Rapid Communication

A magnetic adsorbent for the mutual separation of Am(III) and Eu(III) from dilute nitric acid medium

A.S. Suneesh [a], R. Kumaresan [a], Rakesh Jain [b], K.A. Venkatesan [a],*, M.P. Antony [a], B.M. Bhanage [b]

[a] Fuel Chemistry Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India
[b] Department of Chemistry, Institute of Chemical Technology, Mumbai 400031, India

ABSTRACT

Iron oxide (Fe_3O_4) particles anchored with 1-butyl-3-methylimidazolium bis(2-ethylhexyl)diglycolamate (Fe–Si-MeIm-DEHDGA) was synthesized and characterized by X-ray diffraction, Raman spectroscopy and scanning electron microscopy (SEM) etc. The adsorption behavior of Am(III) and Eu(III) in Fe–Si-MeIm-DEHDGA was studied from dilute nitric acid medium to examine the feasibility of using Fe–Si-MeIm-DEHDGA for the magnetic assisted mutual separation of trivalent actinides and lanthanides. The effect of various parameters such as the duration of equilibration, concentration of nitric acid and diethylenetriaminepentaacetic acid (DTPA) in aqueous phase on the distribution coefficient (K_d) of Am(III) and Eu(III) was studied. The distribution coefficient of ~10^4 mL/g was obtained for both Am(III) and Eu(III) at pH 3 and it decreased with increase in the concentration of nitric acid. Rapid adsorption of metal ions in the initial stages of equilibration followed by the establishment of equilibrium occurred within 2 h. The study indicated the possibility of using Fe–Si-MeIm-DEHDGA particles for the magnetic separation of Eu(III) from Am(III) with high separation factors.

© 2016 Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

The spent nuclear fuel (SNF) discharged from the nuclear reactor contains fissile elements such as plutonium, depleted uranium, and several short-lived and long-lived radioactive nuclides [1]. The SNF is reprocessed for the recovery of uranium and plutonium by liquid–liquid extraction [1] and the aqueous raffinate rejected after the extraction is known as high-level liquid waste (HLLW) [2,3]. The radiotoxicity of HLLW is essentially due to the presence of alpha emitting trivalent actinides such as ^{241}Am and ^{243}Cm [2,3]. One of the options for minimizing the radiotoxicity of HLLW is to partition these trivalent metal ions from HLLW and transmute them into short-lived or innocuous products [2,3]. In this context, a large number of methods have been developed for the separation of trivalent actinides from HLLW by liquid–liquid extraction mode [4,5]. However, the separations based on solid phase extraction are very limited.

In the recent past, the task specific ligands anchored on inorganic solid supports such as silica, titania, iron oxide are receiving increased attention and they are being investigated for the adsorption of radiotoxic metal ions [6–13]. Among the various solid supports, the magnetic solid phase separation (MSPS) is emerging as the promising technique, owing to some exceptional merits discussed elsewhere [6, 9,10]. Since this technique exploits the application of external magnetic field for separation, the particle size of the adsorbent can be lowered down to nano-levels for enabling the adsorption of radioactive metal ions from aqueous feeds in a single contact and in a short span of time. Unlike the conventional solid phase extraction methods, there is no need to pack the adsorbent particles in a column as the MSPS is usually operated in a batch adsorption mode and the phase separation can be quickly achieved by the application of external magnetic field. As a consequence, a large number of studies have been reported in literature on the separation of radioactive metal ions from aqueous waste [11,12] that use either iron oxide or task specific ligands anchored iron oxide. For instance, iminodiacetic acid grafted magnetic adsorbents have been reported [13] for the sequestration of rare earths from dilute solutions. However, the iron oxide modified with task specific room temperature ionic liquid moieties and their application on the separation of radiotoxic metal ion have not been reported in literature.

Room temperature ionic liquids (RTILs) are organic salts molten at temperatures lower than 373 K [14,15]. They have several fascinating properties suitable for industrial exploitation [14]. When the cationic or anionic part of the ionic liquid is tethered with organic functional moiety, they are known as task specific ionic liquids [16]. In this paper, we report the tethering of the task specific ionic liquid, 1-butyl-3-methylimidazolium bis(2-ethylhexyl)diglycolamate, on iron oxide (Fe_3O_4) magnetic particles and study on the extraction behavior of Am(III) and Eu(III) from dilute nitric acid medium. Since the alkyl diglycolamic acid was a promising ligand [17] for the separation of trivalent metal ions from nitric acid medium, it was chosen as the anionic moiety in the present study for tethering.

---

* Corresponding author.
  E-mail address: kavenkat@igcar.gov.in (K.A. Venkatesan).

The magnetite (Fe_3O_4) particles were prepared by the co-precipitation method described elsewhere [18], and the reaction scheme is shown in Fig. S1 (please see supplemental). The silylation reaction on iron oxide was carried out by the procedure described elsewhere [19, 20]. Briefly, the Fe_3O_4 magnetic particles (10 g) were reacted with the ammonia solution (10 mL, 28 wt.%) and tetraethoxysilane (TEOS, 20 mL) for about 10 h at room temperature. During this mixing, the surface hydroxyl groups present on iron oxide react with TEOS to form a bonding of siloxane over the surface of iron oxide. The silylated iron oxide, designated as Fe–Si (Fig. S2, (please see supplemental)), was collected and washed with surplus ethanol and water, and dried in air, overnight. In a separate reaction, 3-(3-methylimidazolium)propyltrimethoxysilane chloride (Si-MeIm) was prepared by reacting 1-methylimidazole (5 g, 60 mmol) with 3-chloropropyltriethoxysilane (13 g, 62 mmol) in presence of acetonitrile at 350 K. The reaction scheme is shown in Fig. S3 (please see supplemental). The product obtained (Si-MeIm, 10 g) was then refluxed with Fe–Si (5 g) in presence of chloroform at 380 K to obtain 1-butyl-3-methylimidazolium chloride anchored on Fe–Si. The product was designated as Fe–Si-MeIm-Cl and the reaction scheme is shown in Fig. S4 (please see supplemental). The chloride form of the particle was then converted to hydroxide (OH^-) form, by treating Fe–Si-MeIm-Cl with excess sodium hydroxide (1 M, 50 mL). The product Fe–Si-MeIm-OH thus obtained was then refluxed with bis(2-ethylhexyl)diglycolamic acid (HDEHDGA) to obtain the imidzolium diglycolamate anchored adsorbent (Fe–Si-MeIm-DEHDGA), as shown in Fig. S4. The functionalized adsorbent was collected and washed several times with toluene, isopropanol, acetone, water and acetone. The structure of the adsorbent is shown in Fig. 1.

The X-ray diffraction patterns (recorded using a Philips 1011 X-ray diffractometer operating with 40 kV and 45 mA, with Cu Kα (1.5406 Å) radiation) of iron oxide (as prepared sample) and Fe–Si-MeIm-DEHDGA are shown in Fig. 2. The XRD pattern compares well with the pattern of standard magnetite, Fe_3O_4 (JCPDS No. 65-3107). The average particle size of Fe–Si-MeIm-DEHDGA, measured using Malvern-Zeta-sizer, was ~50 μm. These particles were further characterized by Raman spectroscopy (Renishaw Raman Imaging Microscope, including a spectrometer connected to a CCD detector). The Raman spectra recorded are shown in Fig. S5 (please see supplemental). Various phases of iron oxide can be easily distinguished by the characteristic traces in Raman spectrum. The Raman spectroscopy studies provided in the supplemental confirmed the structure of magnetite (Fe_3O_4) in the core, which is functionalized with the organic moiety on the surface of iron oxide in Fe–Si-MeIm-DEHDGA.

The SEM image of Fe–Si-MeIm-DEHDGA shown Fig. 3 indicates that the average particle size of the adsorbent ranges from 10 to 20 μm, which is in good agreement with the particle size measured using Zeta sizer (~50 μm). The EDX pattern of the particles showed the presence of Fe, Si, C, N, O elements in the sample. The FT-IR spectrum of Fe–Si-MeIm-DEHDGA shown in Fig. S6 (please see supplemental) exhibits the transmittance bands corresponding to amidic carbonyl (1650 cm^{-1}) of diglycolamate anion, imidazolium moiety (1560 cm^{-1} characteristic of C=C stretching in imidazolium ring) and 2950 cm^{-1} characteristics of C—H stretching, 1460 cm^{-1}

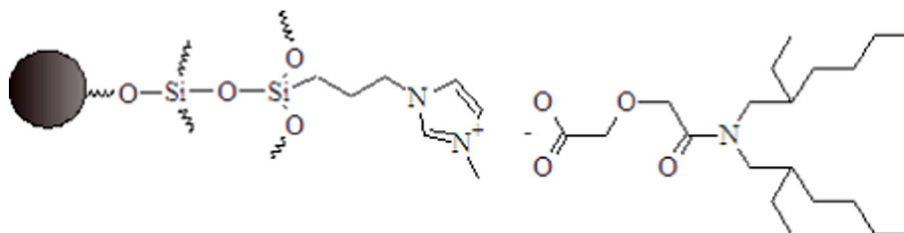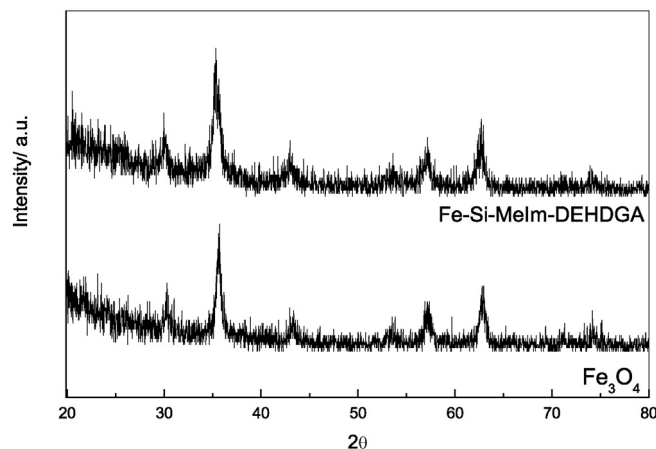**Fig. 2.** Powder X-ray diffraction of as prepared Fe_3O_4 and Fe–Si-MeIm-DEHDGA.

characteristics of C—C stretching, 1070 cm^{-1} characteristic of Fe—O—C rocking vibrations. All these features confirm the presence of imidazolium diglycolamate moiety on iron oxide particles.

The rate of adsorption of Am(III) (or Eu(III)) was studied by the batch equilibration of 0.05 g of the adsorbent (Fe–Si-MeIm-DEHDGA) with 10 mL of nitric acid solution (0.001 M to 0.1 M) spiked with ^{241}Am(III) or $^{(152 + 154)}$Eu tracer at 298 K. The mixture was equilibrated in a 20 mL capacity stoppered test tube immersed in a constant temperature water bath and rotated in a upside down rotation. The equilibration was stopped at a pre-fixed interval of time. The magnetic particles were separated from the aqueous phase by using a permanent magnet, as shown in Fig. S7 (please see supplemental). An aliquot was taken from the aqueous phase at various intervals of time and the radioactivity of $^{(152 + 154)}$Eu or ^{241}Am present in the aqueous phase, before and after equilibration, was measured using a well-type NaI(Tl) scintillation counter. The percentage adsorption of Am(III) or Eu(III) was calculated by the following equation.

$$Percentage\ of\ extraction = \frac{A_0 - A_f}{A_0} \times 100$$

where A_0 and A_f are the initial and final radioactivity of aqueous phase. Rapid adsorption of Am(III) or Eu(III) is observed in the initial stages of equilibration followed by the establishment of equilibrium occurring in 10 min of equilibration, as shown in Fig. S8 (please see supplemental). Therefore, for all subsequent equilibration experiments the aqueous and adsorbent phases were equilibrated for about one hour.

The effect of nitric acid on the adsorption of Am(III) or Eu(III) was studied to assess the feasibility of using the adsorbent for the separation of trivalent metal ions from nitric acid waste solution. The concentration of nitric acid in the waste (TRUEX product [17]) usually ranges from 0.001 M to 0.1 M. Therefore, the adsorbent (0.05 g) was equilibrated with nitric acid (0.001 M to 0.1 M) solution, spiked with ^{241}Am(III) (or $^{(152 + 154)}$Eu(III) (both 20 mg/L). After one hour of equilibration the magnetic particles were separated and the radioactivity of $^{(152 + 154)}$Eu or ^{241}Am present in the aqueous phase was measured.

Fig. 1. Illustration of the structure of Fe–Si-MeIm-DEHDGA.