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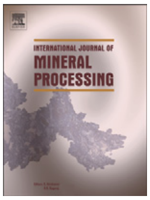

Selective separation of U(VI) from its solutions using amine modified silica gel produced from leached zircon

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ABSTRACT

A solution of sodium silicate produced from the alkali fusion of Egyptian zircon mineral as a waste was used to prepare silica gel in the pH range 6–7. The surface of the obtained silica was functionalized with diethylenetriamine (DET) and tetraethylenepentamine (TEP) to give triamine modified silica (TAMS) and pentamine modified silica (PAMS), respectively. The success of functionalization process was confirmed by means of FT-IR, energy dispersive X-ray analysis (EDX) and elemental analysis. The surface properties of the modified silica obtained were also investigated. The uptake behavior of the modified silica towards U(VI) ions at different experimental conditions of pH, time, concentration and temperature was studied. The maximum uptake values at 25 °C were found to be 90.3 and 112 mg/g for TAMS and PAMS, respectively. Kinetics and thermodynamics studies showed an endothermic pseudo-second order adsorption process. Regeneration of the loaded silica was performed using 1 M HNO_3. The investigated silicas have successfully been applied for extracting of U(VI) obtained from alkaline leaching of Egyptian monazite sand.

1. Introduction

Uranium mainly occurs in association with different rare earths. So its separation from them has always attracted the attention of researchers. The most used methods for separation and preconcentration of uranium include precipitation (Mellah et al., 2007), co-precipitation (Aydin and Soylak, 2007), solvent extraction (Agrawl et al., 2000), membrane dialysis (Kuhu, 1972), chromatographic extraction (Dietz et al., 2001), ion exchange (Ladeira, and Morais, 2005), flotation (Rao et al., 2006) and adsorption (Donia et al., 2009a; Jung et al., 2008). Most of these methods suffer from technical, economic and health problems related to selectivity, long time of extraction and large quantity of hazardous materials used.

Solid phase extraction (SPE) has commonly been used as a technique for preconcentration/separation of various inorganic and organic species. This technique has advantages of higher enrichment factor, absence of emulsion, safety with respect to hazardous samples, minimal costs due to low consumption of reagent, environment friendly, flexibility and easier incorporation into automated analytical techniques (Chen et al., 2006; Zaporozhets et al., 1999). A number of sorbents such as polymeric resins, activated carbon, naphthalene and silica gel etc. … have been developed for effective extraction. However, some of them suffer from a number of drawbacks such as long preconcentration time, low mechanical stability, slow kinetics, irreversible adsorption and swelling (Dev et al., 1999; Santos and Airoldi, 1996; Jal et al., 2001). So, there is still a need for developing good and commercial extractants for metal ion separation in the hydrometallurgical industries.

Silica gel is an amorphous inorganic support which has an ability to react with organosilyl compounds, giving organosilyl silica intermediates (Sylwester et al., 2000; Yousefi et al., 2009). These intermediates in role react with different organic species to give the modified silica precursors (Metilda et al., 2005; Jamali et al., 2006). Recently, a number of silica gel sorbents functionalized with chelating ligands were used for selective extraction of U(VI) from various matrix components (Dev et al., 1999; Santos and Airoldi, 1996; Jal et al., 2001; Venkatesan et al., 2004).

In this study a low-cost silica gel was obtained from sodium silicate solution produced from leaching of zircon during the extraction of zirconium and hafnium from zircon mineral. The silica obtained was analyzed and subjected to surface modification by 3,3-glycidoxypropyltrimethylsilane (GPS) and functionalized with different polyaliphatic amines with different chain length and amino group content. The adsorption behavior of the modified silicas towards U(VI) will be studied at different experimental conditions. The effect of amine type on the kinetics of the adsorption process as well as the maximum adsorption capacity will be also investigated. Finally, the application of the modified silicas for selective separation of U(VI) from Th(IV) in real sample of Egyptian monazite sand will be demonstrated.

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2. Experimental

2.1. Materials

Sodium silicate was obtained as a by-product through leaching of zircon. 3,3-glycidoxypropyltrimethylsilane (GPS) was purchased from Fluka, Italy; diethylenetriamine (DET), tetraethylenepentamine (TEP), and Arsenazo III were from Sigma-Aldrich Chemical Co., Germany; $UO_2(NO_3)_2 \cdot 6H_2O$ was used as a source for U(VI). All other chemicals were ADWIC products, Egypt.

2.2. Preparation of silica gel

A sample of 250 g of zircon concentrate was mixed with 312 g of sodium hydroxide and fed to the electric furnace for 2 h at 650 °C. The fusion product was mixed with distilled water and stirred for 2 h at 60 °C to dissolve the formed water soluble sodium silicate (Daher, and Mohammed, 2002; Abdelkader et al., 2008).

A 25 mL of solution obtained in the above step was diluted up to 100 mL using 1 M HNO_3. The pH of the solution was adjusted in the range of 6–7 using ammonia solution. The mixture was stirred vigorously for 30 min at room temperature where silica gel was precipitated (Munoz-Aguado and Gerorkiewitz, 1997). The precipitate was filtered off, washed with water and ethanol and then dried at 50 °C.

2.3. Modification of silica surface

Glycidoxy modified silica (GMS) was prepared by reaction of silica gel with GPS. 2 mL of GPS was dissolved in 100 mL of distilled water acidified with acetic acid (pH 4). 2 g of activated silica gel (dried in an oven at 150 °C for 18 h) was added to the silane solution and stirred for 2 h at room temperature. The product was filtered off and kept in an oven at 120 °C for 4 h at room temperature. The dried product was washed repeatedly with water, ethanol, and acetone several times for removal of unreacted materials and then dried in the oven at 120 °C for another 2 h (Donia et al., 2009a; Atia et al., 2009; Newalkar and Komarneni, 2000).

Pentamine (PAMS) and triamine (TAMS) modified silicas were prepared as follows: 1 g of the epoxy modified silica obtained in the previous step was treated by 4 mL of TEP or DET dissolved in 12 mL dimethylformamide (DMF) and heated for 72 h at 75–80 °C in an oil bath. The products were then filtered off, washed repeatedly with distilled water, ethanol and dried in air (Donia et al., 2009b; Atia et al., 2009; Newalkar and Komarneni, 2000).

2.4. Characterization of the adsorbents

BET surface area, BJH pore volume and average pore diameter was of the original silica and its modified forms were measured at 77 ± 1 K by a Quanta chrome NOVA automated gas sorption system using nitrogen as the adsorbate. All measurements were taken after heating the samples up to 403 K and evacuation at a pressure of 10^{-4} Torr for 4 h. FT-IR measurements were performed in KBr disks using Nexeus-Nicolite-640-MSA FTIR. Energy dispersive X-ray measurements were measured using Environmental Scanning Electron Microscope (ESEM) EXL 130 attached by energy dispersive spectrometry (EDX) unit system. Elemental analysis was carried out using Perkin Elmer 2400 CHN elemental analyzer.

2.5. Uptake experiments

2.5.1. Preparation of metal ion solutions

Freshly prepared synthetic stock solution of 1000 mg/L of U(VI) was prepared by dissolving 2.11 g of uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ in 1 L of 0.05 M HNO_3.

A study of Egyptian monazite ore samples from Rosetta has been made by the Nuclear Material Authority of Egypt. The natural sample of uranyl nitrate was obtained from the Egyptian Rosetta monazite concentrate. Egyptian monazite (purity 97%) has been analyzed and was found to assay 5.9% ThO_2, 0.44% U_3O_8 and 61.9 rare earths (RE_2O_3). Firstly, monazite was leached with hot concentrated caustic soda. The hydrous oxide concentrate obtained from alkaline processing of monazite is leached with hot hydrochloric acid at 80 °C, and then diluted with water. The separation of thorium and uranium from REES is carried out by selective neutralization of solutions with ammonia solution up to pH = 5.8–6 (Lothongkum et al., 2009; Desouky et al., 2009). Thorium–uranium cake obtained from the hydrous oxide cake concentrate free from REES and iron was dissolved in 4 M HNO_3 to produce uranyl nitrate and thorium nitrate solution which was used in the extraction studies.

2.5.2. Adsorption studies

Uptake of U(VI) at different time intervals was done by placing portions of 0.025 g of PAMS or TAMS in a series of flasks containing 50 mL of U(VI) at initial concentration of 150 mg/L. The contents of the flasks were shaked on a Vibromatic-384 shaker at 300 rpm and at 25, 30 and 40 °C. 5 mL of the solution of each flask was taken at different time intervals and then filtered off. The residual concentration of U(VI) was determined and the uptake was calculated using the following equation:

$$q = \frac{(C_i - C_f)V}{W} \qquad (1)$$

where q is the uptake (mg/g), C_i and C_f are the initial and final concentrations of metal ion (mg/L), V is the volume (L) and W is the weight of the resin (g).

Uptake experiments under controlled pH were carried out following the above procedures and keeping the equilibrating time at 2 h for PAMS and TAMS in the pH range 3–6. Nitric acid was used to study the uptake in acidic media whereas ammonia solution was used to study the uptake at alkaline media.

The effect of U(VI) concentration on the adsorption on PAMS and TAMS was carried out at 25, 30, 35 and 40 °C by placing portions of 0.025 g of modified silicas in a series of flasks containing 50 mL of metal ion solution at desired concentration and pH. The flasks were equilibrated at 300 rpm for 2 h. Later on, the residual concentration was determined where the U(VI) uptake was calculated.

2.5.3. Elution experiment

Elution experiments were performed by placing 0.1 g of PAMS or TAMS in a column with width of 0.4 cm and length of 5 cm then loaded with U(VI) ions at flow rate of 1 mL/min. The maximum uptake was reached in the first run, thereafter the adsorbent was washed carefully by flowing distilled water through the column. The resin loaded by U(VI) was then subjected for elution using 1 M HNO_3. After treating the adsorbent with the eluent, it was carefully washed with distilled water to become ready for reuse for the second run of uptake.

3. Results and discussion

3.1. Materials characterization

The silanol ($\equiv$Si – OH) groups on the silica surface play an important role in the surface modification by forming covalent bonds with GPS in a very slow condensation reaction (Donia et al., 2009a; Atia et al., 2009) The synthesis routes of PAMS and TAMS are shown in Schemes 1 and 2. The characteristics of the modified silica obtained were investigated by means of FT-IR and TGA measurements as shown in Fig. 1. FT-IR spectrum of the free silica displays a number of characteristic bands at 3442 (broad), 1079 (vs), 954 (m) and