

SOLID LIQUID EXTRACTION OF RARE EARTHS FROM AQUEOUS SOLUTIONS: A REVIEW*

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1. Introduction

According to the IUPAC definition, the Rare Earths (REs) are a family of elements in the periodic table that includes the 15 elements called lanthanoids and scandium and yttrium, characterized by similar physical and chemical properties. Based on their location in the periodic table and their atomic weights, it is possible to classify these elements into light REs or LREs (lanthanum, cerium, praseodymium, neodymium, promethium and samarium, with atomic number 57–62) and heavy REs or HREs (europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium atomic no. 63–71) (Connelly, 2005). The abundance of the RE elements taken together is quite considerable. Cerium, the most common RE, is more abundant than cobalt; yttrium is more abundant than lead, whereas genuinely rare REs such as Lu and Tm are as abundant as antimony, mercury, bismuth and silver. Promethium in RE minerals is present only in amounts of < 10-19% as a result of nuclear actions (McGill, 2000).

Nowadays there is an increasing need of REs due to their usage in numerous high-technology applications such as: magnets, phosphors, metal alloys, catalysts, ceramics, glass and polishing. Furthermore, they are becoming increasingly important in the transition to a green, low-carbon economy. This is due to their essential role in permanent magnets, lamp phosphors, rechargeable NiMH batteries and catalysts (Binnemans et al., 2013). Each of these applications requires specific RE elements and they are not interchangeable (Iannicelli-Zubiani et al., 2013). Increasing demand for the different products containing REs has resulted in a restriction of supply from producing Countries, particularly China, which currently holds 60% of the reserves and produces 97% of the world's REs (Massari and Ruberti, 2013). Increased demands in modern electronics as well as simultaneous shortfall in their supply made REs metals and compounds to be considered the most critical raw materials group by the European Commission (EU, 2010).

The main objective of this study is to review the different SLE extraction systems proposed for REs separation with particular focus on the different kinds of solid sorbents used (resins, nanotubes, clays and modified clays, membranes, silica and ion-imprinted polymers) evaluating advantages and critical issues of the different systems.

This work is divided in three main parts:

- an overview about the different available methods recovery for REs;
- a focused review about SLE extraction system, evaluating in particular the different kinds of solid matrices used;
- a comparative analysis of advantages and disadvantages of the different considered systems.

2. Methods for REs recovery

Two principal types of process are used for the extraction of RE elements from mineral ores:

1. solid-liquid systems using fractional crystallization, precipitation or ion exchange.
2. liquid-liquid systems using solvent extraction (McGill, 2000).

In fractional crystallization, one or more REs in a mixture are precipitated by changing the salt concentrations in solution through evaporation or temperature control. Fractional crystallization was the first process for separating REs (McGill, 2000): it was used until the early part of the twentieth century but it revealed to be uneconomical for processing large quantities of lanthanides since many recrystallization steps were required to recover high purity products (Sabot and Maestro, 2000).

Chemical precipitation involves adding a precipitating agent to selectively remove a metal from solution. It is used mainly to operate a crude separation of the REs mixture into

three groups: light, medium and heavy (Sabot and Maestro, 2000). Nowadays it is also used in recycling processes from electronic scraps, in the particular case in which the initial mixtures are not as complicated as the ones coming from ore digestion (Pietrelli et al., 2002; Innocenzi et al., 2013).

Ion exchange was proved to be effective in the separation of high purity REs, but generally involves the processing of very dilute aqueous solutions. In the 1950s, the commercial separation of the REs was dominated by ion exchange methods, but technical and economic limitations have restricted its use in industrial scale separation processes (Sabot and Maestro, 2000). Nowadays ion exchange processes are used in the production of small quantities of higher value RE elements (McGill, 2000) (generally used in electronics or analytical applications (Xie et al., 2014)) and based on the use of cation exchange resins: the H^+ cations readily exchange with other cations in solutions that percolate through a bed of the material. Mixed REs in aqueous solutions are trivalent cations and are strongly adsorbed by the resin. The REs are then recovered by elution. If a complexing agent exhibiting significantly different affinities for the various lanthanides is added to the eluent, then a separation occurs (Sabot and Maestro, 2000).

Solvent extraction is the REs separation process most extensively used in commercial and industrial scale (Iannicelli-Zubiani et al., 2012). It essentially involves selective extraction of metal value of interest from its aqueous solution into an immiscible organic phase. The immiscible organic phase consists of an extractant, a diluent and a phase modifier and is referred as the solvent phase. The selectivity of extraction is controlled by varying the chemical nature of the solvent and aqueous phase. Thus variables such as the initial acidity, metal concentration, extractant concentration play an important role. The separation process is governed by equilibrium considerations which are, in general, difficult to quantify and predict (Anitha and Singh, 2008). The solvent extraction of REs from the leach liquor presents some advantages: it not only concentrates the REs, but also separates REs from main impurities; the raffinate solution can be recycled adding some leaching agents back to leaching new ores; thus no wastewater is generated (Jun et al., 2011) and above large volumes of dilute pregnant liquors can be handled (Xie et al., 2014). Different phosphorus based extractants, tertiary and quaternary amines, sulphoxides, carboxylic acids, etc., are being employed for separation of REs (Singh et al., 2006).

5. Solid Phase Extraction

SPE is in growing development as an alternative approach to liquid-liquid extraction: SPE intends to solve, in fact, some of the limits and disadvantages of solvent extraction processes, such as:

1. the need of many process steps;
2. the consumption of large amounts of chemicals;
3. the use of large amounts of water.

The principle of SPE is similar to that of liquid-liquid extraction (LLE), involving a partitioning of solutes between two phases. However, instead of two immiscible liquid phases, as in LLE, SPE involves partitioning between a liquid (sample matrix) and a solid (sorbent) phase. This sample treatment technique enables both concentration and purification from solution by sorption on a solid sorbent. The basic approach involves passing the liquid sample through a column, a cartridge, a tube or a disk containing an adsorbent that retains the elements or species of interest. After all of the sample has been passed through the sorbent, retained materials are subsequently recovered upon elution properly changing the conditions or the solvent (Camel, 2003). This technique employs adsorbents in cartridge, disk, or membrane format and typical adsorbent materials include inorganic oxides, low-specificity sorbents (e.g., carbon, porous organic polymers etc.), organosiloxane-bonded silica materials, and class-

specific sorbents (e.g. molecularly imprinted polymers (Huck and Bonn, 2000), immunosorbents, surface-bound macrocyclic ligands (Rahman et al., 2013), restricted access materials (Poole and Poole, 2012) and often the same sorbents used in liquid-liquid extraction but immobilized on solids). Recently, the use of SPE is obtaining more and more attention in the recovery of REs because of its advantages of high recovery, short extraction time, high enrichment factor, low cost and low consumption of organic solvents over liquid-liquid extraction (Li et al., 2011). In the following, different kind of solid sorbents will be considered.

Extraction resins for the separation of metal ions have been under development since the mid-1970s (Park et al., 2005) and acquired great importance because they combine the advantages of high selectivities typical of solvent extraction with high efficiencies typical of chromatographic separation (Jia et al., 2004). The resins are generally porous polymeric materials modified with particular solvents that are characterized by high selectivities towards the metal ions of interest. Resins often occur in form of beads or microcapsules (Warshawsky, 1974). In fact, various new dimensions have been explored and reported in the field of metal extraction and the advantages of the use of polymeric beads extends due to large surface area, minimal use of organic solvents (environment friendly) and absence of phase separation phenomenon (Yadav et al., 2013).

In recent years, *nanostructure material* as a new adsorbent for the preconcentration/separation of substances has drawn growing attention in analytical sciences owing to its small size, large specific surface area, excellent mechanical strength, high chemical stability, and unique electrical properties. Some nanometer-sized substances have been successfully used as solid-phase extractants for preconcentration/separation of metal and nonmetal ions as well as adsorption of organic compounds (Chen et al., 2013). Since the first report in 1991, carbon nanotubes (CNTs) have shown great possibilities for a wide variety of processes and applications, which include their use as electrodes, sensors (gas, enzymatic etc.), nanoprobe, electronic materials, field emitters etc. The combination of structures, dimensions and topologies has provided physical and chemical attractive properties that are unparalleled by most known materials. Their applications have also reached the analytical chemistry field in which CNTs are being used as matrices in matrix assisted laser desorption ionization, stationary phases in either gas chromatography, high performance liquid chromatography or capillary electrochromatography, also as pseudo-stationary phases in capillary electrophoresis, etc. as well as new SPE materials. Concerning this last application the number of works has considerably increased in the last five years (Ravelo-Pérez et al., 2010).

Iannicelli-Zubiani et al. (2013) affirmed in their work that *clays* are characterized by some outstanding advantages, such as low cost, high mechanical intensity, good acid tolerance, convenient solid-liquid separation and excellent reusability. Furthermore clay minerals show a natural adsorption behaviour towards REs (Coppin et al., 2002; Moldoveanu and Papangelakis, 2012) so they are often used for their recovery, both as source both as sorbent solid-phase. Iannicelli-Zubiani et al. (2013) and Iannicelli and Zubiani (2013) modified two different clays (STx-1b and SWy-2 belonging to the smectite family) with different polymers in order to obtain new materials able to capture and release RE elements. Li et al. (2011) synthesized a new material for samarium adsorption using dry process to activate the mineral clay bentonite followed by N-(2-hydroxyethyl) ethylenediamine connecting chlorosilane coupling agent.

In the recent years, the separation of ions with very low concentration has been focused on *liquid membrane (LM) techniques*. LM can carry out simultaneous extraction and stripping processes in the same stage, and benefits a non-equilibrium mass transfer and up-hill effect, where the solute can move from low- to high concentration solutions. Main types of liquid membrane systems include supported liquid membrane (SLM), emulsion liquid membrane (ELM), bulk liquid membrane (BLM), flowing liquid membrane (FLM) and electrostatic pseudo liquid membrane (EPLM) (Wannachod et al., 2011). The LM acts generally as a

solvent for a transported solute, which is governed by its solubility in the membrane. This technique likened to that of conventional solvent extraction and stripping in which a thin liquid film is used to transport the solute from the feed to the product side. Organic solvents such as D2EHPA, PC-88A and Aliquat-336 dissolved with kerosene or common sulphonated kerosene are generally the most used extractants for RE metal ions while the strippants in the receiving phase include mineral and carboxylic acids (Gaikwad, 2012; Pei et al., 2012).

Silica is an extraction support very used because of its thermal and mechanical resistance, its great resistance to organic solvents, its lack of swelling and its hydrophilic properties. Several chelating agents were immobilized on silica support according to different methods of functionalization in order to improve the selectivity, the capacity and the rate of sorption of trace metals (Bou-Maroun et al., 2006). Concerning REs, Cornejo-Ponce et al. (Cornejo-Ponce et al., 1998) described a liquid-solid extraction procedure for praseodymium, neodymium, samarium and yttrium mixtures. Zhang et al. (2008) prepared a new material starting always from silica gel and modifying it with 4-(2-morinyldiazenyl)-N-(3-(trimethylsilyl)propyl)benzamide. This new sorbent was studied for separation and preconcentration of Sc(III).

Molecular imprinting is a versatile technique for preparing polymeric materials that are capable of high molecular recognition. Molecular imprinting polymeric (MIP) materials are prepared by the copolymerization of functional and crosslinking monomers in the presence of the target analyte (the imprint molecule) that acts as a molecular template. The functional monomers initially form a complex with the imprint molecule and, following polymerization, the functional groups are held in position by the highly crosslinked polymeric structure. Subsequent removal of the imprint molecule reveals binding sites that are complementary in size and shape to the analyte. Thus, a molecular memory is introduced in to the polymer, which is now capable of binding the analyte with high specificity (Prasada Rao et al., 2004).

6. Concluding remarks

SPE is a process in growing development because of its advantages of high recovery, short extraction time, high enrichment factor, low cost and low consumption of organic solvents over liquid-liquid extraction. The separation of the particular elements REs by SPE was reviewed and the different solid sorbents used were analysed.

Extraction resins combine the advantages of high selectivities typical of solvent extraction with high efficiencies typical of chromatographic separation and are characterized by large surface area, minimal use of organic solvents (environment friendly) and absence of phase separation phenomenon. Nanostructure materials as nanotubes are advantageous for small size, large specific surface area, excellent mechanical strength, high chemical stability, and unique electrical properties.

Clays are characterized by low cost, high mechanical intensity, good acid tolerance, convenient solid-liquid separation and excellent reusability. Furthermore clay minerals show a natural adsorption behaviour towards REs so they are often used for their recovery, both as source both as sorbent solid-phase.

Liquid membrane techniques can carry out simultaneous extraction and stripping processes in the same stage, and benefit a non-equilibrium mass transfer and up-hill effect, where the solute can move from low- to high concentration solutions.

Silica is an extraction support very used because of its thermal and mechanical resistance, its great resistance to organic solvents, its lack of swelling and its hydrophilic properties. Molecular imprinting is a versatile technique for preparing polymeric materials that are capable of high molecular recognition, ensuring very high specificity.

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