N- and O- ligand doped mesoporous silica-chitosan hybrid beads for the efficient, sustainable and selective recovery of rare earth elements (REE) from acid mine drainage (AMD): Understanding the significance of physical modification and conditioning of the polymer

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GRAPHICAL ABSTRACT
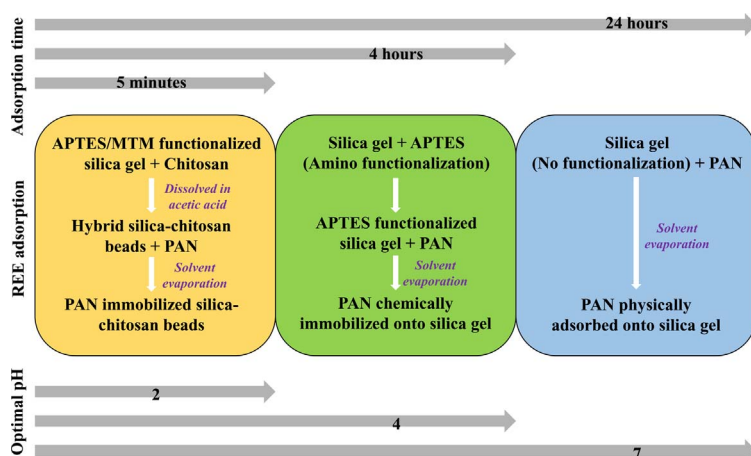
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ABSTRACT

Silica-chitosan hybrid beads were synthesized via three different methods to investigate the selective recovery of REE from AMD. The influence of amino/non-amino silanes, high molecular weight/high viscous chitosan and N-/O- based ligands were studied and their effects on REE removal efficiencies were analyzed. The adsorption efficiencies of three various groups of modified beads were inspected with respect to feed pH, in a single and a multi-component system, and their affinities towards the light and heavy rare earth elements (LREE/ HREEs) were interpreted to understand the intra-series REE separation behavior. The focus of the study was mainly directed towards utilizing these fabricated beads for the recovery of valuable REEs from the real AMD obtained at three different sampling depths which was found rich in iron, sulfur and aluminum. Moreover, the selectivity of the beads towards REEs improved with silanized and ligand immobilized gels and their impacts on REE recovery in the presence of competing ions were successfully presented in this paper. Also, the synthesized beads showed rapid REE adsorption and recovery within a process time of 5 min. Group II adsorbents, synthesized by

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forming silica-chitosan hybrid beads followed by PAN/acac modifications, showed superiority over the other groups of adsorbents.

1. Introduction

REE represents a group of elements with a common electron configuration (6 shells), that include 2 pseudo lanthanides (scandium, Sc, and yttrium, Y) and 14 lanthanides. They possess large ionic radii and oxidation (III) states. Among the REEs, the elements with atomic numbers ranging from 57 (lanthanum, La) through 64 (gadolinium, Gd) are categorized as light rare earth elements (LREEs) while elements from 65 (terbium, Tb) through 71(lutetium, Lu) are termed as heavy rare earth elements (HREEs). Owing to the similarities in their properties, Sc is often categorized as LREE and Y as HREE. Their comparable oxidation states and unchanging valences (mostly trivalent except Ce^{4+} and Eu^{2+}) with increasing atomic number, contribute to the fact that they occur in a combined state and are enriched in Earth's crust (lithophile elements) [1]. There has been an escalating demand for such REEs in recent years, attributed to their several modern applications such as lasers, high strength permanent magnets, electronic devices, superconductors and catalysis [2]. This serves as a motivation for the development of new techniques, both economical and sustainable, aimed at their recovery from secondary sources like mining tailings and industrial residues [3,4].

Polluted mine water has always been considered a waste product and in the present scenario, the mining industry is in constant search of economically viable options to purify the mine water. The purified water can then be decanted into receiving streams after disposing of the concentrated sludge/brine. During the course of this procedure, the valuable components are dissipated and several techniques are being investigated, aimed at their recovery. The accompanying challenges often include the acidity of the effluents, with variable compositions of the ionic species present. Also, the amounts of recoverable elements, such as REEs, occur in small quantities. Hence, the development of novel processes focusing on the selective recovery of such elements at low concentrations, from the mining effluents, is of high priority [5]. There are several existent technologies including ion exchange, solvent extraction, bio-sorption and adsorption for REE recovery [6–9]. The most efficient one, in practice, for the removal of target elements from aqueous solutions is adsorption [10–14].

The development and utilization of nanomaterials, green adsorbents and hybrid conjugates/composites for the selective removal and recovery of valuable metals have attracted enormous attention over the last decade [15–20]. Chitosan, a linear polysaccharide produced by the deacetylation of chitin, is biodegradable and non-toxic in nature. Chitin occurs in natural sources such as the exoskeleton of crustacea (crabs and shrimp shells), making it both abundant and procurable at a low cost. The presence of pH-responsive functional groups with primary amino and hydroxyl groups contribute to chitosan's hydrophilicity. Hence, they can serve as effective sites for the chelation process, while the immobilization of ligands would further enhance the selectivity of the adsorbent [21–25]. Owing to the poor mechanical properties and porosity, chitosan is occasionally hybridized with supports such as silica that provide stability and increased surface properties. From earlier works in literature, it can also be understood that the supports such as Chitosan and silica are favorable for the process of metal ion recovery from wastewater [26–28].

This study was targeted on the removal of REEs from acidic media such as mine wastewater, even at a lower pH value of 2. In our earlier works, the functionalization of silica gels for REE removal was performed using the silanes, 3-aminopropyl triethoxysilane (APTES), 3-aminopropyl trimethoxysilane (APTMS), Trimethoxymethoxymethylsilane (MTM) and Chlorotrimethylsilane (TMCS) [29]. In a further extension of the work, the

ligands, (1-(2-pyridylazo) 2-naphthol (PAN) and acetyl acetone (acac)) immobilized silica gels were compared for their effectiveness in REE removal and the adsorption parameters were optimized [30]. From a pH value of 4, the silica-based adsorbents showed excellent REE adsorption. In this work, novel hybrid beads were synthesized for selective REE recovery from the acidic mine drainage, attempting to shift the optimal adsorption pH value to 2. The analysis provided us with a better acumen of the significance of adsorbents' form and their methods of preparation in the successive removal of low concentrated REEs in a highly acidic medium. From the experimental data, it could be safely concluded that the bead form was highly preferable to the flake form. The augmentation of adsorbent selectivity towards REE recovery from acid mine drainage (AMD) through APTES/MTM silane modifications, different chitosan types and N-/O- donor atoms containing ligands, was explored for the first time and their distinct advantages over traditional silica-chitosan hybrid beads were also brought into the light, especially in terms of REE selectivity after silanization and ligand functionalization step.

Hence, the aim of the current study was to utilize various PAN/ acac grafted silica-chitosan hybrid beads for REE recovery from acidic media. The hybrid beads, prepared and modified, using three different methods, were tested in both single and multi-component system, for REE recovery from wastewater. The intra-series REE behavior was studied to understand the separation trend and the adsorbents' affinity towards LREEs/HREEs. The validation of the process was conducted using real AMD to ascertain the selectivity of the adsorbents towards REEs in the presence of competing ions. The impact of ligand modification, method of preparation, type of chitosan and silane used, was also investigated to optimize the adsorption process. Fourier Transform Infrared Spectroscopy (FTIR), organic elemental and zeta potential (ZP) analyzer were used for the characterization as well as to understand the REE adsorption behavior of the materials.

2. Experimental section

2.1. Chemicals

APTES ($\geq 99.0\%$ pure), MTM ($\geq 99.0\%$ pure), PAN and Acac were supplied by Sigma Aldrich. High molecular weight chitosan C1 (310000–375,000 Da; 800–2000 mPa.s; deacetylated chitin; Poly (D-glucosamine)) and chitosan of high viscosity, obtained from crab shells C2 (> 400 mPa.s; Poly-(1, 4-β-D-glucopyranosamine)), were also procured from Aldrich. Mesoporous silica of particle and pore size of 0.015–0.040 mm and $60 - 70\,\text{Å}$, and glacial acetic acid, used for the gel bead preparation were supplied by Merck and VWR chemicals, respectively. The chloride salts of the REEs were utilized for the preparation of solutions of desired concentrations for the adsorption tests. The conditioning of the polymer beads was performed using Sodium hydroxide (NaOH pellets, from Merck) alkaline coagulation bath.

2.2. Synthesis of hybrid beads

The gel beads were prepared using prior techniques described in the literature with some alterations [31], where equal parts of silica gel and chitosan were mixed in acetic acid (4% w/w) and the resulting viscous solution was dropped into 2.5 M NaOH bath and left undisturbed for 5–6 h. This was followed by the washing and drying (100 °C in the oven) of the beads until a constant weight was attained. Three different bead preparation methods, depicted in Table 1, were exploited, with aim of gaining a sound knowledge on the effect of their adsorbent efficiencies and selectivity towards REEs. To summarize the methodologies: (1) Group I adsorbents were synthesized by dissolving ligand