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Coordination and silica surface chemistry of lanthanides (III), scandium (III) and yttrium (III) sorption on 1-(2-pyridylazo)-2-napththol (PAN) and acetylacetone (acac) immobilized gels

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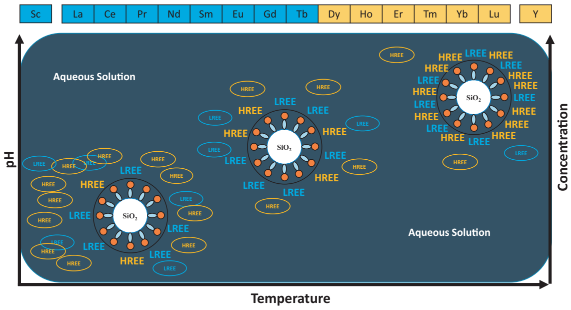
HIGHLIGHTS

- Coordination chemistry of PAN immobilized silica for REE adsorption was studied.
- Strategy for LREE and HREE separation in water was developed.
- Distinct observations between d and f block elements have been observed.
- Sc demonstrates superior removal while La and Y show poor adsorption.
- HREE separation shows positive temperature dependance.

GRAPHICAL ABSTRACT



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ABSTRACT

This article focuses on identifying the coordination and silica surface chemistry of PAN immobilized mesoporous silica gel in the adsorption of Rare earth elements (REE) in comparison to acetylacetone (acac) immobilized gel. PAN is used as an analytical reagent since it has both acidic (pKa 1.9) and basic (pKa 12.2) properties. A strategy for the adsorption of REE has been developed through the analysis on the adsorption of light rare earths (LREEs) and heavy rare earths (HREEs). In this study, the separation of REEs is achieved via the –N group of pyridine/ azo and –OH group of PAN modified silica, at different conditions. The REEs were studied based on different parameters such as pH, kinetics, metal loadings, binding sites, temperature etc. and distinct differences have been observed in separation between 'd' and 'f' block elements. Ionic radii, lanthanide contraction and REE tetrad effect impact the adsorption process for different pH and metal loading conditions. This eventually influences the binding mechanism as well. The affinity of the modified gel was towards LREEs at lower pHs and HREEs in higher regime. As a validation attempt, the developed separation strategy has been employed in investigating under natural water conditions for varying REE concentration and pH in the presence of competing ions. Silica gel with PAN (SEP) modifications performed superior to Acac modifications (SEA) in terms of REE adsorption under all conditions. The behavior was coherent for both single and multi-component systems where HREE adsorption showed temperature dependency. As SEP demonstrated adsorption even in the acidic range (pH 2), it has the potential to serve a wide range of applications involving acidic industrial waste such as mine water.

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1. Introduction

The REE group belong to the IIIA members of the periodic table representing generally 16 elements of 14 Lanthanides (Ln–La through Lu) and 2 Pseudo Lanthanides (Sc and Y). The separation of individual REEs from aqueous solutions is a difficult process owing to their similar physiochemical properties, as summarized in Table S1 (Supplementary material) [1]. Due to their rare and unique physicochemical, magnetic and optical properties, they are engaged in varied applications in technological advancements such as Fluorescent and LED lighting, digital camera lenses, petroleum refinery, automotive catalytic converters, high performance permanent magnets etc [2]. However, due to the increased consumption and demand along with their price being volatile, the need for the separation and purification of such REEs has become an important field with renewed industrial and economic interests, along with government incentives [3–5]. Their demand is expected to grow highly in future as a result of their utilization in the development of low carbon and sustainable energy technologies [6,7].

Despite the existence of several techniques such as solvent extraction, biosorption, ion exchange, adsorption etc. [8–14] for lanthanide extraction, adsorption process with its focus on coordination chemistry utilizing donor ligands containing N and CO groups has gained popularity [12,14–16]. Such a process of ligand immobilization with amino and carboxylic groups [17], when conducted with appropriate support materials with efficient properties such as surface area, pore volume and size, can eliminate several disadvantages of secondary effluent problems and emulsification associated with conventional solvent extraction processes. Also lanthanides and transitional metals are capable of forming coordination complexes with ligands that would facilitate visual detection through colored solutions [18,19]. Silica is one such support material which has been extensively studied for the separation and recovery of REEs due to its high surface area and thermal resistance [20–27].

Ramasamy et al. have studied the recovery of REEs (La, Sc, Er, Eu and Y) from the waste water using the modified silica gels synthesized by chemical immobilization as well as physical adsorption methods [18]. The study concluded that the silica gels prepared by chemical immobilization method (SEP) yielded better results in comparison to the physically adsorbed gels (SP). Also, REE removal was evident from a pH value of 4 for the case of SEP while SP demonstrated REE adsorption only at higher pHs (>7). The results were based on a set of 5 elements with processing conditions being pH, contact time, temperature, dosage etc., eventually optimizing the ideal conditions for adsorption. As stated before, there are few articles in literature dealing with PAN physically adsorbed on silica gel [26,27] and Acac chemically immobilized silica gel (SEA) [2] for metal recovery.

With the first attempt of using SEP for REE recovery and yielding better results during the previous study, the emphasis in the current work was set to investigate the adsorbent in detail with regarding REE adsorption for the whole series to gain more insights into the intraseries (within the series) behavior. Hence, this study is mainly focused on identifying the separation trend for all the REE elements with PAN modified silica gel in comparison to Acac modified silica gel, as a point of reference. This research work is also targeted towards understanding the affinity of PAN ligand immobilized gel to Sc, Y and Ln in relation to coordination chemistry and complexation mechanism. The Lanthanide separation trends (HREEs and LREEs) have also been studied with respect to different factors influencing the underlying experiments. In this article, the factors such as effect of pH, initial concentration, contact time, binding sites and functional groups are analyzed. The utilization of O– and N– donor ligand immobilized adsorbents for lanthanide coordination is an interesting and promising aspect for the effective and stable complexation mechanism during the sorption process. The Table 1 displays the list of abbreviations and notations used throughout this paper.

2. Materials and methods

2.1. Simulated and natural waste water

The experiments were conducted using natural (collected from central laboratory waste, Laboratory of Green Chemistry, Mikkeli, Finland) and artificial waste water. The test water, prepared from ICP standard stock solutions of 1000 ppm, consists of 1–2 ppm each of Ln^{3+}, Sc^{3+} and Y^{3+} ions along with the competing ions. The competing ion (Al^{3+}, Au^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Pd^{2+}, Pt^{2+}, S^{6+}, Sb^{3+}, Si^{4+} and Zn^{2+}) concentration was around 20–30 ppm. For most of the tests, the solutions of LREEs (Sc^{3+} and Ln^{3+} – from La^{3+} till Tb^{3+}) and HREEs (Y^{3+} and Ln^{3+} – from Dy^{3+} till Lu^{3+}) were used throughout the study, prepared from their nitrate or chloride salts, purchased from Sigma Aldrich.

2.2. Synthesis and modification of mesoporous silica

Based on the methodology discussed in the article [18,28], chemical immobilization of silica gel was performed using PAN and Acac ligands. The solvent evaporation was carried out using APTES functionalized silica gel and PAN/Acac (in the solvent) in a ratio of 1:20. The properties of the silica gel are summarized in Table S2 (Supplementary material). The notations SEP and SEA were used for PAN chemically immobilized APTES functionalized silica gel and Acac chemically immobilized APTES functionalized silica gel in authors' previous work [18] and the same notations were followed over the entire course of this paper.

2.3. Characterization

Vertex 70 by B Bruker Optics (4 cm^{-1} resolution from 400 to 4000 cm^{-1}) was employed to obtain the FTIR spectra before and after adsorption. The spectra were collected at a rate of 100 scans per sample to investigate the surface functional groups. BET from

Table 1
Abbreviations and notations used in this study.

S. No	Abbreviation/ notation	Definition
1	PAN	1-(2-Pyridylazo)-naphthol
2	Acac	Acetylacetone
3	APTES	3-Aminopropyl triethoxy silane
4	APTMS	3-Aminopropyl trimethoxy silane
5	REE	Rare Earth Element
6	HREE	Heavy Rare Earth Element
7	LREE	Light Rare Earth Element
8	LED	Light Emitting Diode
9	Ln	Lanthanides
10	SEP	PAN chemically immobilized onto APTES functionalized silica gel
11	SEA	Acac chemically immobilized onto APTES functionalized silica gel
12	STP	PAN chemically immobilized onto APTMS functionalized silica gel
13	STA	Acac chemically immobilized onto APTMS functionalized silica gel
14	SP	PAN physically adsorbed onto silica gel
15	SA	Acac physically adsorbed onto silica gel
16	FTIR	Fourier Transform Infrared Spectroscopy
17	BET	Brunauer-Emmett-Teller
18	ZP	Zeta potential