



Two-stage selective recovery process of scandium from the group of rare earth elements in aqueous systems using activated carbon and silica composites: Dual applications by tailoring the ligand grafting approach

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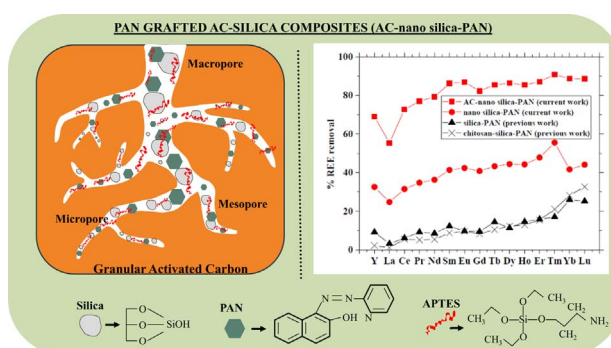
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HIGHLIGHTS

- Two different ligand grafting techniques were explored.
- Grafting via solvent evaporation method was found to be effective for REE recovery.
- Ligand doped activated carbon demonstrated selective scandium recovery.
- Hybrid composites with ligand attachments depicted selective REE recovery.
- Two-stage recovery technique was also validated using real mining effluents.

GRAPHICAL ABSTRACT



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ABSTRACT

A steady, reliable and enhanced scale of scandium (Sc) supply is of paramount importance in the current industrial sector, specifically, in the production of solid oxide fuel cells and scandium based aluminum alloys. Despite an expensive price quote, the remarkable physical properties of Sc drive the need to foster alternate supply pools, including industrial wastes and stockpiles, to tackle the ever-increasing need in global markets. However, they are most often obtained as a combined by-product with other metals, Sc-Y silicate minerals or rare earth elements (REE). To achieve this, activated carbon (AC) was utilized together with nano silica to synthesize two groups of adsorbents varying in terms of the ligand grafting technique. The study revealed that the Method II composites were highly effective in REE recovery, even under the process conditions of high salinity and water hardness, and in the presence of oil and organic compounds. As a conclusive step, the REE adsorption process was also successfully validated with real acidic mine drainage (AMD). Additionally, the synthesized adsorbents were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Brunauer-Emmett-Teller (BET), X-ray diffraction spectroscopy (XRD), organic elemental and zeta potential (ZP) analysis to gain a better insight into the underlying mechanism characterizing the adsorption process.

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1. Introduction

The demand and cost of REEs are in a state of constant escalation, attributed primarily to their potential in accelerating the path towards a low-carbon, clean and circular economy. Some present-day applications include nickel metal hydride batteries in electric vehicles, permanent magnets in wind turbines and disk drives, compact fluorescent lights, magnetic resonance imaging machines, and catalytic converters. REEs, in general, include 15 metallic elements of the lanthanide series, along with scandium (Sc) and yttrium (Y). They are further subdivided into light rare-earth elements (LREEs) from lanthanum (La) to europium (Eu) and heavy rare-earth elements (HREEs) from gadolinium (Gd) to lutetium (Lu). Among the REEs, Sc is the most valuable element, with its market price being 5000 US\$/kg (as scandium oxide, 99.9% purity) [1]. Also, a non-interrupted supply of Sc is an important part of the industrial chain in the manufacture of aluminum alloys, high voltage tension wires and, state of the art 3D printing techniques. The aviation sector is heavily reliant on the usage of Sc in the direction of developing lightweight aircraft components. REE recovery from secondary resources such as industrial waste streams, processing residues, leachate liquors, mine tailings, bauxite residue, electrical and electronic waste (end-of-life consumer goods), seems to be a promising option to overcome high supply risk [2]. Especially, mine tailings and mine waters, such as AMD containing considerable REE amounts, facilitate an easy and efficient means of procurement. Also, such a recovery path would serve beneficial in the remediation of mine sites, which is an added advantage from the economic and environmental standpoint. However, due to similar chemical properties, separation of individual REEs is extremely complicated. There is a persistent search looking for viable options to develop and optimize innovating technologies in utilizing these secondary REE resources, taking the model process economics, energy use and environmental impact into the consideration.

Several technologies such as solvent extraction, adsorption, biosorption, ion exchange process and precipitation, have been explored in the recent years to recover REEs from industrial wastes [3–6]. Among these, solvent extraction is usually preferred for recovery and recycling of REEs from concentrated aqueous waste systems. However, this process is not recommendable for usage with diluted streams as the organic solvents could cause an imminent contamination of the aqueous phase. Leaching process is also widely used for metal recovery from wastewaters, but, it also possesses certain disadvantages such as high acid consumption and complications in the reuse of residues. Thus, adsorption and ion exchange processes are preferred for recovery processes involving diluted aqueous waste streams and relatively extensive attention has been paid to these technologies over the last decade [7–10].

Silica and activated carbon (AC) are one of the exhaustively used adsorbents for metal removal from the aqueous phase, supported by their versatility, high surface area, better thermal and mechanical stability [11–14]. The unique chemistry of REEs by virtue of properties such as high charge density, variable coordination number, and slightly differed atomic radii from each other, the functionalization of the adsorbents with potential ligands would enhance their selectivity in separation from gangue elements and for intra-element separation from mixed REE concentrates [15]. In our prior works, the functionalization of mesoporous silica gel (particle size of ~40 µm) was performed with the most common silane, 3-aminopropyl triethoxysilane (APTES), by attaching the organic amino-polycarboxylic acid groups to the inorganic support. APTES functionalized silica gels revealed to be highly successful in recovering REEs and the adsorbent selectivity was further enhanced by the ligand attachment of 1-(2-Pyridylazo) 2-naphthol (PAN) to the organic–inorganic silica support via solvent-evaporation process [16].

In this study, nano silica (~12 nm particle size) and AC (0.8 mm pellets) were utilized to augment the adsorbent effectiveness through the modification of physical and chemical attributes, to develop

affinities towards REEs. Two different types of PAN grafting techniques were adopted to investigate the REE removal efficiencies via individual (AC-P, silP) as well as hybridized (AC-silP) adsorbents. This novel analysis on the chosen combination of ligand and adsorbent yielded interesting and promising results that can facilitate the development of Sc separation strategy from REE mixtures, using a two-stage setup, by merely tailoring the hybridization and ligand grafting approach. The existent literature focusses on simple (usually single component) systems with elevated individual REE concentrations. However, there is an absolute need to test the efficiencies of the functionalized adsorbents under conditions of real wastewater compositions in the presence of increased salinity, water hardness, and environmentally relevant industrial impurities. Hence, investigations were also performed using real AMD to understand the REE separation behavior from mixtures, as they occur so in real wastewater.

Hence, the objective of this study was to ascertain the selective separation of Sc^{3+} from REE mixtures by means of the synthesized adsorbents. This would motivate the production of economically feasible REE concentrates from low concentration industrial effluents, which are available in ample amounts. This objective was established through the following steps: (a) functionalization of AC, silica and hybrid AC-silica with ligands, (b) identification of the significant ligand grafting procedure, (c) characterization of the synthesized adsorbents to understand the physio-chemical aspects and the underlying mechanism, (d) investigation of REE adsorption efficiencies in real water conditions, and (e) validation of process parameters for REE recovery and selective Sc^{3+} separation from AMD in a two-stage process.

2. Experimental section

2.1. Chemical agents, materials, and methods

Activated Carbon, AC (Norit ROW 0.8 mm pellets, steam activated, CAS: 7440-44-0) and silica (nanopowder, 12 nm particle size, CAS: 7631-86-9) were obtained from Alfa Aesar and Aldrich, respectively. REE salts (in the form of chlorides or nitrates), APTES silane (for silanization), PAN (for ligand grafting) and Toluene (reagent grade, > 99%, for synthesis) were attained from Sigma Aldrich as well. For the synthesis step, PAN solution was prepared by dissolving 0.2% w/w PAN in reagent grade acetone. Two different types of ligand grafting procedures, adopted from our earlier works [16–18], were utilized in this study. Briefly, ligand grafting was done simultaneously by reacting PAN solution along with supports (AC and silica with APTES or just silica with APTES) in Toluene mixture, referred to as Method I. These PAN impregnated Method I adsorbents are denoted as 1AC-silP (AC and silica with APTES), 1silP (silica with APTES) and 1AC-P (just AC). On the other hand, in Method II, PAN grafting was achieved via solvent evaporation process onto hybrid composites, i.e. AC and APTES functionalized nano-silica. These PAN grafted supports are referred to as 2AC-silP, 2silP and 2AC-P, analogous to the naming convention followed for Method I adsorbents. The notations expressed in Table 1 were used throughout the course of this paper. The chemical structures of APTES, PAN and silica are provided in the graphical abstract for the better understanding of the readers.

2.2. Instrumentation

The infrared spectroscopy measurements were conducted by FTIR (Vertex 70 by B Bruker Optics) in order to ascertain the ligand modification, by identifying the vibrational frequencies in the functional groups of the adsorbents using 4 cm^{-1} resolution at 100 scans rate per sample ranging from 400 to 4000 cm^{-1} wavelength. The ligand modification and hybridization process were also investigated by means of XRD measurements (PANalytical instrument with the empyrean program) using $\text{CoK}\alpha$ irradiation at $\lambda = 1.78\text{ \AA}$. The SEM analysis (SU3500 fitted with Thermoscientific UltraDry SDD EDS) provided information

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