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Preparation and characterization of magnetic iron oxide nanoparticles functionalized by L-cysteine: Adsorption and desorption behavior for rare earth metal ions

Radwa M. Ashour[a], Ahmed F. Abdel-Magied[a,b,*], Ahmed A. Abdel-khalek[c], O.S. Helaly[a], M.M. Ali[a,*]

[a] Nuclear Materials Authority, P.O. Box 530, El Maadi, Cairo, Egypt
[b] Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm, Sweden
[c] Department of Chemistry, Faculty of Science, Beni-sueif university, Beni-sueif, Egypt

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ABSTRACT

In this work, magnetic iron oxide nanoparticles functionalized with L-cysteine (Cys-Fe_3O_4 NPs) was synthesized and fully characterized by transmission electron microscopy (TEM), X-ray powder diffraction (XRD), Fourier transform infra-red (FTIR), thermogravimetric analysis (TGA) and zeta potential measurements. The synthesized Cys-Fe_3O_4NPs has been evaluated as a highly adsorbent for the adsorption of a mixture of four rare earths RE^{3+} ions (La^{3+}, Nd^{3+}, Gd^{3+} and Y^{3+}) from digested monazite solutions. The influence of various factors on the adsorption efficiency such as, the contact time, sample pH, temperature, and concentration of the stripping solution were investigated. The results indicate that Cys-Fe_3O_4 NPs achieve high removal efficiency 96.7, 99.3, 96.5 and 87% for La^{3+}, Nd^{3+}, Gd^{3+} and Y^{3+} ions, respectively, at pH = 6 within 15 min, and the adsorbent affinity for metal ions was found to be in order of $Nd^{3+} > La^{3+} > Gd^{3+} > Y^{3+}$ ions. Using the Langmuir model, a maximum adsorption capacity of La^{3+}, Nd^{3+}, Gd^{3+} and Y^{3+} at room temperature was found to be 71.5, 145.5, 64.5 and 13.6 mg g^{-1}, respectively. The Langmuir isotherm and pseudo-second order model fitted much better than the other isotherms and kinetic models. The obtained results for the thermodynamic parameters confirmed the spontaneous and endothermic nature of the process. Moreover, the desorption was carried out with 0.1 M nitric acid solutions. In addition, Cys-Fe_3O_4 NPs can be used as a highly efficient adsorbent for the adsorption of La^{3+}, Nd^{3+}, Gd^{3+} and Y^{3+} ions from digested monazite solutions.

1. Introduction

Rare earth elements (REEs) play an important role in many fields as crucial industrial materials with unique uses; such as permanent magnet, super conductors, electronics, medical and nuclear technologies, therefore, industrial demand for them has increased [1–3]. The discovery of REEs has taken long time due to very similar physico-chemical properties [4,5]. REEs recovery and separation from monazite mineral using various techniques such as precipitation, solvent extraction, adsorption and ion exchange chromatography have been studied extensively [5]. Solid-phase extraction (SPE) technique has become one of the most widely used sample pretreatment techniques for the extraction of heavy metals or REEs, due to it is simple to implement, usually high preconcentration factor to be attained, rapid separation, and can be easily incorporated into automated analytical techniques [6–13]. The type of adsorbent has a crucial function in SPE-based methods because it determines the selectivity, affinity, and capacity. In general, an ideal SPE adsorbents are expected to have large specific area, low blank, high stability, fast adsorption and desorption rates, reversible adsorption, high selectivity and finally high recovery efficiency.

Due to the clear advantages of SPE technology, considerable efforts have been made to find new materials that can be used as a selective sorbents [5,14–21]. Several types of nanomaterials, including magnetic iron oxide nanoparticles (Fe_3O_4 NPs) have unique advantages SPE adsorbents such as favorable chemical stability, low cost, easily retrieved from solution with a magnet. Coating the surface of the magnetic nanoparticles with functional

* Corresponding authors at: Nuclear Materials Authority, P.O. Box 530, El Maadi, Cairo, Egypt.
E-mail address: ahmed.fawzy@su.se (A.F. Abdel-Magied).

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groups can help to avoid the aggregation of iron oxide nanoparticles and increase the REEs removal efficiency. L-Cysteine (Cys), a non-essential, water soluble, with three functional groups (-SH, $-NH_2$, $-COOH$), has a binding affinity to coordinate with Fe_3O_4 NPs surface. In Cys molecules, the divalent sulfur (-SH) add an extra functional group and act as antioxidant, while the amine ($-NH_2$) and carboxylic (-COOH) in Cys molecules facilitate the functionalization of Fe_3O_4 NPs surface in order to have high dispersibility and solubility in aqueous solutions [22,23].

Herein, the general scope of this paper is to develop an SPE method by using iron oxide nanoparticles coated with L-cysteine (Cys-Fe_3O_4 NPs) materials for the extraction and selective separation of our target rare earth ions La^{3+}, Nd^{3+}, Gd^{3+} and Y^{3+} ions from the nitric liquor generated from the monazite digest process [La and Nd as light rare earth elements (LREEs) and Gd and Y as heavy rare earth element (HREEs)]. In the batch adsorption tests, different parameters were evaluated such as loading capacity, adsorption kinetics, thermodynamics parameters and influence of pH. Optimizing the adsorption and desorption conditions in order to acquire knowledge that will help for the development of highly efficient SPE adsorbents for the commercial production.

2. Results and discussion

2.1. Characterization of monazite

The Egyptian purified monazite was identified and fully characterized by using EDX, SEM, XRD and ICP-OES as shown in Fig. 1 and Table 1, respectively. The sample analysis shows that it contains 70.7% LREEs, 6% Gd, 10% Dy and 13.26% Y. The SEM image of the treatment monazites ore is shown in Fig. 1b, where the major amount of monazite contains particle of size ranging 100–200 mesh, indicting that no size reduction occurred to the monazite sample during the purification process. The XRD is shown in Fig. 1c, where sharp reflections peaks of relatively high amplitudes of REOs were observed, which is in agreement to other reported work [24].

Table 1
Concentration of REEs in the purified monazite sample.

RE^{3+} ions	REEs concentration (ppm)
La^{3+}	25
Nd^{3+}	22
Gd^{3+}	16
Y^{3+}	19
Na^{2+}	18
Ca^{2+}	0.9
Dy^{3+}	18
Ce^{3+}	20

2.2. Cys-Fe_3O_4 NPs characterization

In order to examine and validate the successful synthesis of Cys-Fe_3O_4 NPs, various physical-chemical techniques have been used. For a morphological Cys-Fe_3O_4 NPs characterization, TEM was used. The TEM images of the synthesized Cys-Fe_3O_4 NPs is presented in Fig. 2a, where it clearly shows that Cys-Fe_3O_4 NPs is made up of monodisperse and had similar distribution size in the range of 12 ± 3 nm. No aggregation was found, indicating the excellent dispersibility of Cys-Fe_3O_4 NPs in water. EDX analysis on the coated Fe_3O_4 NPs (Fig. S1) shows that the main components in the samples are iron, oxygen, and sulfur. The results obtained suggest the presence of an amount of sulfur on the Fe_3O_4 NPs. XRD pattern of the synthesized sample is presented in Fig. 2b and shows five characteristic peaks for Fe_3O_4 nanoparticles corresponding to (2 Theta) = 30.136, 35.554, 43.2, 53.529 and 57.012 for (2 2 0), (3 1 1), (4 0 0), (4 2 2) and (5 1 1) planes, respectively. These peaks are well matched with the magnetite characteristic peaks confirming that the functionalized process did not result in the phase change and the magnetic nature of Cys-Fe_3O_4 NPs was validated as Fe_3O_4 NPs [25].

FT-IR spectroscopy was used to confirm the successful functionalization of Fe_3O_4 NPs with L-cysteine moiety. As represented in Fig. 2c, bands at 620 cm^{-1} was attributed to the Fe–O of a spinal structure, indicating the formation of particles, and 2955–3178 cm^{-1} attributed to the $—NH_2$ stretches. A strong

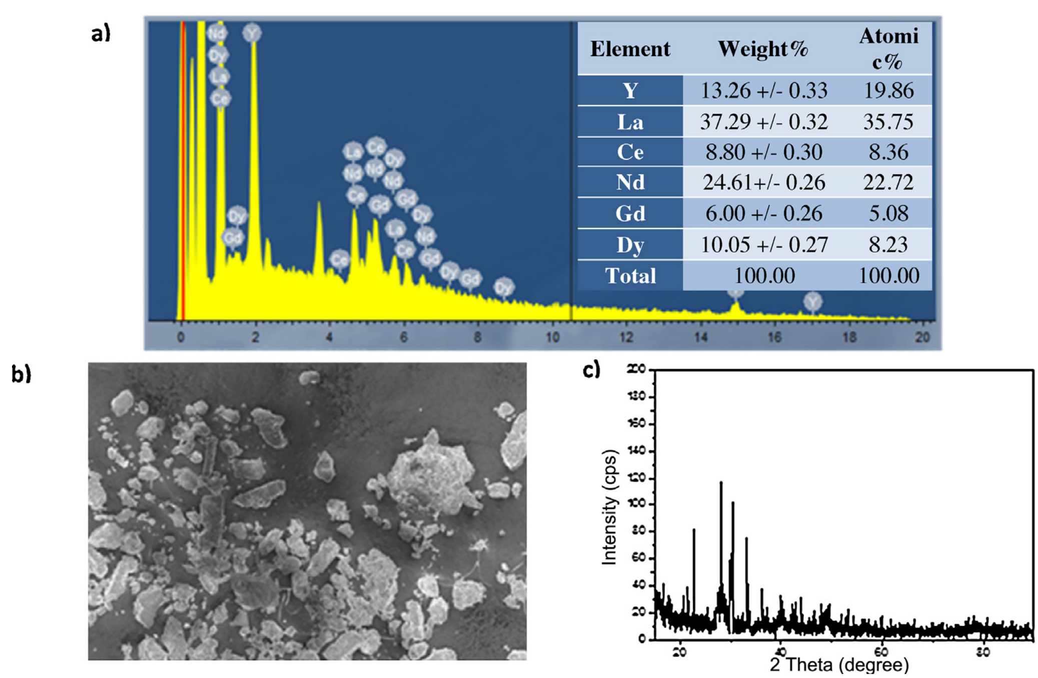

Fig. 1. a) EDX, b) SEM and c) XRD for final concentrate monazite sample after treatment.