STUDIES ON CNT DOPED D2EHPA IMPREGNATED POLYMERIC BEADS FOR YTTRIUM EXTRACTION

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Abstract

Novel polyethersulfone based composite beads encapsulating di-(2-ethylhexyl)-phosphoric acid (D2EHPA) in combination with different additives, such as, PEG, PVA, LiCl and multiwalled-carbon nanotube (MWCNT) have been prepared by non-solvent phase inversion method. These beads were characterized by scanning electron microscopy, thermogravimetry and infra-red spectroscopy. Effect of additives on bead structure, encapsulation capacity, extractability and stability has been examined to compare their usability for extraction of yttrium from acidic medium. Microstructural investigation confirmed the role of additives in modifying the pore structures in beads, responsible for varied degree of yttrium extraction. PES/D2EHPA/MWCNT/PVA beads were found to be superior for Y extraction.

Introduction

Polymeric matrix based composite beads encapsulating organic extractants have recently been investigated for the extraction of metal ions from aqueous solution due to large surface area, minimal use of organic solvents (extractant, diluent), reusability, stability and absence of phase separation phenomenon [1]. Polymeric composites encapsulating organophosphorus type of extractants have been studied for metal ion extraction from aqueous solution [2]. There is not much information available for the extraction and separation of rare earths using polymeric beads. Rare earths are considered as important elements due to their importance in high tech materials such as superconductors, lasers and magnetic materials. Extraction of Y(III) by polymeric beads has been reported recently[3]. With the objective of extraction of rare earths from aqueous phase, different types of novel composite beads having PES as the base matrix encapsulating D2EHPA with various additives like polyethylene glycol (PEG), polyvinyl alcohol (PVA), lithium chloride (LiCl) and multiwall carbon nanotubes (MWCNT) have been prepared and evaluated for yttrium extraction from chloride medium. Different analytical tools including SEM, TGDTA and FTIR have been utilized to acquire information related to morphology, pore size distribution and encapsulation capacity. The analysis of the beads by these techniques provided the basis for the selection of multiwall carbon nanotubes containing PES/PVA/D2EHPA beads for extraction of yttrium.

Materials and methods

PES was obtained from local vendor and used without any further purification. Chemicals like N-methylpyrrolidone (NMP), PVA, PEG and LiCl were purchased from Merck India. Organic extractant D2EHPA (>95% diester), Albright & Wilson, USA was...
used as received. MWCNT was prepared by chemical vapour deposition method from acetylene using ferrocene as a catalyst in our laboratory [4]. Different types of beads namely, PES/PVA /D2EHPA, PES/PEG /D2EHPA, PES/LiCl /D2EHPA, PES/PVA (as blank), PES/PVA/MWCNT/D2EHPA were prepared by non-solvent induced phase inversion method under optimized preparatory conditions [5]. Polymeric composite beads were characterized by SEM and FT-IR. ICP-AES (JY Ultima 2) was used to determine the yttrium concentration in aqueous solution. Y(III) extraction data was interpreted by evaluating weight distribution ratio (D_w), using following equation [6]

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D_w = \frac{(C_f - C_r)}{C_r} \times \left(\frac{V}{w}\right)
\]  

Where C_f (mg/L) and C_r (mg/L) are the aqueous phase Y(III) ion concentrations before and after equilibration, respectively; w(g) is weight of dry polymer and V (mL) is the volume of aqueous phase.

**Results and Discussion**

Cross sectional SEM images of all types of composite beads are illustrated in Fig 1(a-f). Fig. 1a shows a blank bead based on PES matrix only. When D2EHPA is encapsulated, the bead becomes more porous with uneven distribution of polymer (Fig. 1 b). Additives were added in order to modify the structure. PVA doped bead (Fig. 1 c) has relatively thinner outer membrane layer whereas, PEG and LiCl doped beads (Fig. 1d and 1 e) have thick outer polymeric shell with varying morphological structures. Polymeric bead containing PVA and CNT both as additives (Fig. 1 f) has more porosity and uniform distribution of pores and polymer matrix in comparison to PVA doped D2EHPA bead (Fig. 1 c). From the images it is evident that the additives not only act as the pore forming reagents, but also change the configuration of PES molecules and affect the dispersive state of D2EHPA in the polymeric system.

The FTIR spectra of the liquid phase D2EHPA, blank PES/PVA bead and D2EHPA impregnated PES/PVA/CNT beads are depicted in Fig. 2(a, b & c). The D2EHPA spectrum in Fig.2(a) shows a doublet at 1460 and 1380 cm⁻¹ due to the C–H deformation vibrations and peaks at the interval 2800–3000 cm⁻¹ corresponding to the radical 2-ethylhexyl. In Fig. 2 b, three peaks between 1600 cm⁻¹ to 1400 cm⁻¹ were attributed to representative aromatic skeletal vibration of PES. In Fig. 2(c), the peaks at 1250-1210 cm⁻¹, which corresponds to P=O group and low intense band around 1680 cm⁻¹, along with characteristic peaks of PES demonstrated that D2EHPA exist in the bead independently within the polymer matrix without any chemical interaction with PES.

The composite beads were evaluated and compared for their extractability towards yttrium from chloride medium. Metal ion extraction by these polymeric matrix based composite membrane beads occurs via formation of metal ion complex and subsequent diffusion of the complex species through the pores inside the impregnated beads [7]. The values of D_w obtained with

![Fig. 1: Cross-sectional images of PES composite beads with different additives by SEM](image-url)
different types of beads are shown in Fig. 3. The extraction of yttrium with additives follows the order: PES/PVA/MWCNT/D2EHPA > PES/PVA/D2EHPA > PES/D2EHPA > PES/LiCl/D2EHPA > PES/PEG/D2EHPA. PES/D2EHPA beads doped with PVA or PVA+CNT resulted in an enhanced extraction of yttrium. The $D_w$ value of Y(III) increased significantly from 14 (PES/D2EHPA) to 72 (PES/D2EHPA/PVA). The increase in $D_w$ value in the case PVA doped composite beads can be attributed to the increased porosity and modified hydrophilicity causing better contact between aqueous and organic phases thereby facilitating the faster ion exchange mechanism [8]. The addition of MWCNT to PES/PVA/D2EHPA beads significantly increased the $D_w$ value from 72 to 128. This may presumably due to functionalization of CNT by attaching additional D2EHPA molecules on its surface, which in turn gets distributed on the surface near peripherals of the beads resulting in ion exchange as well as adsorption phenomenon taking place simultaneously. MWCNT/PVA doped composite beads were evaluated for their reusability by repeated extraction and stripping operation and even after 10 cycles there was no sign of physical degradation or decrease in extraction capacity of the beads.

Conclusions

D2EHPA impregnated PES composite beads with different additives were successfully prepared and tested for Y(III) recovery from aqueous media. Morphology and encapsulation capacity of the beads could be controlled by suitably selecting the additives. Composite beads doped with PVA and CNT were found to be superior among the tested beads for the recovery of yttrium even at higher acidities. These beads were found to be stable even after 10 cycles of operations without loss of D2EHPA.

References