Extraction of lanthanides and iron from acidic matrix solution produced from monazite processing using chemically modified resins

Thesis

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استخلاص اللانثانيدات والحديد من المحاليل الحامضيه الناتجه من تجهيز خام المونازيت باستخدام راتنجات معدله كيميائيا

رسالة مقدمة من

يهلى عاخطك لمعل زيخيءح لخ عهص

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Aim of the work

Nowadays chelating polymeric materials represent efficient materials in environmental and industrial applications due to their efficiency, selectivity, durability, easy handling and availability from both synthetic and natural sources. The necessity to separation and extraction Rare earth metals (REMs) because They are becoming increasingly important because of their unique chemical and physical properties and their applications in the field of chemical engineering, metallurgy, nuclear energy, optical, magnetic, luminescence and laser materials, high temperature superconductors and secondary batteries, etc.

Chitosan and Alginate are an important natural polymer because of its unique properties like biodegradability, biocompatibility.

The major goal of the present thesis is the preparation and characterization of modified chitosan and Alginate resins. The adsorption behaviour of the resins obtained towards lanthanides and iron will also studied using batch methods. The study will proceed according to the following program:

1. Loading of chitosan with different chelating groups such as, amine, and amino acid group.
2. Synthesis Magnetic nano¬composite alginate beads
3. . Studying the uptake behavior of the obtained resins towards lanthanides and iron in aqueous solutions at different experimental conditions of pH, time, temperature and pollutant concentration.
4. Kinetic and thermodynamic characteristics of adsorption reaction will also investigate.
5. Studying the regeneration of the loaded resins.
6. Application the obtained resin on real sample.

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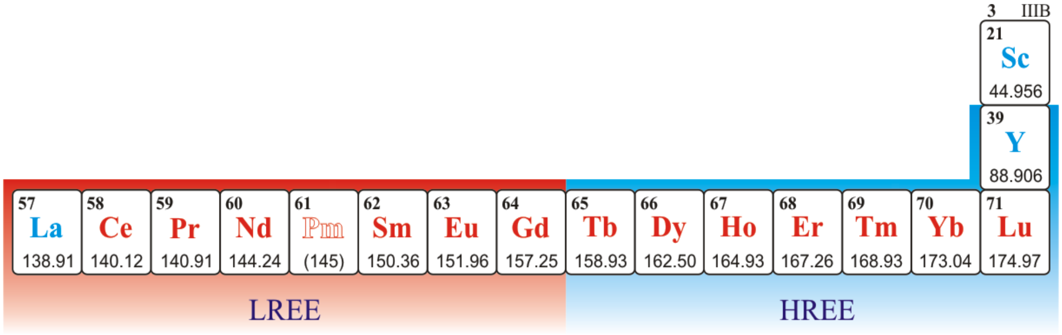
Introduction

1-Rare earth elements

Rare earth elements (REEs) are a group of 17 elements. The group consists of the 15 lanthanides chemical elements (atomic number 57 to 71) along with scandium and yttrium. Which are indicated in the following table [1-4]



REEs share many similar properties, which is why they occur together in geological deposits but their distribution and concentrations vary. They were originally obtained as earths or oxides from relatively rare minerals, thus they were named rare earths. Despite their name, rare earth elements (with the exception of the radioactive promethium) are not rare but relatively plentiful in the earth's crust. The more abundant REE are each similar in crustal concentration to commonplace industrial metals such as chromium, nickel, copper, or lead. Even the least abundant REE, thulium, is nearly 200 times more common than gold. However, in contrast to ordinary base and precious metals, REE have very little tendency to become concentrated in exploitable ore deposits. Therefore they are also referred to as rare ‘They are not especially rare, but they tend to occur together in nature and are difficult to separate from one another. However, because of their geochemical properties, rare earth elements are typically dispersed and not often found concentrated as rare earth minerals in economically exploitable ore deposits. .

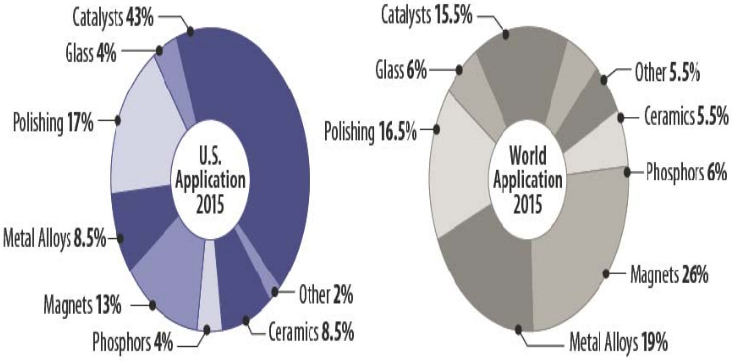
REES generally fall into two categories. light rare earths (LREE) and heavy rare earths (HREE), with varying levels of uses and demand. The LREEs are defined as lanthanum through gadolinium, atomic number 57 to 64. The HREEs are defined as terbium through lutetium, atomic number 65 to 71, and also yttrium (atomic number 39). All the HREEs have 'paired' electrons whereas the LREEs have unpaired electrons, from 0 to 7. Yttrium is lighter than the light rare earths, but included in the HREEs group because of its similar ionic radius, chemical properties and physical associations with heavy rare earths in natural deposits. Scandium is also trivalent; however, its other properties are not similar enough to classify it as either a LREE or HREE. The HREEs are relatively less common in nature but more valuable. The individual REEs can vary widely in their relative natural abundance, ranging from cerium, the most abundant, to promethium which is virtually unknown in ore deposits because it undergoes radioactive decay. [5].

Generally, REEs with low atomic numbers are more abundant in the earth crust than those with high atomic numbers. Although yttrium is the lightest rare earth element, it is usually grouped with the HREEs to which it is chemically and physically similar [6, 7]

1.1. Applications of REEs

Rare earth metals (REMs) are the surface active elements, which play an important role in the metallurgy of materials, such as refinement of microstructure, alloying and purification of materials and metamorphosis of inclusions [8] They are becoming increasingly important because of their unique chemical and physical properties and their applications in the field of chemical engineering, metallurgy, nuclear energy, optical, magnetic, luminescence and laser materials, high temperature superconductors and secondary batteries, etc.[9.10]. Lanthanum has different applications such as Batteries, catalysts for petroleum refining; electric car batteries; high-tech digital cameras; video cameras; laptop batteries; X-ray films; lasers.

The demand for mineral commodities is a derived demand which differs from consumer goods demand. Minerals are used as inputs for the production of goods and services. Consumers have no direct need for the commodity itself as a consumer good. The demand for rare earth elements is derived from the production of their end use products, such as flat panel displays, automobiles, catalysts, etc. As a result, the demand for REEs (as with other minerals) depends on the strength of the demand of the final products for which they are inputs. An increase in the demand for the final product will lead to an increase in demand for REEs.



Source: IMCOA, 2011

1.2. Resources of REEs

About 95% of all the world rare earth resources occur in just three minerals, bastnasite, monazite, and xenotime. These three therefore are the principal ore minerals for rare earth extraction. In which, bastnasite occurs most frequently, monazite, and ~~xenotime is the distant~~ third. Other rare earth minerals that have been used as resources of rare earth include apatite, brannerite, euxenite, gadolinite, loparite, and uraninite. The minerals allanite, apatite, and other phosphorite sources, eudialyte, fergusonite, floreneite, parisite, perovskite, pyrochlore, zircon, and a few other naturally occurring rare earth bearing materials are also considered potential rare earth resources, the following table indicate the important rear earth mineral. Countries whose manufacturing or technology base depends on imported metals have started looking for alternative sources. Other countries and companies, including Toyota, dependent on rare earths are racing to secure control of mines in Australia, South Africa and Greenland. China has already realized the availability of rare earth metals and now provides 97% of the world's supply of rare earth metals [16] .This raises the issues about security of supply. Four rare earth metals, viz. cerium, lanthanum, neodymium, and yttrium, constitute more than 85% of the global production. Recovery for each of these metals is possible, but remains a challenge [17]. Other rare earth metals are generally used in much lower quantities, whose recovery would be difficult due to the technical and scientific challenges associated with separating the rare earths from their ores.

2.Monazite

The mineral monazite is a phosphate, mainly of the REES , thorium and uranium. Monazite is found in many geological environments. It occurs as an accessory mineral in acidic igneous rocks, in metamorphic rocks, and in certain vein deposits. Due to its chemical stability it also develops into detrital mineral in placer deposits and beach sands.The primary monazite deposits have been useful as rare earth resources in a few instances. Notable among them are occurrences in Van Rhynsdorp and Naboomspruit (South Africa), in Colorado (U.S.) and in Bayan Obo (China). The most important monazite resources have been the beach placers. Alluvial, stream, and aeolian deposits have been much less significant. Beach sand deposits contain, in addition to monazite, other heavy minerals like ilmenite, rutile, magnetite and zircon. Sometimes monazite co-occurs with placer tin deposits. Monazite-bearing heavy mineral sand deposits are found in large quantities principally in Australia, Brazil, China, India, Malaysia, South Africa, and the United States. The rare earth content and individual rare earth element distribution in monazite are variable, as is its thorium content, depending on the location. Usually monazite contains about 70% REO, and the rare earth fraction is constituted by 20 to 30% Ce_2O_3; 10 to 40% La_2O_3; significant amounts of neodymium, praseodymium, and samarium; and lesser amounts of dysprosium, erbium, and holmium. Yttrium content may vary from a trace to ~5% Y_2O_3, and thorium content of 4 to 12% is common. According to a United States Geological Survey Circular there are 123 important rare earth deposits in the world and they are located in 20 countries. Most of the deposits are located in the United States, followed by Australia, Brazil, Canada, India, and China. These deposits have been categorized either as placers or as hard rock type. Numerically, placers are more in number. There are 71 placer deposits in the world and 52 hard rock deposits. Mostly the placers are found in recent or ancient shorelines and less frequently along present or former river banks. Monazite is the predominant rare earth mineral in the placers. The countries having major placer deposits are Australia, Brazil, the United States, India, China, and New Zealand. Placer deposits are also found in Argentina, Egypt, Mozambique, South Africa, Sri Lanka, and Uruguay. The data given in the U.S. Geological Survey Circular .

In Egypt monazite occurs as large reserves in black sand (1.06%) that are found along the beaches of northern parts of the Nile Delta around Rosetta to Damietta [18,19]Several methods are used for industrial processing of monazite in order to extract its content of thorium, uranium and lanthanides contents. These involved acid (sulfuric acid) leaching, alkaline leaching (with sodium hydroxide solutions), sintering with sodium carbonate and with sodium carbonate flux, sintering with sodium hydroxide, chlorination with a mixture of coal, and lime [20]. Commercially, both the alkaline (sodium hydroxide) and the acid (sulfuric acid) leaching are the commonly used methods. The hydroxide cake obtained from alkaline processing of monazite is leached with HCl (at 80 C), and then diluted with water. In order to separate thorium and uranium from lanthanides, selective neutralization of solutions with ammonia (at pH = 5.8–6) is carried which leads to complete precipitation of thorium and uranium as a concentrate (containing about 3% lanthanides). On the other hand uranium, thorium and rare earth elements could be recovered from the sulfate leach liquor obtained from the sulfuric acid dissolution of monazite by the following methods, namely; direct precipitation, ion exchange and solvent extraction [21-24].

3. Methods used for recovery of REES

Different methods have been proposed for separation and preconcentration of REEs, such as co-precipitation, solvent extraction, ion-exchange, solid-phase extraction, etc.[25–28] The traditional methods have some disadvantages, such as high consumption of reagent and energy, low selectivity, high operational cost and generation of secondary metablites[33] Therefore, there is a need to develop a cost effetive and eco-friendly method to recover rare earth metals from aqueous environment. Solvent extraction and ion-exchange are the two most common methods for the preconcentration and separation of REEs from various matrices. While, solvent extraction is inefficient due to the requirement of large volume of solvent, which may create health problems [29]. In addition, solvent extraction procedures are usually time-consuming and labor-intensive [30–32]. In recent years, research attention has been focused on biosorption, a cost effective biological method which has been demonstrated as rapid, reversible, economical and ecofriendly technology compared to conventional methods for the recovery of rare earth metals [34]. Alginate is a natural biopolymer extracted from various species of brown seaweed and various bacteria (e.g. Pseudomonas spp. and Azotobacter spp.), composed of chains of 1,4-linked β-D-mannuronic and α-L-guluronic has attached attention because it is non toxic selectivity, efficient and inexpensive [35].It has been demonstrated that the alginate are capable of binding metal ions through carboxyl group [36]. Moreover, nanomaterials have received great attention for synthesis of new nanostrucured sorbents due to their high specific surface area and the absent of resistance to interaparticle diffusion [37] .The adsorption behaviors of lanthanum(III) from an aqueous chloride medium, using iron oxide loaded calcium alginate beads were studied using equilibrium batch and column flow techniques [38]. The effect of pH, contents of loaded iron oxide, ionic strength, adsorbent dose, contact time, and temperature on adsorption capacity of the magnetic beads was investigated. The optimum pH value was defined to be 5.0 at temperature 298 K. Kinetic and isotherm experiments were carried out at the optimum pH. It was enough to reach the adsorption equilibrium at28 h and the maximum uptake capacity was 123.5 mg/g. Complexation, ion exchange and electrostatic interaction were all believed to play a role in lanthanum adsorption on magnetic beads. The equilibrium adsorption data were fitted to second-order kinetic equation. The Langmuir adsorption isotherm models were used for the description of the adsorption process. Furthermore, column breakthrough curves were obtained and the La (III) loaded magnetic beads were regenerated using 0.05 mol/L of CaCl2 solution.

Lunhong et al. [39] reported a simple ionic polymerization route for the fabrication of a magnetically separable adsorbent, that is, activated carbon/cobalt ferrite/alginate composite beads, for effective dye removal from aqueous solution. Adsorption characteristics of the as-made magnetic beads were assessed by using methylene blue (MB) as an adsorbate. The isotherms, kinetics, and thermodynamics of the adsorption of MB onto the magnetic beads have been studied at various experimental conditions. The prepared magnetic beads had a high magnetic sensitivity under an external magnetic field, which provides an easy and efficient way to separate the beads from aqueous solution.The adsorption and desorption kinetics of lanthanum (La) on micro algal cells was investigated [40] The internal transcribed spacer (ITS) and 18S ribosomal RNA gene (rRNA) were used for molecular identification of the species. The algal species were found to have 95–98% identities to Desmodesmus multivariabilis, Scenedesmus acuminutus, Chloroidium saccharophilum and Stichococcus bacillaris. The species were cultured and tested independently. D. multivariabilis was found to be the most efficient at adsorbing lanthanum with a maximum sorption capacity of 100 mg/g and a high affinity of 4.55 L/g.