



Solvent impregnated carbon nanotube embedded polymeric composite beads: An environment benign approach for the separation of rare earths



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ABSTRACT

An environment benign process for the separation of rare earths has been delineated for the first time by developing polyethersulfone based composite beads through phase inversion method, where the use of hazardous organic diluents could be circumvented. The porosity and pore structure of these beads were controlled through different additives, of which, polyvinyl alcohol and multiwall carbon nanotubes proved to be the most efficacious. The extraction efficiency of rare earths was ameliorated by four fold with the application of the developed nanotube incorporated beads. The influence of various process parameters, namely, aqueous phase acidity, metal ion concentration, presence of other competitive ions and temperature on the separation of representative yttrium ion has been elaborated in the present investigation. The experimental results attribute to the excellent stability and reusability of the developed beads. The feasibility of employing this novel technology in large scale has been established by successful operation in continuous column mode. The developed assay exhibits profound application towards a greener approach due to the elimination of hazardous organic diluents and prevention of significant organic extractant loss during the process of recovery of rare earths from aqueous media.

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1. Introduction

Ever increasing indigence of rare earth utilization in the arena of modern electronics, high end technological products and green technology coupled with shortfall in their supply have led to growing interest in the exploration and exploitation of new sources and techniques for extraction. As a consequence, reopening of old mines and erections of new processing plants are underway throughout the world [1,2]. Further, supply risk of rare earths have necessitated the need of recovering rare earths from e-wastes, tailing of mines and lean solutions of processing plants to augment the supply through regular mines [3]. The unique properties of magnetism, luminescence, and strength of rare earth elements endow them with wide applicability in high-tech and clean-energy products. These properties, derived from partially occupied 4f electron orbitals in most rare earth elements, make these elements superior. Normally, the separation factor for different rare earth ions show minimal differences owing to their similar valence and ionic radii. That is why separation and purification of individual rare earth is perhaps the most challenging task in analytical chemistry. Solvent extraction technique has been used on industrial scale to

separate rare earths from lean solutions and their concentrates [4,5]. This technique uses large inventories of hazardous organic extractants, diluents and modifiers, thereby leading to severe environmental problems [6]. Various new techniques based on membrane technology, such as, supported liquid membrane, emulsion liquid membrane, hollow fibre membrane, and polymer inclusion membrane have been reported to separate metal ions from aqueous solutions, where the inventory of organic extractants and solvents were controlled, with an aim to restrict the hazardous impact of organic extractants into natural system without affecting the extraction efficiencies [7,8]. However, the stability of these membranes and loss of extractants after long term use remain major concerns. The last decade has seen phenomenal growth in the use of ionic liquids in this field [6]. Though ionic liquids have shown promising results for selective separation but its physical properties, toxicity and cost remains a challenge for sustainable industrial applications [9]. Developing a new extraction system, including novel extraction material, synergistic extraction system and ionic liquid extraction, with improved efficiency and elimination of organic waste release in aqueous streams has always been challenging [10]. In this context, solvent impregnated resins/beads are being developed as attractive alternatives in separation technology nowadays [11–14]. They offer ease in phase separation and have the dual advantage of solvent extraction and ion

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exchange in terms of comparatively faster mass transfer and higher selectivity [13].

Literature survey unveils that solvent impregnated resins containing organic extractants have been reported for metal ion separation from aqueous solutions. Kondo et al., have investigated the extraction behavior of rare earths (Nd, Eu, Gd) with divinyl benzene based microcapsules encapsulating organic extractant [15]. Uranium separation from phosphoric acid solution by bipolymeric microcapsules of calcium alginate containing di-2-ethylhexyl phosphoric acid (D2EHPA) is also reported [16]. Removal of Cr(VI) from aqueous systems by polysulfone microcapsules containing Cyanex 923 extractant has been reported by Ozcan et al. [17]. The reported polymeric beads are mainly based on polystyrene, polyether ether ketone, and alginate types of polymer and have sizes in micron to sub-millimeter range [18,19]. Therefore, the holding capacity of these beads/capsules for extractants is rather limited. In addition, the leaching of organic extractant from the previously developed resins after repeated cycles of operation adversely affects the reusability and stability of the beads. Polyethersulfone (PES) which is an environment friendly matrix material in water purification membranes have been recently reported for the preparation of solvent impregnated beads to recover metal ions from chloride medium [13,20–23]. It has high glass transition temperature, good mechanical properties and excellent thermal and chemical stability, which makes it suitable as a base matrix for the preparation of solvent impregnated bead. Owing to the above advantages of PES, an attempt has been made to modify the internal microstructure and surface morphology of PES beads by introducing various types of additives, namely, polyvinyl alcohol (PVA), multiwall carbon nanotube (MWCNT), lithium chloride (LiCl) and polyethylene glycol (PEG). The developed composite beads have been characterized by techniques like thermogravimetry (TG), scanning electron microscopy (SEM) and Fourier Transform Infra-Red (FTIR) spectroscopy. Subsequently, all types of composite beads have been evaluated for the sorption of rare earths under comparable experimental conditions. The feasibility of recovering rare earths from aqueous chloride solution has also been investigated in continuous column operation mode, taking Y(III) as the representative of rare earth. Additionally, stability and reusability of MWCNT embedded composite beads have also been evaluated and reported. To the best of our knowledge, the use of MWCNT–PES composite beads encapsulating D2EHPA for the recovery of rare earths is being reported for the first time. Moreover, the possibility of use of diluent free extractant impregnated inside the beads has been shown, which is otherwise not practiced in normal solvent extraction process.

2. Experimental section

2.1. Materials

PES (average molecular weight of 30,000) was obtained from Gharda Chemicals, India and used as received. N-methyl pyrrolidone (NMP), PVA (molecular weight 31,000–50,000), PEG and LiCl were procured from Merck India. D2EHPA (diester > 95%) was obtained from Heavy Water Board, India and was used without any further purification for preparing composite beads. Rare earth (such as Y(III), Sm(III) and La(III)) solutions were prepared by dissolving their oxides (>99% purity, IREL, India) in hydrochloric acid and individual working solution were prepared by the appropriate dilution of the stock solutions. MWCNTs were having an average diameter of 20 nm were prepared in our laboratory by chemical vapour deposition method [24]. Purification of MWCNT was achieved by treating it with hydrochloric acid (HCl) following thermal oxidation prior to its use in the present investigation. All the chemicals have purity >95%.

2.2. Preparation

Five types of polymeric composite beads namely PES/PVA (as blank), PES/PVA/D2EHPA (PES-I), PES/PVA/MWCNT/D2EHPA (PES-II), PES/PEG/D2EHPA (PES-III), PES/LiCl/D2EHPA (PES-IV) with different additives were prepared by non-solvent phase inversion method under optimized preparatory conditions (10–15% w/w PES in NMP with 1:5 D2EHPA to polymer solution) using the experimental set up and procedure developed by us [13]. The concentration of the constituents was optimized in such a way that the resultant composite beads resulted in spherical shape. The concentrations of additives in different polymeric beads were 1.5%, 0.25%, 1%, and 1% w/w for PVA, MWCNT, PEG and LiCl respectively.

2.3. Characterization

Morphology and internal structure of the composite beads were examined by SEM (Seron Technology AIS2300C). The internal diameter, distribution of polymer and void volume of various types of beads were evaluated from SEM images. TG (Mettler Toledo TG/DSC STAR System) was performed by heating the samples up to 1000 °C, at a heating rate of 10 °C/min, in N₂ atmosphere. TG data were used to determine the weight of the encapsulated extractant per unit weight of PES. Further the beads were characterized by FTIR (Shimadzu IR Affinity-1) as a confirmatory tool to substantiate the characteristic functional groups of D2EHPA in the PES bead matrix.

2.4. Metal ion sorption studies

Sorption (uptake) study of Y(III) by polymeric beads was investigated in batch as well as column mode. In the case of batch mode, sorption studies have been performed by contacting known amount of all types of polymeric beads separately with aqueous chloride solutions containing Y(III) (80–3300 mg/L) at varying concentrations at an appropriate solid to liquid ratio (10 g:100 mL: 1:10) for 24 h to make sure that the system had reached the equilibrium. The solid–liquid mixture was stirred constantly to avoid mass transfer resistance. In general, the experiments were performed at ambient temperature (30 ± 1 °C), except for temperature variation study. To study the effect of a particular experimental parameter on sorption of Y(III), sorption test was carried out in similar way by keeping the other variables constant. Once the system reached the equilibrium the polymeric beads were removed and the aqueous phase was analyzed for its Y(III) content by ICP-AES (JY Ultima 2). The concentration of sorbed Y(III) was determined by the difference in the initial and equilibrium concentration in aqueous solution. For material balance the composite beads sorbed with Y(III) was stripped either with 40% HCl or 25% H₂SO₄ and analyzed for Y(III) content by ICP-AES. The material balance was found to be within the error of ±5%. The equilibrium adsorption (q_e) in mg/g and weight distribution coefficient, K_d were evaluated using following equations:

$$q_e = (C_o - C_e) \frac{V}{w} \quad (1)$$

$$K_d = \left(\frac{C_o - C_e}{C_o} \right) \frac{V}{w} \quad (2)$$

where C_o and C_e are concentration of Y(III) in mg/L or ppm at initial time and at equilibrium, respectively; w is the weight of polymeric beads (polymer and extractant); and V is the volume of aqueous phase in liters for q_e and mL for K_d evaluation.

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