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Unique reversibility in extraction mechanism of U compared to solvent extraction for sorption of U(VI) and Pu(IV) by a novel solvent impregnated resin containing trialkyl phosphine oxide functionalized ionic liquid

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ABSTRACT

Novel Solvent Impregnated Resin (SIR) material was prepared by impregnating a trialkyl phosphine oxide functionalized ionic liquid (IL) into an inert polymeric material XAD-7. A series of SIR materials were prepared by varying the IL quantity. Sorption of both U(VI) and Pu(IV) were found to increase with increasing IL concentration in SIR up to an optimum IL concentration of 435 mg g^{-1} of SIR beyond which no effect of IL concentration was observed. A change of mechanism of sorption for U(VI) by SIR was observed in comparison to solvent extraction. The dependency of U(VI) sorption with nitric acid concentration showed a reverse trend compared to solvent extraction studies while for Pu(IV) the trend remained same as observed with solvent extraction. Sorption of both the radionuclides was found to follow pseudo second order mechanism and Langmuir adsorption isotherm. Distribution co-efficient measurements on IL impregnated SIR showed highly selective sorption of U(VI) and Pu(IV) over other trivalent f-elements and fission products from nitric acid medium.

1. Introduction

Ionic liquids are a new class of solvent having many encouraging properties [1–3] to replace the volatile organic diluents presently being used for recovery of various actinides, lanthanides and fission products from spent nuclear fuel origin. Large number of literature reports are available on the use of ILs as diluents with conventional organic extractants for extraction of U(VI), Pu(IV), Am(III), Sr(II) etc. [4–12]. The extent of extraction as well as mechanism of extraction has been reported to be widely different from that of molecular diluents presently employed in industrial scale [13–15]. Inspite of possessing many unique solvent properties, industrial scale application of ILs in the field of actinide, lanthanide and fission product extraction is still in its infancy. The major obstacles for IL based processes in nuclear spent fuel management are high viscosity, loss in aqueous phase etc [3]. An alternative way to prevent the loss of IL in aqueous phase is to functionalize the ionic liquid cationic moiety with proper metal extracting functional groups, the concept which is known as task specific ionic liquid (TSIL) [16–22]. Different TSIL having various novel functionalities have been reported in literature for extraction of U(VI), Pu(IV), Am(III) etc. Our group is also involved in the synthesis of novel task specific ionic liquids for extraction of different radionuclides from nitric acid medium [23,24]. We have recently reported a novel trialkyl phosphine oxide functionalized TSIL and shown that this TSIL is highly selective for U(VI) and Pu(IV) over other minor actinides and lanthanides [24]. In the study we have used phosphine oxide (PO) functionalized IL (PO-TSIL) diluted in two different ionic liquids as diluents in solvent extraction (SX) mode. Though SX is the preferred technique for industrial scale separation of metal ions, IL based SX has a basic disadvantage due to inherent high viscosity associated with ILs. Hence application of IL in industrial scale separation of metal ions requires alternative methods.

Solvent impregnated resins possess unique properties which combine the efficiency and selectivity of the extractants as well as preventing their dispersion in aqueous phase [25]. For ILs, impregnation in a porous polymeric matrix also nullifies the effect of high viscosity of the ILs to a greater extent. Literature reports are available on the application of ILs impregnated in inert polymeric matrix for metal ion separation and in these studies ILs has been used as an extractant as well as diluents with other extractants. Recently, Mohapatra and coworkers [26–28] have used imidazolium based ionic liquids in the presence of conventional extractants like TODGA, CMPO etc in extraction chromatographic resins to study the uptake of various actinides

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from nitric acid medium. Significant enhancement of distribution coefficient values for the actinide ions was observed for the extractants in the presence of ionic liquids. Guibal and co-workers have studied tetraalkyl phosphonium ionic liquid impregnated in synthetic resin Amberlite XAD-7 for separation of Hg(II), Pd(II), Cd(II), Au(III), Bi(III) from HCl medium [29–33]. The solid phases containing phosphonium ionic liquids were found to be very effective for the targeted metal ions. Phosphonium based ionic liquids have also been impregnated in XAD-7 for separation studies of Cr(VI), Tl(I) [34,35]. In spite of such large number of literature reports on the applicability of ILs in SIR mode for separation of metal ions, to the best of our knowledge there is no report available on the applicability of TSIL impregnated SIR for the uptake of actinide ions. Herein we report for the first time, the preparation and characterization of a novel PO-TSIL impregnated SIR. We also report the sorption behavior of U(VI) and Pu(IV) from nitric acid medium using the impregnated SIR. In depth study on the mechanism of extraction, kinetic modeling of extraction, adsorption isotherm are also performed and presented. Desorption of the loaded actinides were also studied to investigate actinide recovery and recyclability of the impregnated SIR. Finally column studies were carried out using the PO-TSIL impregnated SIR to investigate the dynamic loading capacity of the resin material and its possible applicability for real situations.

2. Experimental

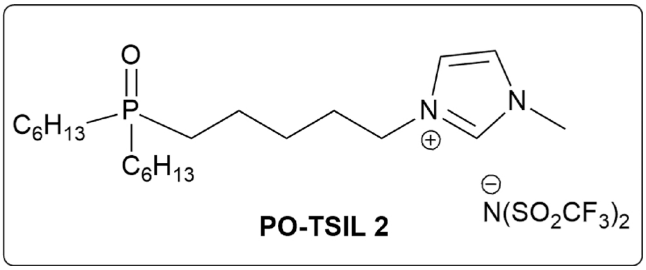
2.1. Materials

2.1.1. Reagents

Trialkyl phosphine oxide functionalized TSIL (Fig. 1) were synthesized as per reported procedure [24] and characterized by NMR and HRMS. Amberlite XAD-7 was received from Sigma-Aldrich. The resin was washed with distilled water, ethanol and acetone to remove the impurities followed by filtration and oven drying at 50 °C for removal of excess acetone. All other reagents were of AR grade and were used without any further purification.

2.1.2. Radionuclides

Radionuclide tracers of ^{233}U, ^{241}Am and Pu (with majority being 239) were purified using standard procedures and radio-chemical purity of the same was ascertained by alpha spectroscopy. Sorption studies for Pu were carried out in different oxidation states. Pu was converted to Pu(IV) using $NaNO_2$ as oxidant and was extracted by Theonyl Trifluoro Acetone (TTA) from a feed solution in presence of 0.5 M HNO_3. The stripping from TTA phase was carried out using 8 M HNO_3 which was used as stock solution. Two different methods were followed to monitor the stability of Pu(IV)-TTA extraction method and spectrophotometry. For dilute solutions, TTA extraction method ensuring a dependence of 4 in the log-log plot of $D_{Pu(IV)}$ and TTA concentration was found to be sufficient whereas for concentrated solution spectrophotometry was used. Pu(III) was prepared by using 0.1 M hydroxyl ammonium nitrate (HAN) as reductant. Other tracers of ^{152,154}Eu, ^{137}Cs and ^{85,89}Sr, purchased from BRIT, Mumbai, were used following their purity check using HPGe based gamma spectrometry.



PO-TSIL 2

Fig. 1. Structure of the PO-TSIL.

The typical concentration range for the radionuclides used in distribution studies were: Am ~ 10^{-6} M, Pu ~ 10^{-5} M, Eu and Cs ~ 10^{-5} M and Sr ~ 10^{-4} M. All other reagents were of AR grade and were used without any further purification.

2.2. Methods

2.2.1. Preparation and characterization of SIR

The PO-TSIL impregnated SIR was prepared by equilibration of known weight of Amberlite XAD-7 solid support and PO-TSIL in presence of sufficient volume of methanol. The equilibration of the slurry was carried out in a mechanical shaker for 24 h. After equilibration, solvent removal was done by flushing nitrogen gas with gentle stirring. After solvent removal, the material was vacuum dried to a constant weight. The prepared SIR was characterized using Fourier- transform Infra Red (FTIR) Shimadzu IRAffinity-1S (for functionalization), Scanning Electron Microscope (SEM) model No Philips 30 (for surface morphology).

2.2.2. Sorption experiments

Batch equilibration studies for the sorption of the radionuclides were carried out by equilibrating a known volume (generally 1 ml) of aqueous phase containing the radio-tracers and known weight of the resin material (~25–30 mg) in a thermo stated water bath (150 rpm). After equilibration, suitable aliquots from the aqueous phase were taken for assaying the radio-tracers. Column studies using the prepared SIR were carried out in a glass column with dimensions (15 cm × 1 cm) and fitted with a stop cock for controlling the rate. 1 g of the resin material was placed inside the column with 4 ml as the bed volume.

Column studies using the prepared SIR were carried out in a glass column with dimensions (15 cm × 1 cm) and fitted with a stop cock for controlling the rate. The column was loaded with 1 g of the resin material with 4 mL as the bed volume.

2.2.3. Estimation of radionuclides

^{233}U and ^{239}Pu assaying were carried out by alpha counting in a Zns (Ag) based alpha counter. Gamma counting using a NaI(Tl) based scintillation counter was used for the determination of ^{241}Am, ^{152,154}Eu, ^{137}Cs, and ^{85,89}Sr. Following formula was employed to calculate the weight distribution co-efficient of metal ions (K_d) on the resin:

$$K_d = \frac{(C0 - C_e)}{C_e} \cdot \frac{V}{W} \tag{1}$$

Where C_0 and C_e are the concentrations of metal ion in the aqueous phase before and after equilibration, V is the volume of the aqueous phase (mL), W is the weight of the resin material (g). Temperature during all the experiments were maintained at (25 ± 2) °C. All the experiments were carried out in triplicate and the error limit was within ± 5% of relative standard deviation.

3. Results and discussion

3.1. Characterization

The synthesized SIR was characterized by FTIR AND SEM. FTIR studies of the XAD loaded with PO-TSIL showed the presence of peaks at, 1450 (C = N), 1351 cm^{-1} (C–F), 1197 cm^{-1} (P = O) and at 1060 cm^{-1} (S = O) (Fig. 2). In the Fig.2 FTIR spectra of pure PO-TSIL, pure XAD-7 support as well as PO-TSIL loaded SIR have been shown. In XAD-7 support material there was no peak at 1450, 1351, 1197 and 1060 cm-1 but these peaks are present in the SIR which clearly proves the presence of PO-TSIL in the SIR. SEM Scanning Electron Microscopy of the SIR showed clear presence of the IL in the pictures with 28× magnifications (Fig.3). The SEM is corresponding to the PO-TSIL loading of 435 mg g^{-1} of SIR. We did not observe any difference in the FTIR spectra of the different SIR corresponding to varying IL loading.