



Research paper

Vermiculite as a potential component of the engineered barriers in low- and medium-level radioactive waste repositories

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ABSTRACT

Vermiculite (VMT) was tested as a low-cost, eco-friendly adsorbent for the removal of cesium(I), strontium(II), europium(III), americium(III), and technetium(VII) radionuclides from aqueous solutions. The raw material was characterized and checked as potential adsorbent. The removal efficiency (E_r , %) was studied as a function of the main factors important for the management of radioactive liquid wastes. It was found that the uptake from the aqueous solutions simulating the radioactive liquid wastes was in the order: Cs(I) - Sr(II) (both about 95%) > Am(III) (about 90%) > Eu(III) (about 80%). When a reducing agent is added to the solution technetium-99 may also be completely removed. The usefulness of VMT in liquid low level radioactive waste management has also been confirmed by checking its radiation stability. Vermiculite can be considered as a promising material for sorption of the radionuclides from radioactive waste solutions and as a potential additive to the engineered barriers in LLRW repositories.

1. Introduction

An increase in the demand for using ionizing radiation and radioactive materials in science, medicine, agriculture, and industry applications has generated a continuously growing amount of radioactive waste. These wastes appear in different physical and chemical forms and contain a wide range of concentrations of radioactive materials. A special problem form low and medium level liquid radioactive wastes (LLRW and MLRW, respectively) because of their large volumes. The high possibility of releasing the radionuclides into different aqueous streams may have adverse effects on the environment, and as a consequence, the health of humans and animals. Therefore safe radioactive waste management has received much attention world-wide.

In Poland, LLRW and MLRW are produced by the research reactor Maria, during the research activities of different scientific laboratories and nuclear medicine clinics, as well as in various industrial processes. In particular, during 2016 the National Radioactive Waste Repository (NRWR, Rozan, Poland) collected about 50 cubic meters of radioactive waste, about 40% being liquid (Polish National Atomic Energy Agency, 2017). In separate studies, it has been found that obtained from the NRWR samples of the liquid wastes (LRW) contain mainly the radioactive metals: ^{137}Cs (587 Bq/L), ^{125}Sb (362 Bq/L), ^{106}Ru (149 Bq/L), ^{60}Co (119 Bq/L), ^{51}Cr (102 Bq/L), ^{134}Cs (12 Bq/L), ^{65}Zn (11), ^{54}Mn (5 Bq/L). Apart from the radionuclides, weighted amounts of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- and NO_3^- have been found, as well as other

cations in the ppb quantity.

In accordance with present regulations, it is prohibited to dilute such liquid radioactive wastes in order to reduce their radioactivity below the levels required to permit their release into the environment.

Currently, search for the novel cost-effective, easy to use and safe methods for elimination of the heavy/radioactive metals from contaminated aqueous samples has intensified considerably. Till now, a great number of physico-chemical techniques have been tested. Among others, one should mention solvent extraction (Onghena et al., 2017), reduction (Majidnia and Fulazzaky, 2017), chemical precipitation (Volkovich et al., 2003), membrane filtration (Hwang et al., 2002), immobilization (El-Kamash et al., 2006) or vacuum membrane distillation (Jia et al., 2017). In addition to these methods, technology based on sorption may be counted as prospective alternative technique. For this purpose, a great number of highly efficient inorganic and organic sorbents have been synthesized. As well as these synthetic sorbents, the removal of metal ions from aqueous media by utilizing different natural sorbent materials or agricultural and industrial wastes has been studied. Examples include: activated carbons (Chegrouche et al., 2009) and carbon nano tubes (Vipin et al., 2014), zeolites (Munthali et al., 2015), hydroxyapatite (Smičiklas et al., 2005), manganese antimonate (Zhang et al., 2016), dolomite powder (Ghaemi et al., 2011), etc. In addition, such biosorbents have been tested as: yeasts (Liu et al., 2016) (Asztemborska et al., 2016), mosses (Marešová et al., 2011), bacteria (Chaalal et al., 2015) or roots of plants (Fuks

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et al., 2016).

Vermiculite (VMT) is a relatively inexpensive, easily available and environmentally friendly clay which contains a small amount of crystalline silica in the form of quartz, as confirmed by XRD analysis (Malandrino et al., 2006), and resembles mica or talc in appearance. World reserves of VMT are large, and the annual need for this material is in the region of tens of thousands of tons. Its well-known applications include construction, horticulture, and agriculture. Of special interest is its usage for adsorptive separation and purification of chemical substances in petrochemical, gas, food, pharmaceutical, and chemical industries.

Vermiculite, a 2:1 sheet aluminosilicate, is composed of two flat layers of silica and alumina tetrahedra (being the tetrahedral sheets) sandwiching a layer composed of apical oxygen atoms together with magnesium or iron atoms and hydroxyl groups (the octahedral structured sheet). Substitution of the Al^{3+} cation for Si^{4+} in tetrahedral sheets, accompanied by Al^{3+} and/or Fe^{3+} substitution for Mg^{2+} in octahedral sheets, results in a negative charge of the aluminosilicate structure. Simultaneously, because of its large surface area and numerous reactive surface sites, VMT has high ability for adsorption of cations (Liu et al., 2010). As a result, vermiculite is suspected to be a promising ion-exchanger for metal ions present in aqueous solutions.

In the literature may be found different chemical formulae, but one of the most popular is $(Na_{0.21}, K_{0.39}, Mg_{0.19}, Ca_{0.13}, 6H_2O)(Mg_5, Fe_{0.2}^{+2}, Fe_{0.8}^{+3})(Si_{5.5}, Al_{2.5}, O_{20})(OH)_4$. The first bracket represents the ion-exchangeable layer, and the components in the second one describe the cations of the octahedral sheet. Finally, the components within the curly brackets are those of the tetrahedral sheet (The Vermiculite Association, 2017).

Working within the framework of other present work, the aim was to study sorption of the model radionuclides, namely cesium(I), strontium(II), europium(III), and americium(III), from aqueous solutions onto the natural inorganic ion-exchanger, vermiculite (VMT). All of the aforementioned radionuclides have been shown to be present in real-world radioactive wastes (Kerrisk, 1985). From an abstract point of view, assessing the sorption ratios of such radionuclides may give more information on the role of ionic charge and atomic radii in the adsorption of these metals. In turn, from the practical point of view our studies will allow us to check the possibility of applying vermiculite as a novel additive material for constructing engineered barriers in radioactive waste repositories.

The use of vermiculite in wastewater treatment has been studied in recent years and experimental results have shown that this material may be a suitable adsorbent for the removal of heavy metals from wastewaters. Checking existing literature for the VMT sorption within the SCOPUS bibliographic database has indicated the existence of about 200 papers published during last 25 years describing their use for the sorption of anions, cations, and also organic dyes. Although this number is not so remarkable when compared to the over 3200 papers published on zeolite sorption over an analogous period. Among the papers dealing with VMT sorption there are only a few dedicated to the problem of adsorption of the radioactive matter. None of them are concerned with the application of this material as potential mitigator for the engineering barriers in radioactive waste management.

In the presented work, adsorption of mono-, di-, and trivalent metals onto VMT has been studied with respect to phase contact time, the acidity of the decontaminated solution, and adsorbent dosage. The impact of competitively chelating agents on the adsorption process was also studied. In addition, the properties of VMT have been examined by SEM, and by determining its zeta potential. FT-IR spectra have been recorded in order to check the radiation stability of the adsorbent.

2. Experimental

2.1. Chemicals

Vermiculite (VMT) was donated by Vermiculite Poland, Ltd. (city Elk, Poland). According to the certificate of analysis provided by the Polish Center for Research and certification the chemical composition of the material is: SiO_2 : 35.0–41.0%; MgO : 14.5–20.5%; Al_2O_3 : 6.0–11.5%; Fe_2O_3 : 6.0–9.5%; K_2O : 3.0–6.0%; P_2O_5 : 0.20–2.0%; CaO : 1.0–4.0%; Mn_2O_3 : 0.05–0.08%; TiO_2 : 0.6–1.4%; Cr_2O_3 : 0.01–0.15%; Cl : 0.0–0.5%; CO_2 : 0.6–2.5%; F : 0.1–0.5%. The hardness of the material is 2–3 Mohs and the mineral density - 2.4–2.7 g/cm³ (Web 1, 2015). Before the experiments were started, the VMT raw material (mean particle size: 0.5 mm) was ground and mechanically homogenized using a 3D-rotating drum.

All chemicals used in the work were of analytical grade purity and used without further purification. They were obtained from Sigma-Aldrich Chem. Co.

In all experiments, deionized water was used.

The carrier-free radionuclides of cesium-137 (radioactive half life - $t_{1/2} = 30.07$ y; energy of emitted radiation - $E_\gamma = 661.7$ keV), strontium-85 ($t_{1/2} = 64.8$ d; $E_\gamma = 514$ keV), europium-152 ($t_{1/2} = 13.5$ y; $E_\gamma = 344.3$ keV), and americium-241 ($t_{1/2} = 432.2$ y; $E_\gamma = 59.5$ keV) were supplied by POLATOM (Otwock-Swierk, Poland) as certificated standard solutions. $Na^{99m}TcO_4$ in 0.9% saline solution (ca 100 MBq cm⁻³) was eluted from a $^{99}Mo/^{99m}Tc$ commercial generator (GE Healthcare, supplied by Biker, Warsaw, Poland). Aqueous solutions of the desired radionuclide concentrations were prepared by gravimetric dilution of these radionuclide standards with 10⁻³ M nitric acid prior to checking their purity by gamma spectrometry.

2.2. Activation of the VMT

The first and second methods of activation of the ground VMT used (10 min; 800–1000 rpm) were adaptations of those proposed by Chmielarz et al. (2010) and by Wypych et al. (2005), respectively. In both variants the VMT clay samples were washed with distilled water and dried for 6 h at a temperature of 80 °C prior to carrying out the appropriate activation procedure.

The first method consisted of the following processes: the 20 g VMT samples were homogenized by stirring with 200 mL of 0.8 M nitric acid at 95 °C overnight. The VMT adsorbent was then filtered, washed with distilled water, and separated into two portions. The first was dried at 80 °C for 12 h, while the second was calcined by heating 600 °C for 6 h.

In the second procedure, two 10 g VMT samples were reacted twice in one day with consecutive 150 mL portions of 2 M hydrochloric acid at 80 °C. Finally, the filtered adsorbent was washed with distilled water and the drying/calcination processes were done in the same way as above.

2.3. Adsorption of the radionuclides

Adsorption properties of the vermiculite (VMT) were studied with respect to all parameters important for liquid radioactive waste management: contact time, acidity of the solution, mass of the adsorbent, and initial concentration of the radionuclides. All tests were carried out at room temperature. An initial aqueous solution containing four radionuclides in nca¹ concentrations was prepared by gravimetric dilution of the radionuclide standards with nitric acid prior to checking their purity by gamma spectrometry. The pH value of the initial solution was determined to be about 3.0. If a different pH value of the

¹ No-carrier added (nca) radioisotope: a quantity of the radionuclide, which is substantially free of the stable isotopes of the element in question, i.e. below than in the weight amount (de Goeij and Bonardi, 2005)

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