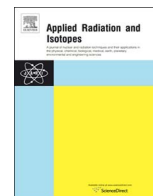




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Retention of barium and europium radionuclides from aqueous solutions on ash-based sorbents by application of radiochemical techniques

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HIGHLIGHTS

- Conversion of plant ash to zeolitic structure materials which can be used as sorbents in the nuclear waste management.
- Characterization of the new materials by several techniques (XRD, TGA, BET).
- Study of parameters influencing the Ba and Eu-sorption using γ -ray spectroscopy.
- The new sorbents exhibited good uptake capacity in Ba and Eu-sorption and low leachability.
- The process is physical sorption, spontaneous and endothermic in nature.

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ABSTRACT

New materials were synthesized for application in sorption of radionuclides from aqueous solutions. The elaboration was performed by conversion of power plant ash using the hydrothermal method under optimum experimental conditions. Sodalite, Na-Y, and analcime were formed from ash precursor during the treatment, exhibiting thermal stability as revealed by the characterization by X-ray diffraction (XRD) and thermogravimetric differential thermal analysis (TG-DTA). The Brunauer–Emmett–Teller (BET) surface area and pore volume were determined and they presented higher values than plant ash. The ability of the new products to retain Ba and Eu radionuclides was studied in aqueous solutions using ^{133}Ba and ^{152}Eu as tracers and γ -ray spectroscopy under batch experiments. The experimental data were modeled by the Langmuir and Freundlich equations, whereas sorption kinetics measurements were performed at 293, 308, and 323 K and thermodynamic parameters were calculated. The release of the sorbed ions into the environment was also tested by leaching experiments. The results of these tests indicated that the synthesized materials are very efficient in removing the aforementioned metals from aqueous solutions and can be considered as potential low-cost sorbents in nuclear waste management.

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1. Introduction

Recently, various techniques such as adsorption, precipitation, and ion exchange have been applied in radioactive waste management to test new materials. Among these materials (inorganic ion exchangers, clays and zeolites, ash-based sorbents) natural and synthetic zeolites are particularly preferred, because they are very effective sorbents. Zeolites are microporous materials widely used

as molecular sieves in environment remediation, radioactive waste, and industrial applications for selective adsorption of positively charged contaminant species (Misaelides, 2011). Their ion exchange capacity is rather high depending on the Si/Al framework ratio, which ranges between 1 and 3.

Zeolites can be synthesized from power station ashes, as the chemical composition of ash shows similarities to some volcanic precursors of natural zeolites (Gross et al., 2007; Gupta et al., 2009; Reijnders, 2005; Wang and Wu, 2006; Wdowin et al., 2014).

At present, the effective utilization and conversion of ash to other materials is an economic and environment-friendly solution

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considering the large quantities of ash (more than 600 Mt), which are worldwide produced every year, creating a disposal problem (Ahmaruzzaman, 2010; Bhangare et al., 2014; Wang and Wu, 2006). Therefore, the modification of ashes and their potential application as sorbents for the removal of hazardous species from waters, wastewaters, soils, and especially radionuclides has attracted increased research interest recently (Buema et al., 2014; El-Naggar et al., 2008; Noli et al., 2015; Penilla et al., 2006).

Various types of zeolites (e.g., A-, P-, and N-type zeolites, sodalite, and faujasite) have been produced depending on the chemical composition of ashes and other parameters such as temperature, concentration of alkaline reagent, reaction time, and solid-to-liquid ratio (Adamczyk and Bialecka, 2005; Ryu et al., 2006).

For example, high-quality zeolites X were synthesized from ash by Fan et al. (2008) using high reaction temperatures and crystallization times (temperature and time up to 550 °C and 26 h, respectively). K-H zeolite ($K_2Al_2Si_4O_{12} \cdot nH_2O$) was successfully produced by Mimura et al. (2001) under optimum conditions (temperature: 160 °C, time: 3 days), whereas Gross et al. (2007) reported the formation of faujasite from fly ash selecting lower synthesis temperatures (50 °C) but longer time (up to 100 days).

The objective of this study was to convert ash to zeolitic materials using a simple and low-cost method for application in nuclear waste management for the removal of Ba and Eu. The retention of barium and europium is of special importance, because Ba is an ideal analog of Ra, which is also important in radioactive waste considerations, and presents high mobility in the geosphere and thus gains more access to the food chain (Toxicological Profile for Barium, 2007; Baeza-Alvarado and Olguín, 2011; Chavez et al., 2010; Chmielewska-Horváthová, 1998; Zhang et al., 2001; Shihwan et al., 2002). On the contrary, Eu is connected with the nuclear fuel cycle and is frequently used as natural homolog of the trivalent actinides (e.g., Am and Cm) (El-Kamash et al., 2007; Moussa et al., 2013; Naveau et al., 2005; Shao et al., 2009; Sharma and Tomar, 2011; Sun et al., 2014; Wenming et al., 2001). The number of studies investigating the sorption of these metals is rather limited in the literature.

The new sorbents were synthesized by selecting optimum experimental conditions, and their characterization was performed by various techniques. The Eu and Ba sorption properties of the synthesized materials were investigated using radiochemical techniques, and modeling and kinetics data were obtained.

2. Experimental

2.1. Materials Synthesis

Ash from a Romanian thermal power plant was used for the synthesis of the new sorbents. The whole procedure was carried out by the direct activation method using 5 M NaOH at temperatures of 70 and 90 °C. Our previous studies have shown that increase of temperature, treatment time, or quantity of the alkali results in the formation of materials with different properties (composition in zeolites, porosity, surface area). High NaOH concentration (5 M) and reaction temperature (90 °C) lead to crystallization of zeolites (10–11). Hence, the following experimental conditions were selected for this study: (i) solid-to-liquid (S:L) ratio, 1:5 and 1:3, respectively; (ii) concentration of NaOH, 5 M; (iii) temperature, 70 and 90 °C; and (iv) reaction time, 4 and 15 h. After the treatment, the synthesized materials were annealed for 18 h at ambient temperature, filtered, washed, and dried.

2.2. Materials characterization

The surface microstructure and chemical composition of the raw material (ash) and the synthesized materials were investigated by scanning electron microscopy–energy dispersive spectrometry (SEM–EDS) using a JEOL JSM 840A microscope equipped with an OXFORD ISIS 300 EDS microanalyzer and QUANTA 3D – AL99/D8229. The mineralogical composition of the materials was investigated by X-ray diffraction (XRD) using an X'PERT PRO MRD equipment. Thermogravimetric analysis (TGA) was applied using the SETA-RAM SetSys-1200 model in N₂ atmosphere, whereas the porosity and specific surface area were measured by the Brunauer–Emmett–Teller (BET) method using an Autosorb 1-MP gas sorption system (Quantachrome Instruments). Nitrogen sorption was carried out at –196 °C, and the samples were degassed under high vacuum at 350 °C for 3 h before analysis.

The zeta potential of the materials was determined using a Brookhaven ZetaPALS instrument (Brookhaven Instruments Corporation, Brookhaven, Holtsville, NY, USA). Very dilute suspensions (5 mg mL^{–1}) of the material in ultrapure water were prepared. The pH was adjusted by adding NaOH or HNO₃ solutions. After achieving equilibrium, the samples were measured at 25 °C, using a refractive index 1.330 for the aqueous phase and a viscosity of 890 cP.

2.3. Sorption experiments

The sorption experiments were conducted by adding approximately 50 mg of the sorbents in 10 mL of the solution of the elements under investigation in polypropylene tubes. The quantity of each sorbent was weighted using a balance KERN 770 ($d=0.01$ mg) and the volume of the solution was measured using an Eppendorf pipette. The samples were agitated at ambient temperature for 24 h. Therefore, in order to optimize the pH for maximum sorption efficiency, experiments have been conducted in the pH range of 2–7 for an equilibration time of 5 h. Stock solutions of BaCl₂ spiked with ¹³³Ba (1.4 Bq/mL) and Eu(NO₃)₃ · H₂O spiked with ¹⁵²Eu (2.1 Bq/mL) with initial concentration between 10 and 1000 mg/L were prepared using analytical grade reagents dissolved in bi-distilled water. Before the sorption experiments, the pH of the solutions was adjusted by adding HCl and NaOH. After separation of the solid from the liquid phase by centrifugation and filtration (0.22- μ m filter), the equilibrium pH was measured by a Metron pH meter (± 0.1) and the element concentration in the liquid phase was determined. The Ba and Eu concentrations in the supernatant solution were determined by γ -ray spectroscopy using a HPGe detector (CANBERRA, REGe detector, efficiency 20%, energy resolution 2.1 keV for the 1332-keV ⁶⁰Co γ radiation) connected with a standard computer-based gamma spectroscopy setup. A small amount (5 mL) of the solution was placed in vials of standard geometry and measured after measuring the blank (labeled solution without sorbent). The counting time varied between 700 and 1000 s to obtain good statistics resulting in activities from 0.88 up to 1.59 counts per second. The overall uncertainty of the measurements was estimated to be 5–7%.

Further experiments concerning the influence of competing cations on the sorption capacity (the presence of background electrolyte 0.1 M NaNO₃), as well as sorption kinetics, were conducted using the most effective sorbent. The kinetics experiments were performed at 298, 308, and 323 (± 0.5) K and the data were modeled using the pseudo-first- and pseudo-second-order kinetic equations (Fan et al., 2008). For the kinetics measurements, 1.25 g of the adsorbent was contacted with 250 mL of the labeled solution of experimental conditions: solution concentration 250 mg/L

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