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Studies on the recovery of Th(IV) ions from nitric acid solutions using amino-magnetic glycidyl methacrylate resins and application to granite leach liquors

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ABSTRACT

Polymeric matrices composed of glycidyl methacrylate/divinylbenzene and glycidyl methacrylate/*N*,*N*′-methylenebis(acrylamide) were prepared concurrently in the presence of dispersed fine magnetite particles. The obtained products were allowed to react with tetraethylenepentamine to produce two amino-magnetic resins named RI and RII. The adsorption of Th(IV) ions on RI and RII from nitric acid solutions was studied using batch and column experiments. At pH 3.7, maximum adsorption capacity values of 0.86 and 0.97 mmol g^{-1} of Th(IV) ions were obtained for RI and RII, respectively. At S/L ratio = 1, removal efficiency values of 86 and 99% from an initial concentration of 0.54 mmol L^{-1} were achieved for Th(IV) ions using RI and RII, respectively. At all S/L ratios, the more hydrophilic resin RII showed better removal efficiency compared to RI. Adsorption experiments were carried out on three granite ore samples to recover Th(IV) ions using the two new resins obtained. The results indicated good recovery percentage and selectivity of the resins towards Th(IV) ions compared to other associated elements. The resins loaded with Th(IV) ions were effectively regenerated using 0.1 M HNO_3.

1. Introduction

Thorium is a naturally radioactive metal existing at minor levels in soil, rocks, water, plants and animals (Habashi, 1997; Alipour et al., 2016). The main implementation of thorium at present is in nuclear reactors and commercial nuclear industry (Vertes et al., 2010; Keogh, 2006). Thorium as nuclear fuel has some benefits over uranium like, more abundant than uranium, more chemically stable, higher radiation resistance, produce low radiotoxicity waste than uranium (Torapava, 2011). The thorium compounds in entering living organisms may cause an expanded risk like lung cancer, pancreatic cancer, and bone cancer (Metaxas et al., 2003).

The removal of Th(IV) ions from its sources is an economic and environmental task. Various physical and chemical techniques like, precipitation, coagulation, flotation, solvent extraction, and adsorption have been adopted by some researchers to perform the removal of thorium ions from water and wastewater (Bose et al., 2005; Sharma et al., 2011; Seader and Henley, 2006). Adsorption is a superior technique compared to other separation and pre-concentration techniques because of cost, simplicity, availability, and effectiveness (Donia et al., 2009). Chelating reagents are promising entities with many advantages, such as higher enrichment factors, lower consumption of reagents, flexibility, and more importantly environmental friendliness. A chelating reagent can be chemically bonded or impregnated onto support matrices, thus providing chelating solid phases (Demirel et al., 2003). In literature, several materials have been produced and used for the selective removal of thorium from aqueous media including, activated carbon (Kütahyal and Eral, 2010), silica (Dolatyari et al., 2015; Yousefi et al., 2009), clays (Guerra et al., 2009), chitosan (Anirudhan et al., 2010), graphene oxide (Jiang et al., 2015) and styrene-divinylbenzene (Ilaiyaraja et al., 2013).

Moreover, chelating resins with magnetic properties are important due to the ease of solid/liquid separation using an external magnetic field improving the recovery and separation process (Atta and Akl, 2015; Hritcu et al., 2012; Wu et al., 2013). Magnetic resins are prepared by coating ferromagnetic material and the size of beads may vary from hundred nanometers to few millimeters (Donia et al., 2009; Ngomsik et al., 2005).

The objective of this work was to studies recovery of Th(IV) ions from granite leach liquors using amino-magnetic glycidyl methacrylate resins. The adsorbents were synthesized from glycidyl methacrylate, magnetite particles, and divinylbenzene or *N*,*N*′-methylenebis(acrylamide) as cross-linkers. The adsorbents obtained were immobilized with tetraethylenepentamine (TEP) to provide the resins with the active

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sites required for the interaction with the targeted metal ions. The amino resins produced were used in the study of the recovery of Th(IV) ions from nitric acid solutions. The different experimental conditions were studied to evaluate kinetic and thermodynamic parameters. The findings of the basic research were applied to real ore samples containing thorium.

2. Experimental

2.1. Chemicals

Glycidyl methacrylate (GMA), divinylbenzene (DVB), benzoyl peroxide (Bz_2O_2), tetraethylenepentamine (TEP) and *N*,*N*′-methylenebis(acrylamide) (MBA) were Aldrich Products. Thorium nitrate pentahydrate, $Th(NO_3)_4.5H_2O$, was Merck product and was used as a source of Th(IV) ions. All other chemicals were Prolab products and were used as received. Table 1 presents the materials used and their chemical formula.

2.2. Synthesis of magnetite nanoparticles

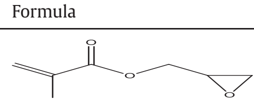
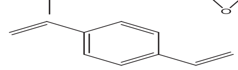
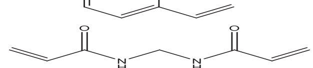
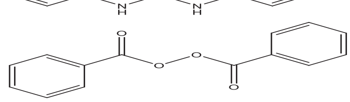
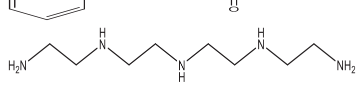
Chemical synthesis of colloidal magnetite has been reported since a long time ago by many authors (Wu and Gao, 2012; Lu et al., 2009; Sun et al., 2004). Nano-magnetite was prepared following the method proposed by Donia et al. (2009): A 0.2 M Fe(III) solution was added to 0.1 M Fe(II) solution followed by the addition of 200 mL ammonia solution (30%) poured to the previously prepared Fe(III)/Fe(II) solution with vigorous stirring. The precipitate was washed with deoxygenated water (water was boiled to repel any gasses then bubbled with nitrogen gas) under magnetic decantation until neutral pH.

2.3. Preparation of resins

Two resins composed of magnetite-GMA/DVB and magnetite-GMA/MBA were prepared through the suspension copolymerization of GMA with DVB or MBA as a cross-linker and Bz_2O_2 as an initiator in a suspension of nano-magnetite particles (Fe_3O_4) following the previously mentioned method (Donia et al., 2009). First, 0.1 g Bz_2O_2 (initiator) was added to the mixture of GMA/DVB or GMA/MBA (9.5:0.5 mol ratio) and mixed well until complete dissolution of Bz_2O_2, then Fe_2O_3 and diluent mixture(isopropyl alcohol/cyclohexane) were added to the solution. Finally, the former solution was added to 1% polyvinyl alcohol solution, point by point and refluxed at 70–80 °C for 4–6 h.

The resins obtained in the previous step were allowed to react with tetraethylenepentamine (TEP) to give the corresponding amine containing resins RI and RII with hydrophobic and hydrophilic properties, respectively. The products obtained were filtered and washed with distilled water, ethanol and dried in air.

Table 1
The materials used and their chemical formulae.

Chemical name	Formula
Glycidyl methacrylate (GMA)	
Divinylbenzene (DVB)	
N,N′-Methylenebis(acrylamide) (MBA)	
Benzoyl peroxide (Bz_2O_2)	
Tetraethylenepentamine (TEP)	
Thorium nitrate pentahydrate	$Th(NO_3)_4.5H_2O$

The synthetic routes of RI and RII are shown in Scheme 1. The characterization of the resins including IR and EDX were presented in detail in previous publications (Atia et al., 2008; Donia et al., 2009; Donia et al., 2013). The analyses proved the presence of resin-embedded magnetite particles and the immobilization of the resins with amine-active sites. The concentration of the surface-active amino sites was found to be 12.4 and 13.8 mmol g^{-1} for RI and RII, respectively. The higher active site concentration of RI and RII may indicate the formation of a porous extended polymeric film on the finely divided magnetite particles.

2.4. Adsorption measurements using the batch method

The effect of pH on the adsorption of Th(IV) ions was proved by placing portions of 0.02 g resin in a series of flasks. In each flask, 100 mL solutions of 0.65 mM Th(IV) ions was added and the pH was adjusted using NaOH and HNO_3 solutions. The flasks were shaken for 3 h at 25 °C. After equilibration, the residual concentration was quantified using Thoron I method (Marczenko, 1986). Metal ion concentration was determined using UV/VIS double beam spectrophotometer of the type LABOMED, INC (U.S.A.). Effect of temperature on adsorption process was studied in the temperature range 25–50 °C and at different initial Th(IV) ions concentrations. After equilibration, the residual concentration of metal ions was quantified to calculate the amount retained by resin.

The kinetics of the adsorption of Th(IV) ions on RI and RII were studied by placing portions of 0.02 g resin in a series of flasks with 100 mL of 0.65 mM Th(IV) ions. At different time intervals after equilibration, the residual concentration of the metal ions was determined and used in calculating the amount retained by resin. The effect of the solid/liquid (S/L) ratio was performed using 100 mL of Th(IV) solution at pH 3.7 and varying the amount of the resin in the range 0.02 to 0.1 g.

Experiments on real samples were conducted using three granite ore samples named G-1, G-2, and G-3. Each sample was digested with 2 M HNO_3 for 6 h. The obtained slurry was filtered, and washed with hot water. The filtrate produced was analyzed for Th(IV), U(VI) and total REEs using UV/VIS spectrophotometer. The filtrate was adjusted to pH 3.7 using NaOH and diluted HNO_3. The adsorption experiments were conducted using the batch method at S/L = 1 of RI and RII and the leach liquor was shaken for 90 min at 25 °C. After equilibration, the residual concentration of Th(IV), U(VI) and the total REE was analyzed and the amount adsorbed metal ions and the removal efficiency was calculated.

2.5. Adsorption measurements using column experiments

The experiments of adsorption of Th(IV) ions on RI and RII under flow conditions were carried out in a plastic column (length 3 cm and diameter 0.8 cm). A small piece of glass wool was placed at the bottom of the column and a specified quantity of the investigated resin was placed in the column to yield the desired bed height. A solution of 0.43 mM Th(IV) ions at pH 3.7 was allowed to flow downwards through the column at flow rates of 1, 2 and 3 mL min^{-1}.

To study the effect of the resin bed height on the uptake of Th(IV) ions, the column was packed with RI or RII resins to give bed heights of 1, 1.5 and 2 cm. The Th(IV) solutions at an initial concentration of 0.43 mM and pH 3.7 were allowed to flow downward at a flow rate of 1 mL min^{-1}. The experiment was terminated when the concentration of the metal ion at the outlet of the column was equal to its initial concentration.

3. Results and discussions

3.1. Effect of pH on batch adsorption process

Effect of pH is one of the most significant factors affecting the adsorption process because it controls the surface charge of the adsorbent