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Research paper

Adsorptive removal of $^{134}Cs^{+}$, $^{60}Co^{2+}$ and $^{152+154}Eu^{3+}$ radionuclides from aqueous solutions using sepiolite: Single and multi-component systems

Mamdoh R. Mahmoud [a],*, Ghada M. Rashad [a], Essam Metwally [a], Ebtissam A. Saad [b], Ahmed M. Elewa [a]

[a] Nuclear Chemistry Department, Hot Laboratories Center, Atomic Energy Authority, P.O. Box 13759, Inshas, Cairo, Egypt
[b] Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

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ABSTRACT

Single and multi-component adsorptive removal of $^{134}Cs^{+}$, $^{60}Co^{2+}$ and $^{152+154}Eu^{3+}$ from aqueous solutions onto sepiolite are studied in the present study. Removal of these radionuclides in single systems is found to be strongly dependent on the initial pH on the solution. Removals >99% (for $^{60}Co^{2+}$ and $^{152+154}Eu^{3+}$) and of about 82% (for $^{134}Cs^{+}$) are achieved at initial pH values higher than 4 and 5, respectively. The kinetic data and the equilibrium isotherms are modeled by two kinetic models, the pseudo-first-order and the pseudo-second-order, and two isotherm models, Langmuir and Freundlich, respectively. The effect of various coexisting cations, Na^{+}, Ca^{2+} and Al^{3+}, at different concentrations on the adsorption processes of the concerned radionuclides in single systems was evaluated. Desorption studies of radionuclide-loaded sepiolite are studied using different concentrations of organic, EDTA and HA (strong complexing agents for radionuclides), and inorganic, HCl, NaCl, $CaCl_2$, $Mg(NO_3)_2$ and $AlCl_3$, desorbing agents. Adsorption mechanisms of radionuclides onto sepiolite are deeply discussed. Multi-component adsorptive removal of $^{134}Cs^{+}$, $^{60}Co^{2+}$ and $^{152+154}Eu^{3+}$ onto sepiolite as a function of adsorbent weight and time was also studied. The influence of the solution pH on co-removal efficiency of radionuclides was investigated in presence of EDTA. Furthermore, the present investigation evaluated the removal efficiency of radionuclides, in multi-systems, in presence of different concentrations either of NaCl or $CaCl_2$.

1. Introduction

The application of radionuclides in medicine, industry, agriculture and research generates large volumes of radioactive wastewaters which have dangerous effects on the environment. The radionuclides $^{134}Cs^{+}$, $^{60}Co^{2+}$ and $^{152+154}Eu^{3+}$ are commonly present in radioactive wastewaters. Owing to their relatively long half-lives (2.06, 5.27, 8.59 and 13.54 for $^{134}Cs^{+}$, $^{60}Co^{2+}$, $^{154}Eu^{3+}$ and $^{152}Eu^{3+}$, respectively) as well as their radiotoxicity, these radionuclides must be removed from radioactive wastes for safe discharge. The traditional chemical and physical methods used for removing radionuclides from aqueous solutions include chemical precipitation, evaporation, solvent extraction, foam separation, membrane separation and adsorption. However, most of these technologies have some disadvantages such as generation of toxic byproduct, generation of high volumes of sludge or solid wastes, low efficiency, time consuming and high energy requirements (Yu et al., 2016; Uzal et al., 2011; Zhu et al., 2014). Alternatively, adsorption is considered the most efficient and extensively used technique for treatment of radioactive wastewater due to its simplicity and efficiency (El Afifi et al., 2016; Zhu et al., 2016; Metwally and Ayoub, 2016; Sun et al., 2014). In the last decades, clay minerals have been widely utilized as adsorbents for the removal of radionuclides from aqueous solutions due to their low cost, availability and high efficiency (Hongxia et al., 2016; Reinoso-Maset and Ly, 2016; Yu et al., 2015; Zong et al., 2015; Sun et al., 2014; Fan et al., 2009).

Sepiolite, a natural clay mineral, is a hydrated magnesium silicate with the unit cell formula of $Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4(H_2O)_8$ (Bergaya et al., 2006). Unlike other layer silicate, sepiolite has not continuous octahedral sheets. Structurally, it contains ribbons of a 2:1 phyllosilicates. One ribbon is linked to the next by inversion of SiO_4 tetrahedral along a set of Si-O-Si bonds (Sparks, 2003). Each structure block of sepiolite is composed of two tetrahedral silica sheets sandwiching a central sheet of magnesium oxide-hydride. Due to the discontinuity of octahedral sheet, oxygen atoms in the octahedral at the edge of the ribbons are coordinated to cations on the ribbon side only, while coordination and charge balance are completed along the channels by protons, coordinated waters and a small number of exchangeable cations (Bergaya et al., 2006). In addition to the exchangeable cations (Ca and Mg), the channels of sepiolite contain two types of water: bound water (molecules coordinating Mg atoms at the broken bond surfaces of the channels) and zeolitic water (clusters filling the empty space in the channels and

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* Corresponding author.
E-mail address: mamdohrefaat@yahoo.com (M.R. Mahmoud).

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hydrogen-bonded to the bound water) (Santos and Boaventura, 2016). Its unique fibrous structure with interior channels allows incorporation of organic and inorganic ions into the structure of sepiolite. The extraordinary performance on the flame resistance, barrier properties, mechanical properties and thermal stability of sepiolite make it valuable clay for innumerable applications and draw the attention of researchers in recent years (Kara et al., 2016). In the field of wastewater treatment, many publications are reported on the use of natural and modified sepiolite as adsorbents for organic and inorganic pollutants (Kara et al., 2016; Santos and Boaventura, 2016; Yu et al., 2016; Duman et al., 2015; Fu et al., 2015; Huang et al., 2015; Cobas et al., 2014). From the economic point of view, natural sepiolite is considered to be better than modified one for treatment of wastewaters. According to our literature survey, few publications are reported on the removal of radionuclides by adsorption onto sepiolite. Furthermore, none of the published papers have applied sepiolite for multi-component adsorption process. Therefore, single and multi-component adsorptive removal of $^{134}Cs^{+}$, $^{60}Co^{2+}$ and $^{152+154}Eu^{3+}$ from aqueous solutions using sepiolite as adsorbent in the main purpose of this study. These radionuclides are selected on the basis that; (i) they have relatively long half-lives and high energy (all are gamma-emitters) as well as their radiotoxicity; (ii) they are representative of a wide range of chemical properties by including the alkali metal Cs, the transition metal Co and the rare earth metal Eu; and (iii) they are exemplify of monovalent, bivalent and trivalent cationic radionuclides.

2. Experimental

2.1. Materials and reagents

Sepiolite, employed as an adsorbent in this study, was purchased from Merck and was used as received without any purification or sieving. The chemical analysis of sepiolite, using X-Ray fluorescence (Axios, sequential WD-XRF spectrophotometer, PANanalytical 2005), showed that it is mainly composed of 71.55% SiO_2, 18.62% MgO, 3.08% Fe_2O_3, 2.74% Al_2O_3, 1.81% K_2O and 0.92% CaO.

Stock solutions of Cs^{+}, Co^{2+} and Eu^{3+} (0.05 M of each) were prepared from CsCl (Sigma-Aldrich, 99.99% purity), $CoCl_2.6H_2O$ (Fluka) and Eu_2O_3 (Merck, 99.99% purity), respectively. Stock solutions of Cs^{+} and Co^{2+} were prepared by dissolving their salts in distilled water, while Eu^{3+} stock solution was prepared by dissolving its oxide in 10 mL conc. HCl, then the solution was heated till complete evaporation and the residual solid was dissolved in acidified water. The working solutions were prepared by diluting the stock solutions with distilled water to appropriate volumes. Sodium hydroxide and hydrochloric acid (provided by Merck) solutions were used for adjustment of the pH of these solutions. Solutions of the irradiated CsCl, $CoCl_2.6H_2O$ and Eu_2O_3 in Egypt Second Research Reactor were prepared by the same procedures followed for preparation of their carrier solutions and were used as sources of $^{134}Cs^{+}$, $^{60}Co^{2+}$ and $^{152+154}Eu^{3+}$ radiotracers, respectively.

The organic reagents, ethylenediaminetetraacetic acid disodium salt (Na_2EDTA, Riedel- de Haen) and humic acid (HA, Sigma-Aldrich), as well as the inorganic ones, NaCl (Chem-Lab), $CaCl_2 \cdot 2H_2O$ (Panreac), Mg $(NO_3)_2 \cdot 6H_2O$ (Merck) and $AlCl_3 \cdot 6H_2O$ (Riedel-de Haen), were used for desorption studies of radionuclides- loaded sepiolite. Of the inorganic reagents, NaCl, $CaCl_2 \cdot 2H_2O$ and $AlCl_3 \cdot 6H_2O$ were used as sources of Na^{+}, Ca^{2+} and Al^{3+} ions for studying the impact of their coexistence with radionuclides on the present adsorption process onto sepiolite.

2.2. Adsorption experiments

Most of the present adsorption experiments of cesium, cobalt and europium ions (50 mg/L for each unless otherwise specified), traced with their radionuclides ($^{134}Cs^{+}$, $^{60}Co^{2+}$ and $^{152+154}Eu^{3+}$, respectively) were performed in a temperature-controlled water bath shaker (Jeio Tech type, BS-21 Model, Korea). The volume/mass ratio was kept constant at 50 mL/g (for Cs) and 100 mL/g (for both Co and Eu).

2.2.1. Effect of solution pH

The impact of the solution pH on adsorption of Cs, Co and Eu was investigated by contacting their traced solutions (5 mL) with sepiolite (0.1 g for Cs and 0.05 g for Co and Eu) in 25 mL glass bottles. The adsorbate solutions were adjusted to the pH values in the range of 2.4–12, 1.5–10 and 2.5–7 for Cs, Co and Eu, respectively. The glass bottles were sealed tightly ad shaken for 24 h (for Cs and Eu) and 48 h (for Co) at 25 °C at a constant shaking speed of 80 rpm. For determination of the precipitation pHs of Co and Eu, the same procedures were followed but in absence of sepiolite. After equilibration, the contents of the glass bottles were centrifuged and the radioactivity of radionuclides as well as the final pH, pH_f, of the supernatant was measured.

2.2.2. Effect of sepiolite weight

Different sepiolite dosages (0.01–0.15 g) were weighed in glass bottles. The adsorbate solution (5 mL, 50 mg/L), adjusted to desired pH value, was then added to bottles and shaken for 24 h (for Cs and Eu) and 48 h (for Co) which was found to be sufficient more than required for equilibration. The radioactivity of the supernated, obtained by centrifugation, was measured.

2.2.3. Effect of contact time

The effect of contact time (5–120 min, 5–4320 and 1–2300 min for $^{134}Cs^{+}$, $^{60}Co^{2+}$ and $^{152+154}Eu^{3+}$, respectively) was studied by adding 5 mL of radionuclides solution (50 mg/L) to a specified amount of sepiolite in stoppered glass bottles. The bottles were shaked at a constant shaking speed of 80 rpm at 25 °C. At certain time intervals, the solid phase was separated by centrifugation and the radioactivity in the liquid phase was measured.

2.2.4. Effect of adsorbate concentration

Concentration series of the adsorbate solutions (5–700 mg/L for Cs, 5–160 mg/L for Co and 5–400 mg/L for Eu) was adjusted, after traced with the radionuclide, to the preliminary determined pH value (~7.0 for Cs and ~3.5 for Co and Eu). The prepared solutions were then added to fixed amounts of sepiolite and shaken for a previously optimized contact time (24 h for Cs and Eu while 48 h for Co) at 25 °C in water bath shaker. After equilibration, the suspensions were centrifuged and the radioactivity in the liquid phase was measured.

2.2.5. Effect of coexisting ions

Adsorbate solutions (5 mL, 50 mg/L) containing a foreign ion at different concentrations (0.0001 M–0.5 M either for Na^{+} or Ca^{2+} and 0.0001 M–0.01 M for Al^{3+} ion) was adjusted to the desired pH value and then was contacted, in 25 mL glass bottles, with constant amounts of sepiolite. After shaking and equilibration, the contents of the bottles were centrifuged for measuring the radionuclide radioactivity in the liquid phase.

2.2.6. Multi-radionuclide adsorption experiments

Adsorption experiments of $^{134}Cs^{+}$, $^{60}Co^{2+}$ and $^{152+154}Eu^{3+}$ in their mixture using sepiolite were carried out by the same procedures followed for their removal in single systems.

2.3. Calculations

A NaI scintillation counter connected to single channel spectrometer (Spectech ST 360 to crystal, USA) was used for measurement of the radioactivity of the radionuclides in the aqueous phase. The removal percentage for the present adsorption processes onto sepiolite was