THERMAL ANALYSIS OF POLYETHERSULFONE BASED COMPOSITE BEADS ENCAPSULATED WITH DI-2-ETHYL HEXYL PHOSPHORIC ACID

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Abstract

A novel polymeric composite bead encapsulating organophosphorus extractant D2EHPA has been developed and tested for rare earths separation. Analytical techniques such as TGA, SEM and IR were employed to characterize the physical and thermal behavior of the bead. Weight loss profile as a function of temperature revealed the extractant encapsulation capacity of the beads. Microscopic examination of the composite bead confirmed central coconut type cavity surrounded by porous polymer layer of the beads through which exchange of metal ions occurs. The composite beads have the potential for rare earths separation from aqueous solutions.

Introduction

There is a considerable interest in evaluating alternative methods for separation of metal ions from various types of aqueous streams. Solid-liquid extraction method, employing polymer based composite in the form of beads, encapsulating organic solvent, has emerged as an effective separation tool over conventional liquid-liquid extraction and ion exchange techniques [1]. The advantages of the use of polymeric beads over other processes extends due to large surface area, minimal use of organic solvents (extractant, diluent), reusability, stability and absence of phase separation phenomenon. A liquid cation exchange type of extractant, D2EHPA(di 2 ethyl hexyl phosphoric acid) has been widely used for the separation of rare earths by liquid –liquid extraction technique [2]. In the present study, we report preparation of polyethersulfone based composite beads(PBC) encapsulating D2EHPA under various experimental condition and their characterization by TGA, SEM and optical microscope. These beads were also evaluated for their usability in the separation of rare earths from aqueous solution.

Experimental

Commercially available polyethersulfone (PES,Molecular weight ~30000),N-methyl pyrolidone (NMP) and poly(vinyl alcohol) PVA (MW 31,000–50,000) were used for the preparation of beads. D2EHPA was procured from Albright and Wilson and used as received. Rare earths (such as Y(III), Sm(III) and La(III)) solutions were prepared by dissolving their oxides (>99% purity) in hydrochloric acid. Polymeric composite beads (PES/PVA/ D2EHPA/NMP/water system) were prepared as per the procedure described elsewhere [3]. Morphology and internal structure of the composite beads were examined by optical microscope and scanning electron microscope (SEM). Thermo gravimetric analysis (TGA, Mettler) of all types of polymeric beads was carried out to evaluate the percentage of extractant, polymer, water and NMP content in the composite bead. ICP-
AES (JY-Ultima -II) was used to estimate rare earths in aqueous samples.

Results and Discussion

Microstructural examination of beads

Three types PBC viz. (a) PES bead without extractant (b) PES bead encapsulating D2EHPA and (c) PVA doped PES bead encapsulating D2EHPA were examined by SEM and optical microscope. Typical SEM micrographs of the PVA doped PES beads encapsulating D2EHPA are shown in Fig. 1(a-e). Figure 1(a) shows the overall image of solvent encapsulated sphere and Fig. 1 (b,c) depict the details of its surface structure at different levels of magnification. These images suggest that beads are almost spherical with uniformly distributed pores (i.d. = 1 μm). The cross-sectional image of doped (Fig. 1d) and normal beads (Fig. 1f) lead to the distinguishing observations as: PBC without additives had relatively thin outer polymeric layer and shell within shell type of internal structure due to uneven distribution of polymer in comparison with doped beads. PBC having PVA as an additive had coconut type of internal structure with a central void (volume~10 mm³) filled with organic extractant (Fig 1d). The internal structure of these beads was found to be more porous (high surface area) in comparison to beads without additive and the porosity decreases from center to circumference of the spherical bead (Fig 1e, contains CNT as coadditive). NMP and PVA both are soluble in water. During phase inversion, not only NMP diffuses out through PES, water also ingress into PES due to hydrophilicity of PVA. This results in more porous, thicker walled bead structure.

Thermal analysis of polymeric composite beads

PES/PVA/D2EHPA beads with different extractant to polymer solution ratio were prepared. Thermo gravimetric analysis of these polymeric beads was carried out to evaluate the percentage of extractant, PES, water and NMP content in the composite material. TGA (Fig. 2) representing change in the weight of sample (beads) with increase in temperature showed mainly three segments of 80-160°C, 230-260°C and 460-560°C. First segment represents evaporation of water and NMP in the range of 80 to 160°C, second zone of weight loss depicts the disintegration of D2EHPA and 460 to 560°C part of the profile shows the weight loss due to dissociation of PES and disintegrated parts of D2EHPA. Evaluation of thermograms revealed that increase in extractant to polymer ratio from 1:15 to 1:4 lead to increase in D2EHPA content from 9% to 25.5% in the beads, whereas polymer content in the beads was in the range of 10 to 16%. These results were in good agreement with the encapsulated amount of D2EHPA (7-25%) taken during preparation of beads. Comparison of TGA profiles of D2EHPA encapsulating beads with the profiles of D2EHPA and PES showed no shift in the mass loss vs. temperature profile of individual compound eliminating any possibility of chemical interaction.
among the main constituents of the extractant encapsulating beads. Further the TGA of PES/PVA/D2EHPA beads were performed to evaluate the extractant loading (L) calculated in grams of extractant per gram of PES. The value of L for PES based material was found to be 1.4±0.2 gram of D2EHPA per gram of polymer.

The feasibility of using PES/PVA/D2EHPA based polymeric composite beads for rare earths separation were tested by performing the extraction experiment with mixed rare earths solution containing 450 mg/L of La(III), Sm(III), Y(III) each at 0.5N HCl. The extraction profiles of these rare earths are shown in Fig. 3(a), which clearly demonstrates the possible use of these beads for separation purposes. The order of extraction of rare earths was La(III)<Sm(III)<Y(III); showing appreciable separation factor between them. Equilibration time of 6 hours was found to be sufficient for >80% extraction of rare earths. Later these beads were subjected for stripping of rare earths with 5NHCl(Fig.3b). It is evident that with 6 hours of contact time >90% rare earths were brought back to the aqueous phase. This study demonstrated that these beads can be used for separation of rare earths from aqueous solution.

Conclusions

TGA and microscopic examination of PES/PVA/D2EHPA PBC has been performed.D2EHPA encapsulationin PBC has been estimated using TGA. Thermal analysis results indicated no interaction between polymer and extractant and thus preserving extractant properties.Feasibility of employing PBC for the separation of rare earths from hydrochloric medium has been demonstrated.

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References