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Adsorption of Cs-137 and Am-241 ions from aqueous solutions on bentonites

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ABSTRACT

As materials used for sealing of landfills and removal of inorganic pollutants, bentonites are also potentially useful for the treatment of radionuclides from aqueous solutions. The ability of two coming from different continents bentonites (Wyoming and Karakaya) to take up the radioisotopes Cs-137 and Am-241 has been examined as a function of contact time and pH of the aqueous solutions. The sorption capacity of bentonites was determined as the decontamination factor (DF) and distribution coefficient K_d. It is demonstrated herein that the Wyoming and Karakaya bentonites seem to be effective sorbents for the removal of radionuclide ions from aqueous solutions. The bentonites are characterized by the decontamination factor equal to 50% for cesium ions (Cs(I)) and 33% for americium ions (Am(III)). Additionally, it was observed that an increase in solution pH negatively influenced the removal of ions. The calculations done by Hydra-Medusa Software were performed to create chemical equilibrium diagrams for Cs(I) and Am(III) species. The porous structure of both bentonites was characterized on the basis of determined nitrogen low-temperature adsorption-desorption isotherms. The surface characteristics were analyzed with the use of scanning electron microscope photographs and the chemical composition was determined by energy-dispersive X-ray spectroscopy analysis. The properties of the sorbent surfaces are important for their usefulness in radionuclide removal. The results of this study indicate the potential application of natural sorbents in treating radioactive effluents. Both used bentonites are readily available in large quantities.

Keywords: Adsorption; Americium-241; Cesium-137; Bentonites; Contact time; Solution pH

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1. Introduction

Liquid radioactive wastes are a serious and increasing worldwide problem because of their relatively large volume. Safe disposal of nuclear wastes, especially aqueous radioactive wastes originating from the reprocessing of spent nuclear fuels, is a matter of great importance. At present, their immobilization into vitreous matrices followed by their final storage in deep geological repository systems, which are composed of natural and engineered barriers to isolate radionuclides from the biosphere, is the most preferred procedure (IAEA-TECDOC-1336, 2003) [1]. Granite rock formations as the host media, and bentonite alone or its mixtures with sand or crushed granite as the back-fill are the favorite materials used for this purpose [2]. It is well known that the usage of these barriers requires a large amount of natural materials exhibiting specific physicochemical and sorption properties [3,4]. For this application, the most promising option is using natural sorption materials with low prices and effective sorption properties. Sorption is amongst the most popular methods because it is cheap, effective, and easy to carry out.

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Moreover, radioactive isotopes of plutonium, americium and cesium released during atmospheric testing of nuclear weapons in the early 1960s, have been detected worldwide [5]. An additional source of radioactive contaminants may be those that are released from the nuclear industry and nuclear accidents. These include americium-241 and cesium-137 [6]. The development of methods for the removal of metallic radionuclides from aqueous solutions are of particular importance. Several methods have been applied to remove radioactive metal ions, including precipitation, ion exchange, membrane technologies or electrochemical processes [7,8], but all of them have technical and economical limitations. Adsorption has been proposed as an alternative for the above-mentioned methods because it is a low cost and simple method [9]. In addition, it is selective and highly effective in the treatment of dilute effluents.

In many reports, effective adsorbents for the removal of radionuclides were made of raw and modified minerals [2,10–15], as well as composite materials or biosorbents [16–19]. Reviews of various adsorbents applied in cesium removal [20,21] show the influence of their properties on the adsorption efficiency of this metal from aqueous solutions. The results of research on the binding of radionuclides to the soil environment [22–24] or sea sediments [25] have been presented in some papers.

Despite numerous studies focused on the adsorptive removal of radioactive metal ions from aqueous solutions, the properties of adsorbents were very rarely characterized in detail. This mainly concerns the lack of information about the specific surface area and surface chemistry. Therefore, in this work, two bentonites of different origin with previously characterized surface properties were used to remove ions of Cs-137 and Am-241 radioisotopes. Both used bentonites are readily available in large quantities. These bentonites showed some differences in porous structure and surface chemistry. The radionuclides used for research are metal ions with extremely different properties, for example, valences (I and III) and the ability to create various species.

2. Experimental part

2.1. Materials characteristics

Two powdered sodium bentonites without any chemical treatment were used in the study – Karakaya bentonite (B-K) and Wyoming bentonite (B-Wy). The materials tested were supplied from mines located in Turkey (Karakaya Bentonite Inc., Karakaya, Reşadiye) and in the USA (Bentonite Performance Minerals, LLC., Colony, Wyoming). According to Erdogăn et al. [4], the main mineralogical components of the Karakaya (Reşadiye) bentonite are smectite, cristobalite, quartz and feldspar. According to Cheshire et al. [3], the Wyoming bentonite (Colony) is composed of Na-montmorillonite with minor amounts of clinoptilolite, feldspar, biotite, cristobalite and quartz. The chemical composition (XRF) of the tested materials was as follows: for the Wyoming bentonite – 61.9% SiO_2, 19.5% Al_2O_3, 1.6% MgO, 0.9% CaO, 4.1% Fe_2O_3, and 2.85% Na_2O; and for the Karakaya bentonite – 61.8% SiO_2, 16.6% Al_2O_3, 1.8% MgO, 4.5% CaO, 3.4% Fe_2O_3, and 2.6% Na_2O.

To characterize the porous structure of both bentonites, nitrogen low-temperature (77 K) adsorption–desorption isotherms were determined using an ASAP 2420 system (Micromeritics, Norcross, GA 30093, USA). Additionally, a scanning electron microscope FEI Quanta 3D FEG (FEI Company, Hillsboro, OR, USA), equipped with an energy-dispersive X-ray spectroscopy detector, was used to determine their surface topography and chemical composition.

2.2. Radionuclide adsorption experiments

Adsorption experiments were performed to obtain the values of optimum pH, contact time, and initial concentration of Cs(I) and Am (III) ions. In all experiments, the ratio of the bentonites to the liquid phase was 50 g to 1 L of the solution. Both bentonite-solution suspensions were shaken in a thermostatic shaker (type MKR 13; Merazet) at room temperature (23°C ± 1°C). Sorption of cesium(I) and americium(III) from the two-component solution with an initial concentration of 10^{-5} M for each radionuclide was studied for contact time in a range of 0 to 3.5 h. Aqueous solutions of the desired Cs-137 and Am-241 concentrations were prepared by weight dilution of the certificated standard solution delivered by the National Centre for Nuclear Research – Radioisotope Centre POLATOM (Świerk, Poland). The acidity of solutions in the pH range from 3 to 7 was controlled by the addition of nitric acid or sodium hydroxide. The ionic strength of the solutions was kept constant with 0.05 mol/L sodium nitrate. The equilibration period averaged 2.5 h and the equilibrium pH was measured immediately prior to sampling using the Agilent Technologies pH-meter (3200P Benchtop). The liquid phase was separated from the solid phase by centrifuging (6,000 rpm, 20 min). Activity concentrations of Cs-137 ($t_{1/2} = 30.07$ y; $E\gamma = 661.7$ keV), and Am-241 ($t_{1/2} = 432.2$ y; $E\gamma = 59.5$ keV) in the initial and equilibrium liquid phases were determined radiometrically using 2480 Wizard2® automatic gamma counter (PerkinElmer, Inc. 940 Winter Street Waltham, MA 02451, USA).

Sorption properties of the bentonites were presented as decontamination factors (DF) [18]:

$$\text{DF} = \left(1 - \frac{A_{\text{eq}}}{A_0}\right) \times 100\% \tag{1}$$

and distribution coefficients K_d, which were defined as:

$$K_d = \frac{A_{\text{bentonite}}}{A_{\text{eq}}} = \left(\frac{A_0 - A_{\text{eq}}}{A_{\text{eq}}}\right) \times \left(\frac{V}{m}\right) \tag{2}$$

where A_0 is the volume activity of the initial solution (cps mL^{-1}), A_{eq} is the equilibrium volume activity of the solution (cps mL^{-1}), V is the volume of the aqueous phase (mL), and m is the weight of the bentonite (g).

2.3. Chemical equilibrium diagrams

The calculations done by Hydra-Medusa Software [26] were performed to create chemical equilibrium diagrams for metal (Cs(I) and Am(III)) species.

3. Results and discussion

3.1. Materials characteristics

The properties of both bentonites show some differences. Nitrogen low-temperature adsorption–desorption isotherms (Fig. 1a) were used to characterize their porous structure. On their basis, the specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation. The Wyoming bentonite has a smaller BET specific surface area than the Karakaya bentonite by slightly around 28%. A similar difference (around 29%) also applies to the micropore volume (Table 1). Surface topography visible in SEM images (Fig. 1b) also suggests a more developed porosity of the Karakaya bentonite. In the case of surface chemical composition, a higher oxygen, carbon and sodium content for the Karakaya bentonite can be observed compared to the Wyoming bentonite (Fig. 1c). A reverse relationship was detected for the remaining elements (Si, Al, Fe, Mg, Ca). The last two elements, titanium and potassium, occur on only the surface of one of the bentonites, Wyoming and Karakaya, respectively.

In the papers [27,28] the dependence of zeta potential on pH of solution was studied and discussed for Wyoming and Karakaya bentonites. The zeta potential was similar and little changed in the greater part of the 2–10 pH range for both bentonites (–35 ÷ –40 mV).

Among the surface properties used to test bentonites, the greatest differences can be observed in the case of porosity. Both bentonites differ in the degree of development of the porous structure: bentonite Karakaya has a larger specific surface area as well as micropore volume than bentonite Wyoming by about 30%. In the case of surface chemistry, the differences between the tested bentonites were much smaller.

3.2. Radionuclide adsorption experiments

Fig. 2 shows the sorption of cesium(I) and americium(III) onto two studied types of bentonites: Wyoming and Karakaya for different initial pH values of solutions. As it can be seen, the adsorption equilibrium of Cs(I) (Figs. 2a, c, e and g) and Am(III) (Figs. 2b, d, f and h) on both examined sorbents was reached usually within 2.5 h. After this time, the distribution coefficient (K_d) was independent from the contact time of the equilibrated phases. In order to examine a wastewater treatment process, it is important to predict the rate of sorption operation. The kinetic studies of americium adsorption on bentonites was described in the paper [11]. It was found that the pseudo-second-order model provides better fit for Am(III) removal from aqueous solutions by the bentonites. Based on the literature, it can be concluded that kinetic studies of cesium also describe the pseudo-second-order model [29].

Decontamination factors (DF) in the case of bentonites were studied as a function of contact time (3.5 h) and initial pH (3–7), respectively (Table 2). The DF at a pH of 3 and a temperature of 23°C ± 1°C after 3.5 h was equal to 41% ± 0.03% for Cs(I) and 23% ± 0.05% for Am(III) in the case of the Wyoming bentonite, and 50% ± 0.04% for Cs(I) and 33% ± 0.05% for Am(III) in the case of the Karakaya bentonite. The DF of the Karakaya bentonite was higher by 22% for Cs(I) and by 43% for Am(III) than the DF of the Wyoming bentonite, which is consistent with the established relations for the specific surface area and total volume of micropores. It can be seen that both materials tested had a higher potential to remove Cs(I) than Am(III) by 78% for the Wyoming bentonite and 51% for the Karakaya bentonite. For the Wyoming bentonite, a clear effect of the initial pH on the degree of Am (III) removal was observed. This can be seen in the smaller values of the DF and distribution coefficient obtained for Am(III) solutions with an initial pH of 7. A similar relationship was observed for the Karakaya bentonite. This can be explained by the changing form of Am(III) depending on the pH of the solution.

Based on the calculations made in Hydra-Medusa software, the only species present in acidic conditions is Am(III) (Fig. 3). However, at pH in the range of 6.5 to 7, monovalent $Am(CO_3)^+$ and divalent $Am(OH)^{2+}$ species may be found in significant amounts [18]. The presence of $Am(CO_3)^+$ and $Am(OH)^{2+}$ affects the sorption of Am(III), which is expressed by the lower values of distribution coefficients in this case. Additionally, for both materials, the lowest values of DF were observed for solutions with the initial pH of 4. Moreover, a negative correlation was observed between the degree of Cs(II) removal and the pH of the solution for the Karakaya bentonite (Table 2), which can be seen in the DF values. It must be noted that according to the Hydra-Medusa software calculations (Fig. 3), Cs(I) is the only species present in the tested range of initial pH of the solutions.

For comparison with the results of our research with the use of bentonites, focus is drawn on the results of Oszczak-Nowińska and Fuks [19] for alginates as adsorbents and Cs(I) and Am(III) radioisotopes as adsorbates. For comparable experiment conditions the obtained $\log K_d$ values were as follows: 2.5–3.4 for Cs(I) adsorption and 3.9–4.4 for Am(III) adsorption in the case of calcium-, barium- and strontium-alginates as adsorbents.

4. Conclusions

The Wyoming and Karakaya bentonites seem to be good radioisotope sorbents from aqueous solutions. Better

Table 1
Parameters of the bentonite porous structure

Bentonite	S_{BET} (m^2/g)	V_{mi} (cm^3/g)	V_t (cm^3/g)	V_{mi}/V_t
Wyoming bentonite	36	0.017	0.099	0.17
Karakaya bentonite	46	0.022	0.093	0.24

S_{BET}, Brunauer–Emmett–Teller specific surface area (m^2/g); V_{mi}, volume of micropores (cm^3/g); V_t, total volume of pores (cm^3/g).

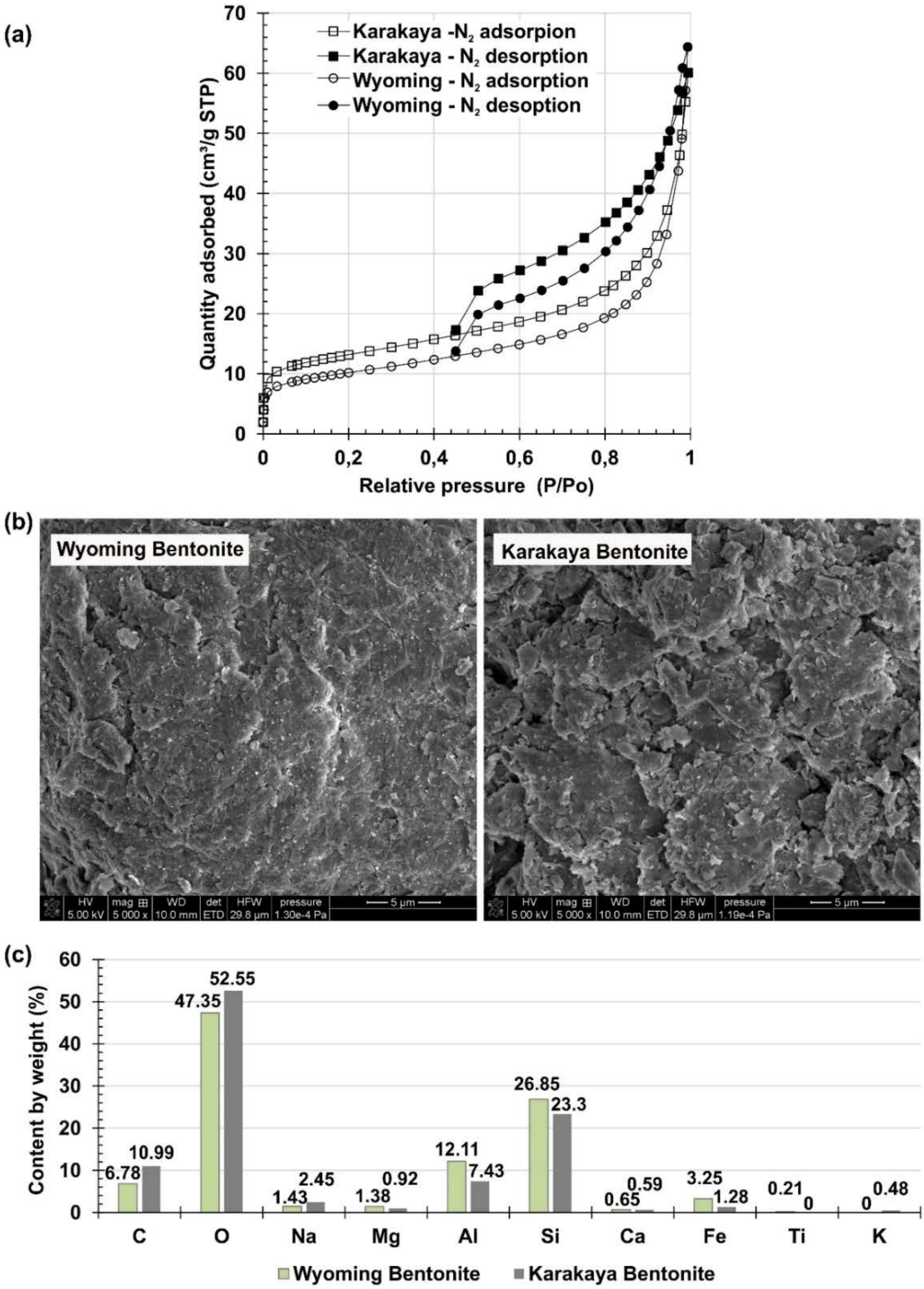

Fig. 1. Low-temperature (77 K) nitrogen adsorption–desorption isotherms (a), scanning electron microscopy images (b), and surface chemical composition from energy-dispersive X-ray spectroscopy (c) of the tested bentonites.

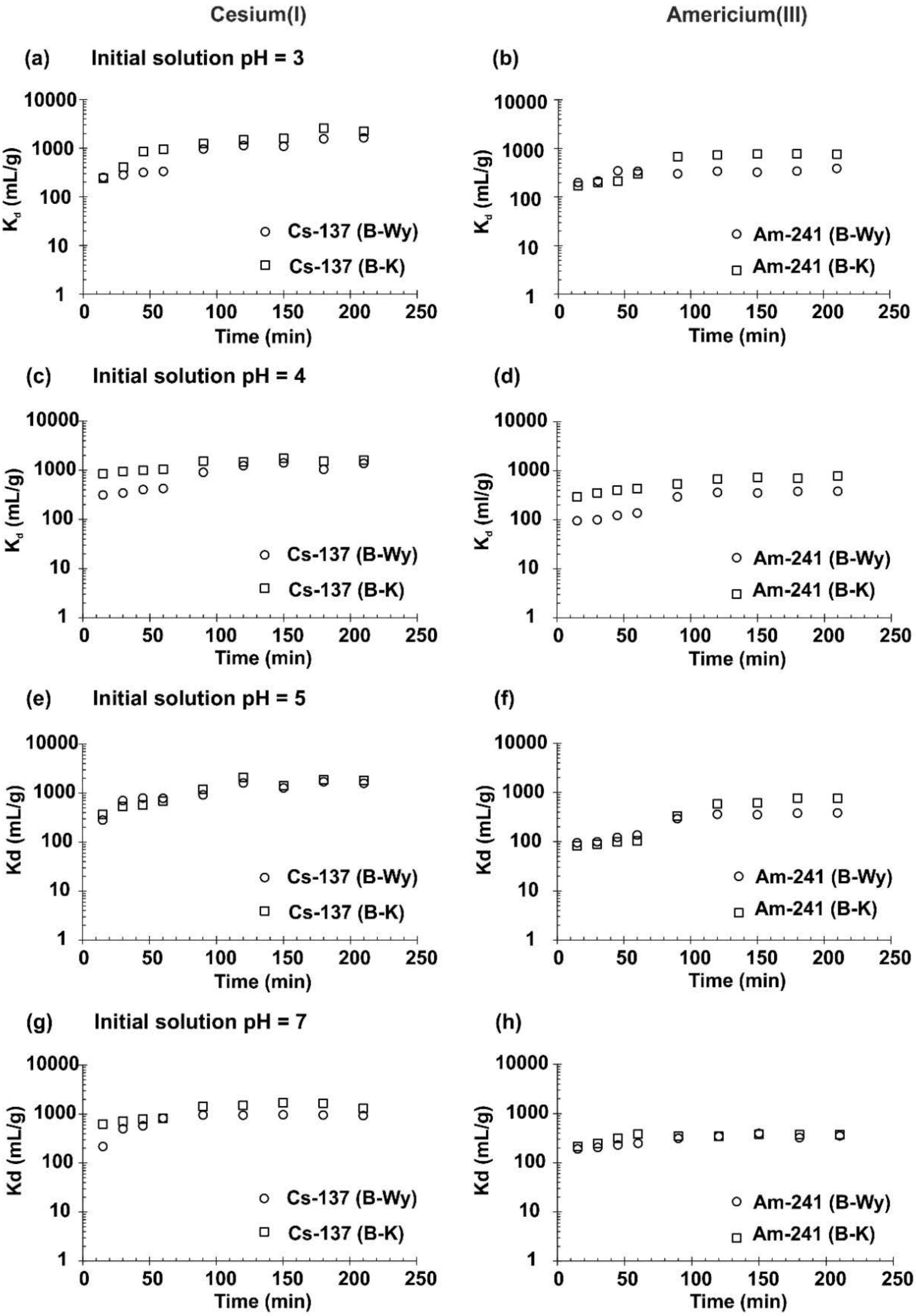

Fig. 2. Effect of contact time and initial pH of aqueous solutions on Cs(I) and Am(III) adsorption on bentonites.

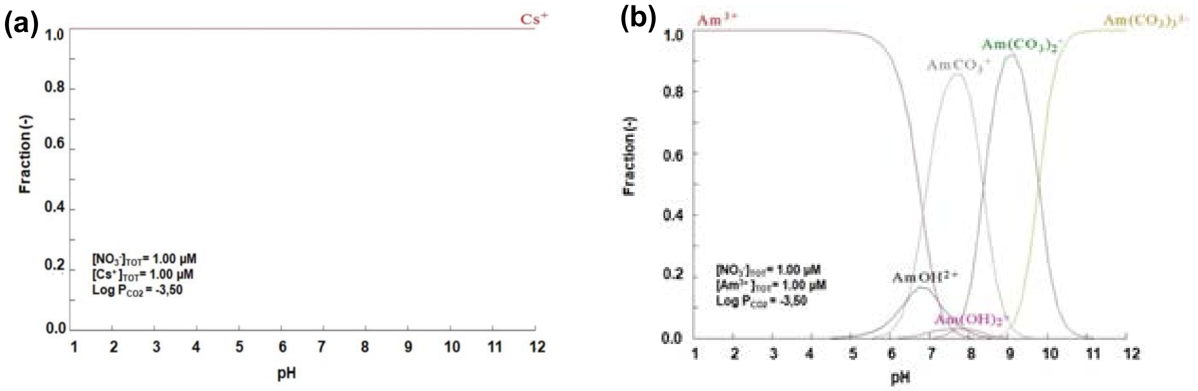

Fig. 3. Diagrams showing the concentrations of Cs(I) (a) and Am(III) (b) for different pH values ($[NO_3^-]_{TOT}$ = 1.00 μM $[Cs^+$ or $Am^{+3}]_{TOT}$ = 1 μM; full exposure to atmospheric conditions with partial pressure $pCO_2 = -3.5$) [26].

Table 2
Distribution coefficients and decontamination factors for Cs(I) and Am(III) for bentonites; 0.05 M $NaNO_3$ solution, pH (3–7), *t* 3.5 h, temperature of 23°C ± 1°C, concentration of radionuclides 10^{-5} M

Radioisotopes	pH	K_d (mL/g)	logK_d	SD	DF (%)
Wyoming bentonite					
Cs(I)	3	1.62×10^3	3.21	±0.03	41
	4	1.54×10^3	3.14	±0.01	39
	5	1.59×10^3	3.20	±0.01	40
	7	1.58×10^3	3.20	±0.03	40
Am(III)	3	3.89×10^2	2.58	±0.05	23
	4	3.85×10^2	2.58	±0.03	23
	5	3.85×10^2	2.58	±0.03	23
	7	3.46×10^2	2.53	±0.06	21
Karakaya bentonite					
Cs(I)	3	2.58×10^3	3.41	±0.04	50
	4	1.62×10^3	3.21	±0.03	41
	5	1.87×10^3	3.27	±0.02	45
	7	1.67×10^3	3.22	±0.04	42
Am(III)	3	7.62×10^2	2.88	±0.05	33
	4	7.85×10^2	2.89	±0.02	33
	5	7.59×10^2	2.88	±0.02	33
	7	3.52×10^2	2.55	±0.04	23

K_d, distribution coefficient (mL/g); SD, standard deviation; DF, decontamination factor (%).

results observed for the Karakaya bentonite compared to the Wyoming bentonite may result from appropriate differences in their specific surface area and total volume of micropores. The adsorption equilibration time was 2.5 h for both bentonites. Kinetics of Am(III) and Cs(I) sorption on both sorbents can be evaluated based on the pseudo-second-order rate equation [11,29]. Karakaya bentonite was characterized by the decontamination factor equal to 50% for Cs(I) and 33% for Am(III), whereas for the Wyoming bentonite – by the decontamination factor equal to 41% for Cs(I) and 23% for Am(III). The distribution coefficient logK_d values for bentonites were: 3.41 for Cs(I) and 2.88 for Am(III) in the case of Karakaya bentonite, 3.21 for Cs(I) and 2.58 for Am(III) in the case of Wyoming bentonite. The sorption order of radioisotopes on the Wyoming and Karakaya bentonites was Cs > Am. For both radionuclides, the contaminant removal by the Karakaya bentonite was more dependent on the solution pH (in the range 3–7). Both the bentonites used are cheap and readily available in large quantities. The performed tests confirmed the application potential of both materials in the removal of Cs(I) and Am(III) from aqueous solutions.

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