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Recovery of uranium, thorium and zirconium from allanite by extraction chromatography using impregnated chromosorb

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ABSTRACT

Chromosorb 102 impregnated with Cyanex 923 was used as a stationary phase in the extraction chromatographic separation of lanthanides, U(VI), Th(IV) and Zr(IV). Batch studies were carried out to investigate the uptake behaviour of these metal ions, along with few other metal ions. The effect of different parameters like equilibration time, concentration of acid, metal ions and extractant has been studied. The distribution data has been used to develop suitable eluting agents. The sorbing and desorbing capacity of the column for U(VI), Th(IV) and Zr(IV) was determined. Results indicate an insignificant change in the efficiency of the column up to 10 such cycles. The practical utility of the column has been demonstrated by the recovery of around 95% of U(VI), Th(IV) and Zr(IV) from allanite sample with a purity of around 97% ± 2%.

1. Introduction

Separation science plays an important role in the development of recovery and purification processes. A variety of separation methods such as solvent extraction, ion exchange, adsorption and

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various forms of chromatography have been explored for the separation and recovery of metal ions. Extraction chromatography, in contrast, has received limited attention. It is a form of liquid–liquid chromatography in which the stationary phase is either an extractant or a solution of extractant supported on an inert support [1]. The technique thus combines the selectivity of solvent extraction with the multistage character of a chromatographic process accompanied by ease of handling. The technique offers tremendous potential for the separation of intricately similar metal ions. The liquid–liquid extraction data provides a database for developing an extraction chromatographic procedure.

U(VI), Th(IV) and Zr(IV) are the vital elements for nuclear energy and the demand for these elements has increased enormously. With the advancement of science and technology lanthanides have found utility in the fields like rechargeable batteries, advanced ceramics, fiber optics, permanent magnets and superconductors. In nature, uranium, thorium and zirconium are invariably associated with lanthanides and their mutual separation is of vital significance. Most of the natural sources of these elements are lean and elegant separation schemes are required to meet the stringent demands of purity and recovery. A number of alkyl phosphorus compounds such as tributyl phosphate [2], di-2-ethylhexyl phosphoric acid [3] and trioctyl phosphine oxide [4,5] have been explored as extractants for these elements. But only in a few reports have the partition data been explored. The alkylphosphine extractants marketed under the trade name of 'Cyanex' have gained prominence as extractants for these elements due to their poor aqueous solubility, good hydrolytic stability and selectivity. These inherent advantages make these extractants attractive alternatives for use as stationary phase in extraction chromatography for the separation of metal ions [6–8]. Literature suggests that several attempts have been made to explore Cyanex extractants for these elements [9–12]. The selectivity of Cyanex 923 for the extraction of U(VI), Th(IV), Zr(IV) and lanthanides has already been investigated by the authors [13–15]. The potential of this extractant as impregnant for the said metal ions still remains to be fully explored. In view of this it was planned to explore this extractant for the separation and recovery of U, Th, Zr and lanthanides from a complex matrix by extraction chromatography.

The present paper deals with the uptake of U(VI), Th(IV), Zr(IV) and lanthanides on Cyanex 923 impregnated chromosorb 102. The effect of shaking time and concentration of acid, metal ion and extractant on the uptake of metal ions has been investigated. The stoichiometries of the extracted species have been proposed. The uptake behaviour of lanthanides [La(III), Yb(III)], Y(III), Fe(III), Al(III), Mn(II), V(IV) and Ti(IV) has also been investigated. Based on the sorption data a separation scheme has been designed. The developed procedure has been applied to allanite for the separation and recovery of U(VI), Th(IV), Zr(IV) and lanthanide fractions. Allanite is an ore with a relatively high content of rare earths and yttrium with small amounts of thorium, uranium and zirconium.

2. Experimental section

2.1. General details

All the chemicals and solvents were of analytical-reagent grade from E. Merck (Germany)/Aldrich (USA)/Fluka (Germany) and were used as purchased. The stock solutions of metal ions were prepared in double distilled water after dissolving their suitable salts containing a minimum amount of the corresponding mineral acid. Cyanex 923 (Avg. Mol. Wt. 348, 93% purity) was received from Cytec Canada Inc (Canada). It was used without further purification. Chromosorb 102 (particle size of 80/100 mesh) was procured from John's Manville, USA. A sample of allanite from Rajasthan (India) was used for the recovery of lanthanides, U, Th and Zr.

The quantification of metals in the aqueous solutions was done using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Calibration of this instrument was carried out by sequential peak measurement of the corresponding emission signal and background. The calibration standards used for the determination of various metal ions ranged from 1 to 100 $\mu g\ L^{-1}$.

Chromosorb 102 was impregnated with varying amounts of Cyanex 923 [0.174–8.7 g] per g of the inert support by making slurry of the former in toluene solution of the latter. The toluene was then evaporated by warming up with gentle stirring.