Selective Solid Phase Extraction and Separation of Rare Earth Elements on Silica Based Nanoparticles before their Determination by Inductively Coupled Plasma Mass-spectrometry

Abstract

Silica based adsorbents with covalently immobilized fragments of N-Benzoyl-N-phenylhydroxylamine (BPHA), 2,6-pyridinedicarboxylic acid (PdCA) and amino-di(methylene-phosphonic) acid (AdMPA) have been obtained in multi-step surface synthesis. Functionalized materials were characterized by elemental, FTIR, solid-state NMR, TGA and XPS analysis. For the materials, degree of functionalization, concentration of surface immobilized groups (C_{BPHA} = 0.3 mmol g^{-1}, C_{PDCA} = 0.36 mmol g^{-1}, C_{ADMPA} = 0.29 mmol g^{-1}), characteristics and surface properties were evaluated. Affinity of the adsorbent to the 16 trivalent rare-earth ions in multi-component system has been investigated in aqueous solution. Adsorbents demonstrate reversible adsorption and very high kinetic characteristics. Complete adsorption/desorption process was observed for 10 min. It has been demonstrated that SiO_2-PdCA and SiO_2-AdMPA can be successfully used as adsorbent for removal of REE ions from aqueous solution at pH $\geq$ 2. The adsorbents provide high recovery (>95%) of all REE in presence of 50-fold excess of Ba^{2+} ions. SiO_2-BPHA quantitatively adsorbs most of REE from solution with pH $\geq$ 5 and provide selectivity towards heavy and light REEs (separation factor, SF Lu/La = 81) in the presence of other ions. Ions, Fe^{3+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Al^{3+} which are predominate in environmental objects in 200-fold excess caused little or no interference on the determination of REE. The adsorbents can be reused up to 5 cycles with no significant loss in REEs recovery using 0.1M HNO_3 as desorbing agent. After adsorption of Eu^{3+} and Tb^{3+} ions, SiO_2-PdCA and SiO_2-AdMPA adsorbents demonstrate strong red and green luminescent and can be used as luminescent probes for monitoring of Eu^{3+} and Tb^{3+} ions in solution.

Keyword: silica based adsorbent, solid phase extraction, preconcentration, separation, rare earth elements (REEs), ICP-MS.