]. Selective extraction of heavy samarium-holmium (Sm–Ho) and light lanthanum-niobium (La–Nd) lanthanides from aqueous solutions using diethylenetriamine-pentaacetic acid (DTPA) functionalized Fe_3O_4 NPs, achieving high SF between heavy-lanthanides and light-lanthanides reaching the maximal value of 11.5 at low pH (2.0) in 30 min was reported by Qiang et al. recently [25].

The choice of appropriate functional chelating groups is a critical factor to obtain maximum adsorption efficiency and selectivity. Citric acid and *L*-cysteine are two major classes of chelating agents that have been studied as chelators for adsorption of metal ions [26]. Citric acid contains three carboxyl groups and a hydroxyl group, while *L*-cysteine is constituted of three different functional groups, amine, thiol and carboxylic acid (Fig. 1). Both citric acid and *L*-cysteine ligands lead to the availability of functional groups on Fe_3O_4 NPs for controlled adsorption but also affects the size, morphology and colloidal stability of the nanoparticles [21].

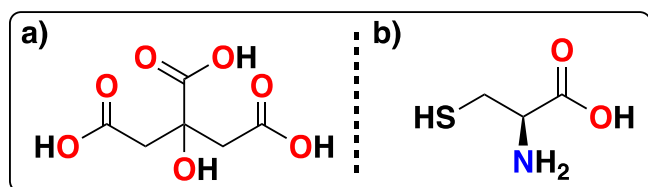


Fig. 1. Chemical structure of the functionalization ligands used in this study: (a) Citric acid and (b) *L*-cysteine.

Herein, we report the synthesis and characterization of magnetic nanoparticles functionalized with citric acid ($CA@Fe_3O_4$ NPs) and *L*-cysteine ($Cys@Fe_3O_4$ NPs) ligands, respectively. We investigate the influence of $CA@Fe_3O_4$ NPs and $Cys@Fe_3O_4$ NPs on the selective adsorption of RE^{3+} ($= La^{3+}, Nd^{3+}, Gd^{3+}$ and Y^{3+}) and the adsorption mechanism from aqueous solution. The dependence of adsorption parameters such as contact time, pH, temperature and initial concentration of metal ions on the adsorption efficiency were studied. In addition, we report the desorption characteristics of REEs from the loaded $CA@Fe_3O_4$ NPs and $Cys@Fe_3O_4$ NPs using different eluents such as NaOH and HNO_3 . Adsorption kinetics and adsorption isotherms were analyzed using a non-linear method and the thermodynamic parameters (ΔG° , ΔH° and ΔS°) were derived from the obtained experimental results.

2. Materials and methods

2.1. Chemicals

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, $\geq 99\%$), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, $\geq 98\%$), ammonium hydroxide (25%), citric acid monohydrate (98%), *L*-cysteine, nitric acid (65%), sodium hydroxide (98%), lanthanum(III) nitrate hexahydrate (99.9%) [$La(NO_3)_3 \cdot 6H_2O$], neodymium(III) nitrate hexahydrate (99.9%) [$Nd(NO_3)_3 \cdot 6H_2O$], gadolinium(III) nitrate hexahydrate (99.9%) [$Gd(NO_3)_3 \cdot 6H_2O$], yttrium(III) nitrate hexahydrate (99.9%) [$Y(NO_3)_3 \cdot 6H_2O$] and standard solutions (1000 mg/L) of $Mg(NO_3)_2$, $Ca(NO_3)_2$ and $Ni(NO_3)_2$ were purchased from Sigma Aldrich. All chemicals were of analytical grade reagents and used as received without further purification. Deionized water with a resistivity of 18 $M\Omega$ cm was used in all the experiments.

2.2. Characterization

High resolution transmission electron microscopy (HRTEM) (HR-FEG-TEM, JEOL JEM-2100, Tokyo, Japan) was used for the characterization of the morphology and size distribution of the synthesized nanoparticles. For structural evaluation X-Ray Powder Diffraction analysis (XRPD, PANalytical Empyrean) was carried out. Fourier transform infra-red (FT-IR) spectrometer (Nicolet Instruments model Avatar-100 equipped with diamond ATR, Madison, WI, USA) was used to study characteristic functional groups on the nanoparticle surfaces in the range of 500–4000 cm^{-1} . Specific surface area calculations were determined by the Brunauer-Emmett-Teller (BET) method with N_2 gas using Micromeritics ASAP 2000 surface area and porosity system (Quantachrome, USA) by first degassing the samples at 150 °C for 1 hour. Zeta potential of synthesized nanoparticles and surface charge of nanoparticles were determined by (Delsa Nano C, Beckman Coulter, CA, USA). The percentage weight loss of $CA@Fe_3O_4$ NPs and $Cys@Fe_3O_4$ NPs were studied in the temperature range of 30–600 °C at a heating rate of 10 °C min in nitrogen atmosphere, using Thermogravimetric analysis (TGA) (Q5000, TA instruments, DE, USA). The concentrations of metal ions were determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) iCAP 6500 ICP from Thermo Scientific (MA, USA). Adjustments of solutions pH were measured by a pH-meter (ORION 410).

2.3. Synthesis of precursor Fe_3O_4 NPs

The detailed synthetic process of Fe_3O_4 NPs (≈ 10 nm) have been described elsewhere [27]. Briefly, 1.988 g (0.125 mol) of $FeCl_2 \cdot 4H_2O$ and 5.406 g (0.25 mol) of $FeCl_3 \cdot 6H_2O$ (1:2 molar ratio) were dissolved in 80 mL of water in a round bottomed flask at room temperature. Then the temperature was slowly increased to

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