

## Article

# The Effect of High-Energy Ball Milling of Montmorillonite for Adsorptive Removal of Cesium, Strontium, and Uranium Ions from Aqueous Solution

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**Abstract:** Clay minerals are widely used to treat groundwater and surface water containing radionuclides. In our study, the method of mechanochemical activation for increasing the sorption capacity of the natural clay mineral montmorillonite was used. By adjusting the grinding time, the increasing sorption parameters of mechanochemically activated montmorillonite were determined. X-ray diffraction method, scanning electron microscopy, and the determination of the specific surface by low-temperature adsorption–desorption of nitrogen to characterize the natural and mechanochemical-activated montmorillonites were used. It was established that the maximal sorption of uranium, strontium, and cesium is found for montmorillonite after mechanochemical treatment for 2 h. It is shown that the filling of the surface of montmorillonite with ions of different natures occurs in various ways during different times of mechanochemical treatment. The appropriateness of the Langmuir and Freundlich models for the sorption parameters of uranium, strontium, and cesium ions on montmorillonite after its mechanochemical activation was established. The effect of natural organic substances—humic acids—on the efficiency of water purification from uranium on mechanoactivated montmorillonite was studied. The obtained sorbents can be effectively used for the removal of trace amounts of radionuclides of different chemical natures (uranium, cesium, and strontium) from polluted surface and ground waters.

**Keywords:** layered silicate; mechanochemical activation; sorption; radionuclides; surface filling; humic acid



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## 1. Introduction

Contamination of surface water and groundwater by radioactive elements such as uranium, cesium, and strontium is caused by several factors. Among these factors are the obtaining of environmentally hazardous toxicants into groundwater from the mining industry, tailings storage facilities, nuclear power plant accidents, and radioactive waste disposal sites from block waters of radioactive sites of nuclear power plants [1–8]. As a result, the ecological balance is disturbed. The concentration of radioactive elements can vary for different reservoirs depending on the type of drained rocks, the chemical composition of the water, and the hydrogeological regime [9].

In water, uranium forms carbonate and, rarely, sulfate anion complexes, uranyl, and hydroxo-uranyl cations, and can also be in a dispersed state in the composition of detrital minerals. These toxicants can be dissolved in surface water and groundwater or exchange ions in soils or sediments by complex reactions with natural organic matter as pure or

mixed mineral phases [3]. In an aqueous medium, cesium exists in a cationic form over a wide pH range. However, for strontium, in addition to the ionic and ion-dispersed form, it is also likely to be found in the form of complex compounds. In surface waters, most of the cesium-137 is transported in the form of positively charged ions, although significant amounts of cesium can be strongly adsorbed on clay particles and transported in the solid phase. The main amounts of strontium-90 in fresh waters are transported in ionic form [10]. There is an interaction of radionuclides with organic components of natural waters, with the formation of sufficiently strong complexes, which can be one of the main channels of transport in the case of a high content of organic substances in waters [11,12].

As a result of migration, radioactive elements enter drinking water sources and are a threat to public health. Because of its radioactivity and toxicity (carcinogenic for humans), uranium is a very dangerous element, and the World Health Organization recommends a limit of 0.015 mg/L for drinking water [13]. Also, U has been added to the US Environmental Protection Agency's National Primary Drinking Water Regulations, with a recommended guideline of 0.030 mg/L [14]. Total beta activity for drinking water consists of  $\leq 1.0$  Bq/L, specific activity  $^{137}\text{Cs}$  consists of  $\leq 2.0$  Bq/L, and  $^{90}\text{Sr}$  consists of  $\leq 2.0$  Bq/L. Therefore, considerable attention is paid to the study of the features of binding of radioactive elements to the components of natural waters—fulvic acids, and humic acids, as well as possible ways of extracting these compounds from the water environment [15–17].

The problem of preventing the migration of radionuclides and heavy metals from mining and other contaminated areas is huge and requires low-cost technological solutions. The using of the sorption method is one of them. Natural sorbents are usually used to create permeable reactive barriers or as filling materials in storage facilities for the long-term disposal of radioactive waste [18,19]. Clay materials have all the necessary qualities for this, including sufficient resistance to radiation exposure [20,21].

However, these materials in the raw state have only moderate sorption properties. To increase the sorption capacity of clay minerals and selectivity concerning certain toxicants, methods of physical and chemical surface modification are widely used [22]. The simple methods seem to be more promising for the processing of large volumes of clay materials. When grinding solids using energy-intensive equipment, it is possible to achieve a high dispersion of final products, as well as to significantly influence the concentration and nature of surface defects. The latter determines the use of mechanochemical activation (MCA) in the technology of catalysts as well as in sorption processes [23–26].

A large number of works are devoted to studies of the properties of MCA-treated layered materials [27]: bentonite [28], montmorillonite [29–32], vermiculite [33], kaolinite [29,32], talc [34], smectite [35], etc. Mechanochemical activation leads to the decreasing of crystallinity (amorphization) of the solid substance, while the surface energy and surface reactivity of the material and, therefore, chemical activity increase [25,26,31,36,37]. As a result of MCA, the clay structure changes. The following changes are observed: delamination and disorderliness of layers, increasing defects, a reduction in the size of the crystallites, a lowering of the temperature of the dehydroxylation, increasing free surface clay particles, and increasing reaction abilities. The greatest influence on the changing properties of clays in the MCA are time and the intensity of processing [25,26].

Montmorillonite has attracted widespread attention as a potential material for the control of harmful elements in the environment [38–40]. The enhancement of adsorption of organic compounds (gaseous toluene, acetone [41,42]) was investigated on ball milling-treated montmorillonite. The increasing of sorption values by twice and more with the use of mechanochemical treatment were shown on the removal of such elements as lead [33,43], cesium, and strontium [25,43]. The first factor that determines the high selectivity of clay minerals to large cations of alkali metals is structural. At the sorption processes it is caused by the presence of ditrigonal holes on the surface of silica grids proportional to the parameters of large cations. The second feature is an increase in the relative contribution of the side faces to their specific surface and the formation of so-called “frayed” side faces at the fine comminution of air-dried samples of these minerals. It leads to the possible

increase in the  $^{137}\text{Cs}$  ions' sorption values [25]. As follows, fine comminution with the use of high-energy aggregates [25,44] contributes to increasing the surface activity of clay minerals and, accordingly, increasing their sorption characteristics.

However, the use of mechanoactivated clays, in particular, mechanoactivated montmorillonite, for water purification from heavy metals and radionuclides is not so widely used. Therefore, the use of cheap natural raw materials in combination with high-energy processing will make it possible to obtain effective sorbents for the removal of radionuclides. Our research aimed to obtain montmorillonite-based materials using mechanochemical activation for increasing sorption characteristics. Such sorbents can provide protection to the aqueous environment from cesium, strontium, and uranium.

## 2. Materials and Methods

### 2.1. Materials and Chemicals

The layered silicate 2:1-type montmorillonite (Dashukivka, Cherkasy region, Ukraine) with a cation-exchange capacity (CEC) of 0.71 meq/100 g and a structural formula of  $(\text{Ca}_{0.12}\text{Na}_{0.03}\text{K}_{0.03})_{0.18}(\text{Al}_{1.39}\text{Mg}_{0.13}\text{Fe}_{0.44})_{1.96}(\text{Si}_{3.88}\text{Al}_{0.12})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$  was used. Coarse mineral impurities such as feldspars, quartz, aluminum and iron oxides, carbonates, etc., were withdrawn from montmorillonite rock. Purified montmorillonite, which was used in the next experiments, was obtained by way of sedimentation from an aqueous-clay suspension, centrifugation, drying at 105 °C, and grinding to the fraction < 0.1 mm. The chemical composition of natural montmorillonite, according to SEM/EDS analysis, followed (% , at.): —52.65, Si—27.70, Al—10.02, Fe—8.38, and Mg—1.25.

Hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), salt of uranyl sulfate trihydrate ( $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ ), cesium chloride (CsCl), and strontium chloride ( $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ) were obtained from Sigma-Aldrich, St. Louis, MO, USA; humic acid was obtained from Fluka. All the chemicals were analytical reagent grade and used without further purification. The solution of the uranium, cesium, and strontium salts were prepared using distilled water. In all experiments, distilled water was used to prepare solutions of different concentrations.

### 2.2. Synthesis Procedure

Planetary ball mill Pulverisette-6 (Fritsch) was used for the mechanochemical treatment of MMT. Si<sub>3</sub>N<sub>4</sub> balls (d = 20 mm, n = 12) with a total weight of 160 g were used as working bodies. The mass ratio of balls and MMT was 1:10. The milling process continued 0.5–4 h. The rotation speed was equal to 300 rpm. Milling was performed in 10 min cycles; subsequently, a reverse was carried out after each cycle.

### 2.3. Characterization Methods

X-ray powder diffraction (XRD) patterns of the natural clay mineral and mechanochemical-activated montmorillonite (MCA MMT) were recorded with a DRON-4-07 diffractometer using  $\text{CuK}\alpha$  (0.154 nm) in the region between 2° and 60° (2  $\theta$ ). The constant pass energy of U = 30 kV and I = 30 mA were used [45].

Scanning electron microscopy (SEM) method (Jeol JSM-6060, Tokyo, Japan) was used for the investigation of the surface morphology of the natural and mechanochemical-activated MMT. The samples of MMT and MCA MMT were sputter coated with gold for 3 min. In the conditions of analysis, secondary images were used with an acceleration voltage of 30 kV and a magnification of 5000-fold.

The sample of natural montmorillonite was analyzed using a JED-2300 X-ray spectrometer integrated with a JSM 6060 LA scanning electron microscope. Energy-dispersive X-ray (EDS) analysis was performed with an accelerating voltage of 15 kV and a magnification of  $\times 500$  using standard software.

The low-temperature N<sub>2</sub> adsorption-desorption method (T = −196 °C) (Quantachrome NOVA-2200e Surface Area and Pore Size Analyzer, Boynton Beach, FL, USA) was used for the determination of the porous structure parameters. The ASiQwinTM V 3.0 software was

used for the results processed. Specific surface area  $S$  ( $\text{m}^2/\text{g}$ ) was estimated using the BET equation. The total pore volume  $V$  ( $\text{cm}^3/\text{g}$ ) was calculated using the maximum adsorbed volume of nitrogen at a relative pressure  $p/p_0 \approx 0.99$ . The distribution of pore size  $dV(r)$  (nm) was determined using BJH and DFT models [46].

Potentiometric titration of the samples was performed using a 781 pH/Ion Meter by the procedure described in [47].

#### 2.4. Adsorption Experiments

The batch-wise method was performed for the adsorption experiment. A series of 0.1 g samples of sorbents to 50 mL aqueous solutions of radionuclides U(VI), Cs(I), and Sr(II) were added. The solutions were prepared from the salts uranyl sulfate ( $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ ), strontium chloride ( $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ), and cesium chloride (CsCl). The ionic strength was created with a solution of 0.01M NaCl. The experiments were conducted in triplicate at pH 6 in a thermostatic cell at 25 °C with continuous shaking for 1 h. After establishing the adsorption equilibrium, the liquid phase was separated by centrifugation (6000 rpm) for 30 min. The effect of humic acid (HA) was studied at a concentration of 100 mg/L for HA and 300  $\mu\text{mol}/\text{L}$  for U(VI).

The spectrophotometric method (UNICO 2100UV, United Products and Instruments, Suite E Dayton, NJ, USA) was used for the determination after adsorption of the equilibrium concentration of U(VI); the wavelength was 665 nm, and Arsenazo III was used as a reagent. The atomic adsorption spectroscopy (AA-6300 Shimadzu, Shimadzu Corporation, Tokyo, Japan) was used for the determination of the equilibrium concentrations of Cs(I) and Sr(II) after adsorption.

The kinetic experiments were conducted on samples of natural and mechanical-activated montmorillonite by uranium sulfate, cesium chloride, and strontium chloride solutions with the same initial concentration of 100  $\mu\text{mol}/\text{L}$  for different selected times ranging from 5 to 360 min.

The presentation of sorption (PS, %) from U(VI), Cs(I), and Sr(II), was calculated by Equation (1):

$$\text{PS} = (\text{C}_{\text{in}} - \text{C}_{\text{eq}}) / \text{C}_{\text{in}} \cdot 100 \quad (1)$$

The adsorption capacity ( $q_{\text{eq}}$ ,  $\mu\text{mol}/\text{g}$ ) of radionuclide ions was estimated by Equation (2):

$$q_{\text{eq}} = (\text{C}_{\text{in}} - \text{C}_{\text{eq}}) \cdot \text{V} / \text{m} \quad (2)$$

where  $\text{C}_{\text{in}}$  and  $\text{C}_{\text{eq}}$  represent the initial and equilibrium radionuclides concentrations ( $\mu\text{mol}/\text{L}$ ),  $\text{V}$  is the solution volume (L), and  $\text{m}$  is the weight of the adsorbent (g).

The distribution of radionuclides between the adsorbent and solution was calculated as the value of the coefficient of distribution  $\text{K}_d$ ,  $\text{mL}/\text{g}$  (Equation (3)):

$$\text{K}_d = (\text{C}_{\text{in}} - \text{C}_{\text{eq}}) \cdot \text{V} / (\text{C}_{\text{eq}} \cdot \text{m}) \cdot 1000 \quad (3)$$

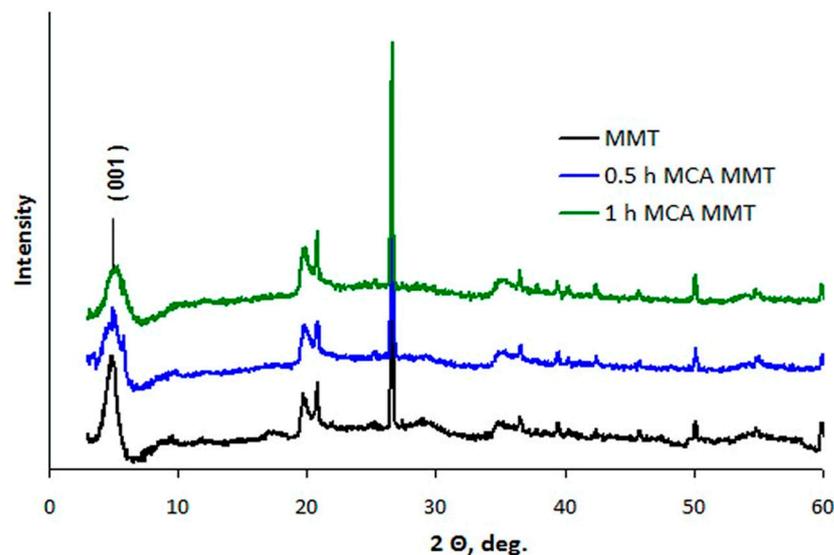
The experimental isotherms of radionuclides adsorption were processed using the Langmuir mathematical model for a homogeneous surface and the Freundlich model for a heterogeneous surface [48].

### 3. Results and Discussion

#### 3.1. Characteristics of Natural and Mechanical-Activated Montmorillonite

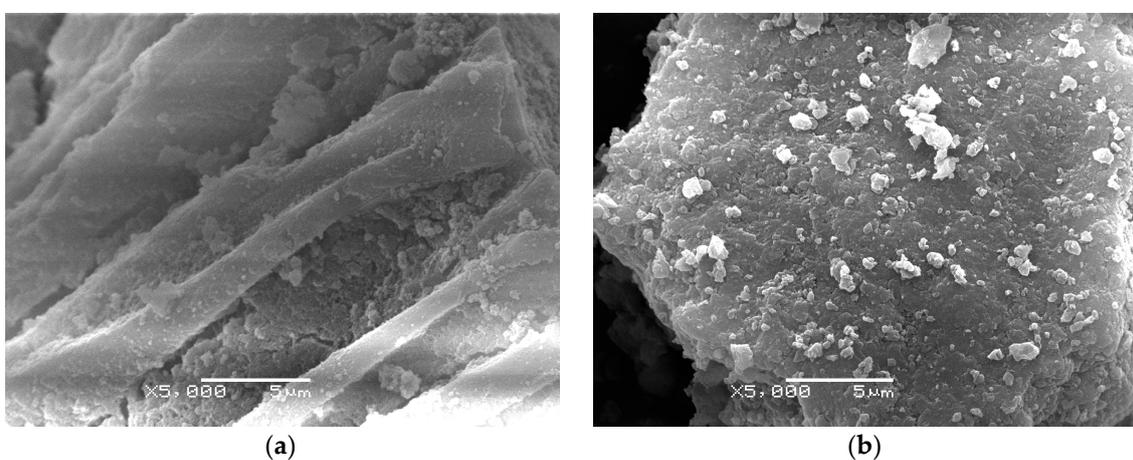
The X-ray diffraction patterns of the MMT and MCA MMT are demonstrated in Figure 1. There were structural changes during the milling process. A gradual destruction of the crystalline phase occurs with the increasing duration of milling. This was evidenced by a progressive decrease in the XRD reflection intensities. Fine grinding leads to a systematic decrease in the intensity of reflections. It is proven to increase the amorphization of the structure of activated MMT during milling. Mechanochemical treatment for 1 h and more leads to the decreasing intensity of the 001 peaks and a shift of the 001 peaks with the concomitant broadening in an asymmetrical fashion. At the same time, the stacking

of layers is disturbed and lost, and the initial structural destabilization of the basal plane begins [45,49]. This is probably due to the partial removal of water molecules from the interlayer spaces and may, according to the work [25], be accompanied by the formation of a disordered mixed-layer phase of montmorillonite: partially dehydrated montmorillonite. The broadening of the XRD reflections (Figure 1) indicated that, along with structural changes, a reduction in particle size occurred: from 6.63 nm for MMT to 4.32 nm for 1 h MCA MMT. With prolonged milling (more than 4 h), montmorillonite was transformed into an amorphous solid [25].



**Figure 1.** X-ray diffraction patterns of the montmorillonite before and after mechanochemical activation: 1-MMT, 2-0.5 h MCA MMT, 3-1 h MCA MMT.

SEM microphotograph samples of the natural MMT and the most reactive sample (MCA MMT 2 h) are shown in Figure 2. Particles of natural MMT have the shape of plates, which can be seen in Figure 2a. For the series of milled montmorillonite samples, the microstructure is changed with increasing the treatment time. Fine grinding of MMT in a planetary ball mill for 2 h changed the structure of MMT (Figure 2b). Contrary to natural MMT, the morphology of the mechanochemically activated sample (MCA MMT 2 h) is more uniform, with a predominance of spheroidal and (quasi)regular particles. As a result of mechanochemical activation, the flaky-edged particles appeared. So, the mechanochemical treatment of MMT samples leads to the formation of new more reactive surfaces [26,29,32].



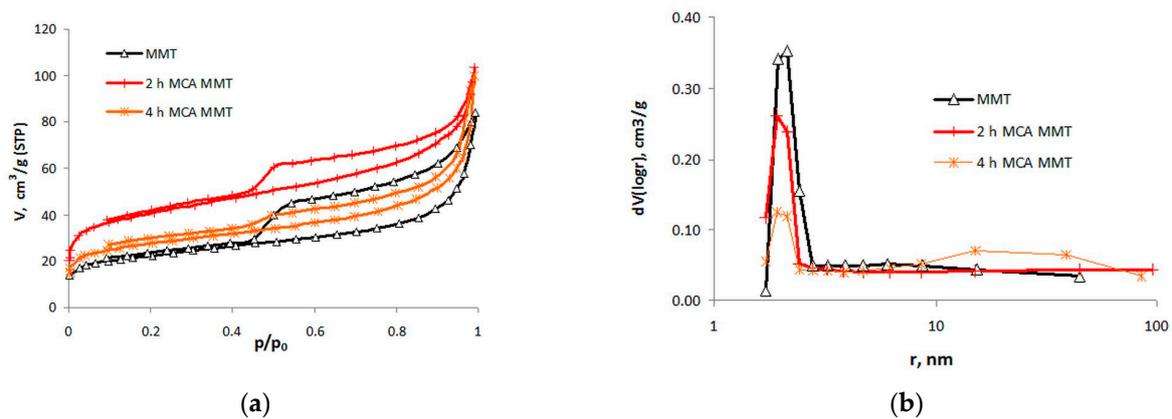
**Figure 2.** SEM microphotographs of the montmorillonite particles before and after mechanochemical activation: (a)—MMT; (b)—2 h MCA MMT.

The MCA treatment leads to a decrease in the structural order and an increase in the specific surface area of clays. The data calculated from nitrogen adsorption/desorption isotherms for MMT and MCA MMT samples showed that the dependence of specific surface area, total pore volume, as well as average pore radius  $r$  from activation time is non-monotonic, although there is a tendency for the values of these parameters to increase (Table 1).

**Table 1.** Characteristics of the porous structure for the montmorillonite before and after mechanochemical activation.

Sample	S, m <sup>2</sup> /g	V, cm <sup>3</sup> /g	r, nm	Distribution of Pore Sizes, nm				
				BJH dV (r)		DFT dV (r)		
				r <sub>1</sub>	r <sub>2</sub>	r <sub>1</sub>	r <sub>2</sub>	r <sub>3</sub>
MMT	89.1	0.078	1.753	1.98	-	1.41	2.75	-
0.5 h MCA MMT	117.4	0.140	2.377	2.142	-	1.17	2.44	0.64
1 h MCA MMT	93.4	0.131	2.811	2.142	-	1.25	2.64	0.64
2 h MCA MMT	146.8	0.161	2.187	1.92	-	1.13	2.64	0.67
4 h MCA MMT	99.1	0.155	3.128	1.90	15.10	1.21	2.54	0.64

Isotherms of the low-temperature nitrogen sorption-desorption (Figure 3a) for all samples have the waveform. According to the IUPAC classification, the obtained isotherms can be attributed to Type II [50]. The observed hysteresis loops in the range of values  $p/p_0 > 0.35-0.4$  can be classified as H3 type, indicating the presence of slit-like pores. Mesopore size distributions were obtained from the low-temperature nitrogen adsorption data according to the currently used Barret–Joyner–Halenda (BJH) method [46]. The maximum in the pore radius  $r_1$  distribution for the natural montmorillonite is centered at 1.98 nm (Figure 3b). This value slightly increases after MCA to 2.14 nm for 0.5 h and 1 h, and again decreases to 1.90 nm for 4 h treatment. In general, the specific surface area of investigated MMT samples increases with the increase in time of mechanochemical activation. The specific surface area increases from 89.1 m<sup>2</sup>/g for natural MMT up to 146.8 m<sup>2</sup>/g for 2 h MCA MMT. The specific surface area for this sample reaches the maximal value (Table 1). However, dependence on the specific surface area from the time of milling is irregular. This is because several different processes, which occur simultaneously, affect the change in specific surface area during the milling of solids, in general, and minerals, in particular. Thus, the first local maximum on this dependence, which is observed after milling for 0.5 h, is caused by the comminution of montmorillonite particles without significant destruction of crystal structure, as in work [32]. On the contrary, a decrease in specific surface area for samples, milled for 1 h, is associated with aggregation, which often takes place when the milling time is increased [26,33]. Milling for more than 1 h results in significant destruction of the crystal structure of montmorillonite and its amorphization, as mentioned above. This is the reason for the increase in the specific surface area for the sample milled for 2 h. A further increase in the time of mechanochemical activation leads to a decrease in the specific surface of montmorillonite samples, similar to the other clays: kaolinite and ripidolite [32]. This occurs due to the aggregation of amorphized particles. It should be noted that there is a similar irregular dependence of specific surface area from energy supplied by the ball mill for sodium montmorillonite [51].

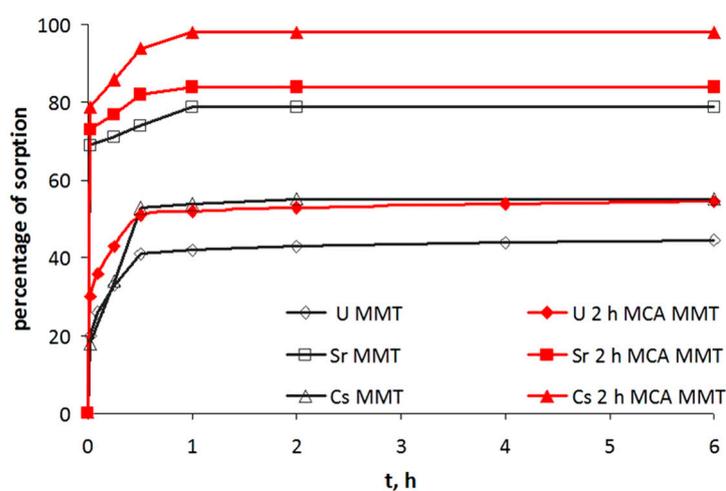


**Figure 3.** Nitrogen adsorption–desorption isotherms (a) and mesopore size distributions (b) of the montmorillonite before and after mechanochemical activation.

So, according to the theory of “mechanochemical activation”, the mechanical stress leads to the shifting of atoms from their equilibrium crystal lattice positions, bringing the solid into a high-energy metastable state, and to a further fracture of particles. The particles reach a critical size and solid materials begin to build up crystal defects and develop amorphous phases or other crystalline morphologies [52].

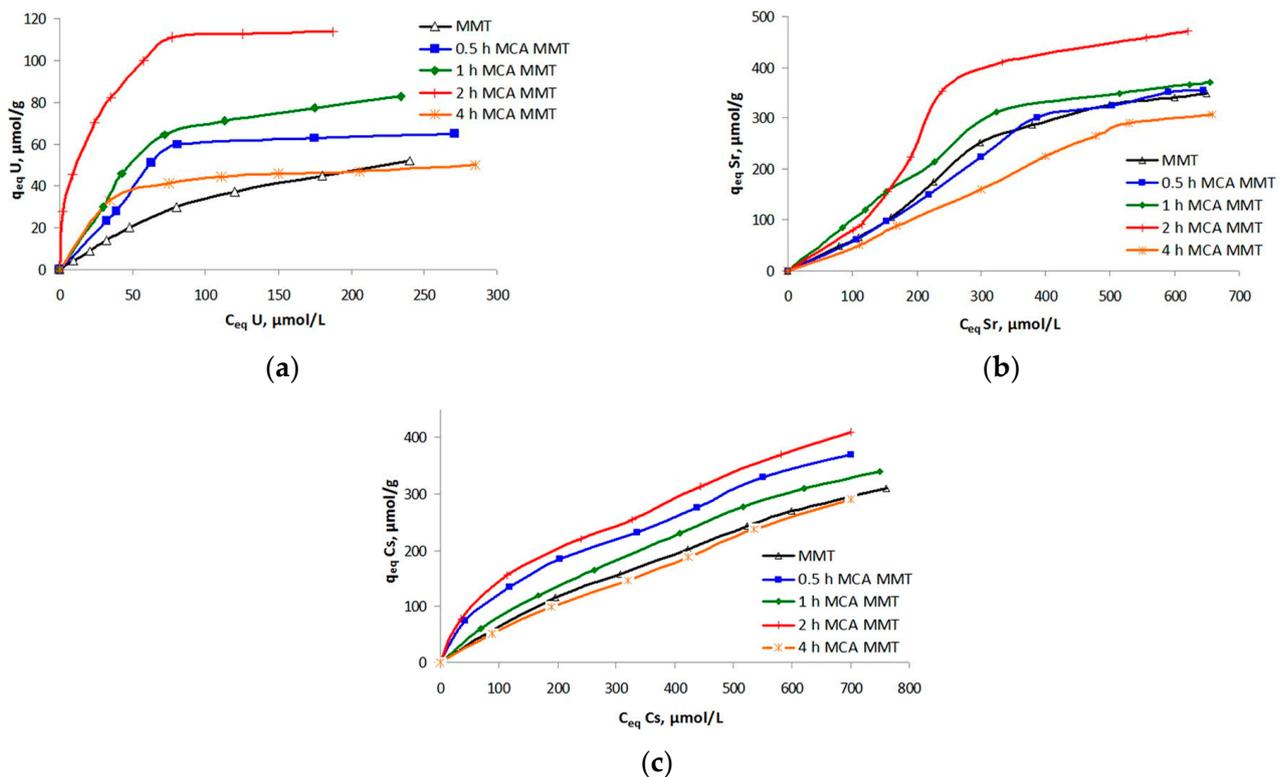
### 3.2. Adsorption Isotherms Study

Adsorption kinetics of uranium, cesium, and strontium ions from the aqueous solutions onto the natural and 2 h mechanochemical-activated montmorillonite was made up to equilibrium. Adsorption of U(VI), Ce(I), and Sr(II) on the natural and 2 h mechanochemical-activated montmorillonite as a function of the contact time is shown in Figure 4. Kinetic curves of the sorption of uranium, cesium, and strontium ions on all the samples indicate a sufficiently fast attainment of sorption equilibrium, within 15–20 min. In all the next sorption experiments, the duration was established as 1 h. The kinetics of U(VI), Ce(I), and Sr(II) adsorption onto natural and 2 h mechanochemical-activated montmorillonite can be significantly better described by the pseudo-second order rate equation.



**Figure 4.** Kinetic study of the sorption of uranium, cesium, and strontium ions on natural montmorillonite and 2 h mechanochemical-activated MMT.

Sorption isotherms of uranium (Figure 5a), strontium (Figure 5b), and cesium (Figure 5c) ions show that the sorption characteristics of the samples for mechanochemically activated MMT are higher compared to those of the natural mineral.



**Figure 5.** Sorption isotherms of uranium (a), strontium (b), and cesium (c) onto the montmorillonite before and after mechanochemical activation.

With an increase in the time of mechanochemical activation, the values of uranium sorption are 77.5, 105.3, and 123.5  $\mu\text{mol/g}$  for samples activated for 0.5, 1, and 2 h, respectively. However, further activation (4 h) leads to a sharp decrease in the amount of uranium sorption, to 53.5  $\mu\text{mol/g}$  (Table 2). For  $\text{Sr}^{2+}$  (Figure 5b) and  $\text{Cs}^+$  (Figure 5c) ions, the improvement in sorption values correlates with an increase in the duration of MCA in a similar way. The sorption values of the studied metals are correlated with the values of the specific surface area of montmorillonite (Table 1), which increases with increasing the activation time (0.5–2 h) from 89.1  $\text{m}^2/\text{g}$  to 146.8  $\text{m}^2/\text{g}$  and decreases with increasing the activation time (4 h) up to 99.1  $\text{m}^2/\text{g}$ .

The obtained sorption values of the studied metal ions on the natural montmorillonite are related to the peculiarities of its structure. Layered silicates are characterized by the presence of two main types of ion exchange centers, which differ sharply in their properties. These are exchangeable cations associated with non-stoichiometric isomorphous substitutions in the structure and are located on the basal surfaces of minerals, as well as broken silica or aluminum oxide bonds localized on the side faces of the crystals.

U(VI) is characterized by the possibility of existence in surface waters not only as uranyl ions ( $\text{UO}_2^{2+}$ ), but also in the form of positively charged, neutral, or even negatively charged products of hydrolysis and interaction with dissolved  $\text{CO}_2$ :  $[\text{UO}_2\text{OH}]^+$ ,  $[(\text{UO}_2)_3(\text{OH})_5]^+$ ,  $\text{UO}_2(\text{OH})_2$ ,  $\text{UO}_2\text{CO}_3$ ,  $[(\text{UO}_2)_2\text{CO}_3(\text{OH})_3]^-$ , etc. [10,11]. The dependence of U(VI) sorption values for montmorillonite on pH has an extreme character, with maximum values in a neutral media, which is characterized by a high degree of dissociation of  $\text{Si}(\text{Al})\text{OH}$  groups on the side faces of the mineral particles, which are mainly responsible for the sorption process, and in the presence of positively charged  $\text{UO}_2^{2+}$  as the dominant form of U(VI) [12].

**Table 2.** Langmuir and Freundlich parameters for the adsorption of uranium, strontium, and cesium ions onto natural and mechanochemical-activated montmorillonite.

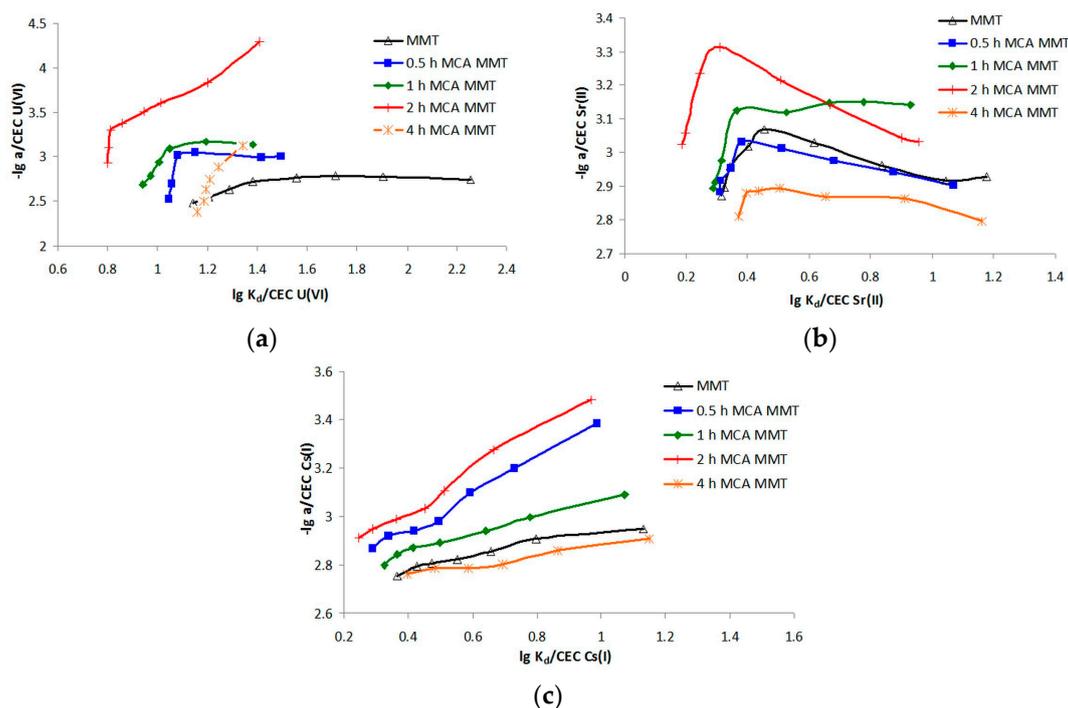
Sample	Radio-Nuclide	Langmuir			Freundlich		
		$q_m$ , $\mu\text{mol/g}$	$K_L$ , $\text{L}/\mu\text{mol}$	$R^2$	$1/n$	$K_F$ , $\text{L}/\mu\text{mol}$	$R^2$
MMT	U(VI)	86.2	6.44	0.995	0.748	9.53	0.980
0.5 h MCA MMT		77.5	21.50	0.967	1.078	19.53	0.765
1 h MCA MMT		105.3	15.83	0.983	0.324	8.49	0.917
2 h MCA MMT		123.5	81.00	0.996	0.317	10.49	0.914
4 h MCA MMT		53.5	46.75	0.999	0.191	6.13	0.953
MMT	Sr(II)	526.3	3.17	0.996	0.984	16.60	0.960
0.5 h MCA MMT		500.0	4.00	0.994	0.984	16.55	0.967
1 h MCA MMT		454.6	7.33	0.999	0.710	15.60	0.956
2 h MCA MMT		588.2	5.67	0.999	0.905	19.09	0.845
4 h MCA MMT		500.0	2.50	0.946	1.055	15.50	0.986
MMT	Cs(I)	714.3	0.93	0.979	0.799	13.52	0.998
0.5 h MCA MMT		384.6	5.20	0.975	0.570	14.20	0.998
1 h MCA MMT		526.3	1.90	0.969	0.729	14.01	0.999
2 h MCA MMT		416.7	6.00	0.967	0.550	14.75	0.998
4 h MCA MMT		588.2	1.06	0.969	0.834	13.32	0.999

$q_m$ —the amount of adsorbate corresponding to complete monolayer coverage;  $K_L$ —Langmuir bonding energy coefficient;  $K_F$ —Freundlich coefficient of adsorption capacity;  $n$ —coefficient of adsorption intensity;  $R$ —correlation coefficient.

Sorption of cesium and strontium ions on natural montmorillonite primarily occurs by the ion-exchange mechanism. Taking into account that the ion exchange on layered silicates is determined by the active centers of the basal faces, which account for the majority of the total exchange capacity, this factor is decisive in increasing the selectivity of montmorillonite to cesium ions.

The sorption of cesium and strontium ions on natural montmorillonite ( $q_m$  calculated from the Langmuir equation) are 714.3 and 526.3  $\mu\text{mol/g}$ , respectively. In addition, the exchange centers of the basal faces show a high affinity for cesium ions, which is due to the manifestation of a structural factor [25,38]. The ditrigonal holes of silica grids on the surface of clay minerals are proportional to the size of the large alkali metal cations. It is possible to localize large alkali metal ions in pseudo-hexagonal oxygen holes of tetrahedral networks of minerals. Cesium sorption occurs not only on the outer surface of particles. Penetration of cesium ions into the interlayer space occurs, replacing the corresponding ion-exchange positions.

Mechanochemical activation significantly improves the sorption properties of natural MMT by achieving a greater equilibrium sorption capacity in the region of low equilibrium concentrations of uranium ions in the solution. This can be seen visually from the slope of the sorption isotherms (Figure 5a) and can be quantified using  $K_d$  values (Figure 6). In the case of the sorption of cesium ions (Figure 6c), a consistent increase in the value of  $K_d$  with the time of MCA was observed. For uranium and strontium ions, the character of the dependence of the distribution coefficients has a more complicated form. The maximum values of coefficients of distribution for MMT/2 h MXA MMT are as follows:  $\text{ml/g}$ : uranium (438/14,000), cesium (641/2191), and strontium (841/1476).



**Figure 6.** The degree of montmorillonite surface filling before and after mechanochemical activation by uranium (a), strontium (b), and cesium (c) ions.

The observed nature of changes in the sorption properties of minerals after mechanical activation can be explained as follows.

The mechanochemical activation of montmorillonite at the initial stage leads to an increase in the fineness of particle grinding and significant structural changes, which is primarily associated with the disordering of the octahedral mesh and significant distortions in the tetrahedral meshes. At the same time, the main structural motif is preserved and, accordingly, ensures an increase in the number of pseudo-hexagonal silicon–oxygen holes, which are the most important active centers of the sorption of large cations [25,28,32,44].

At the same time, the mechanical activation of air-dried samples leads primarily to the fracture of lamellar particles of clay minerals and, thus, to an increase in the relative contribution of the side faces to the total surface of the samples. A high affinity of the most high-energy sorption centers localized on the so-called cleaved side faces to metal ions is observed. At the same time, it is possible to form strong surface complexes with uranium, cesium, and strontium ions, in the formation of which both surface hydroxyl groups and oxygen atoms of partially destroyed ditrigonal holes participate. Therefore, in the interlayer space of minerals near the side faces, the area easily accessible to metal ions increases [25,38,43].

The presence of various defects on the surface of the mineral determines the significant energy heterogeneity of the sorption centers. These structural defects, and, therefore, the functional groups of different compositions (exchangeable cations, surface hydroxyl groups, and oxygen of the tetrahedral network), play the role of active centers during adsorption and catalytic reactions. Surface  $\equiv Si-OH-$ ,  $=Al-OH-$ , etc., groups of the side surface of minerals behave like a mixture of acids of different strengths. During the mechanical activation of samples in air, the growth of the total specific surface area of the particles is largely due to the development of side faces, with partial destruction of the basal faces. It was established that in the process of mechanochemical activation, the number of acid groups per unit mass of the montmorillonite sample increases and amounts to 2.5 meq/g for natural MMT, 0.5 h MCA MMT, and 1 h MCA MMT, while for 2 h MCA MMT is 3.5 meq/g and for 4 h MCA MMT is 4.5 meq/g.

The applicability of the Freundlich equation (Table 2) to the description of sorption data indicates the significant energy heterogeneity of the sorption centers located on the surface. The measure of the energy heterogeneity of the surface is the coefficient  $1/n$ : the closer that the value of this coefficient is to unity, the more homogeneous the surface is. The obtained results indicate a noticeable increase in the energy heterogeneity of the sorption centers as a result of the mechanical activation of the samples. For cesium ions, the Freundlich correlation coefficient is very high: ( $R^2 = 0.998$ – $0.999$ ).

For the Langmuir monomolecular sorption equation, which indicates the energy homogeneity of active centers and, accordingly, the proximity of ion sorption energies as the surface is filled, the correlation coefficient is  $R^2 = 0.946$ – $0.999$ .

Figure 6 shows the filling of the mineral surface with metal ions. On the abscissa axis,  $\lg(q/CEC)$  is represented, characterizing the degree of surface filling, where  $q$  is the concentration of metal ions in the solid phase ( $\mu\text{mol/g}$ ) and  $CEC$  is the exchange capacity ( $\mu\text{mol/g}$ ). The ordinate axis shows  $\lg(K_d/CEC)$ , where  $K_d/CEC$  is the specific distribution coefficient.

Noticeably different natures of surface filling for uranium, strontium, and cesium ions can be observed in Figure 6. For cesium,  $\lg(K_d/CEC)$  changes as the montmorillonite surface is filled in the range from 1.13 to 0.37 for the original and from 0.97 to 0.24 for the 2 h mechanochemically activated mineral, which corresponds to the distribution coefficients of 641 and 408 for the original and 2191 and 586 for the mechanically activated for 2 h mineral. For uranium ions, as for strontium ions, there is a gradual filling of the surface with metal ions for the original mineral:  $\lg(K_d/CEC)$  increases from 2.26 to 1.14 for uranium per MMT with distribution coefficients of 400 and 217, respectively. The much faster filling occurs for mechanochemically activated samples: 2 h (1.41–0.80) and 4 h (1.34–1.16) for uranium, corresponding to distribution coefficients 14,000 and 608 (2 h) and 960 and 176 (4 h).

### 3.3. Effect of Natural Organic Compounds

It was established that at a uranium concentration of  $300 \mu\text{mol/L}$ , the sorption curves without and in the presence of  $100 \text{ mg/L}$  humic acid (HA) have a similar appearance (Figure 7). However, the values of uranium sorption in the presence of HA are significantly lower. This is determined by the fact that the presence of natural organic substances in the water environment, in particular, fulvic acids [12,17,53], significantly changes the values of uranium (VI) sorption. Namely, the formation of stable humate complexes with uranium leads to a decrease in sorption indicators for both natural MMT and MCA MMT.

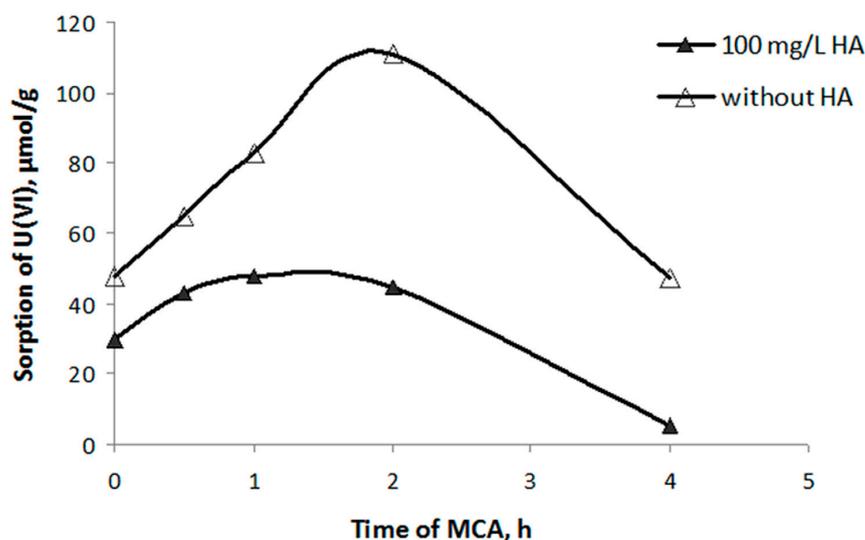


Figure 7. Effect of humic acids on uranium sorption at montmorillonite before and after mechanochemical activation in dependence of MCA time.

#### 4. Conclusions

Mechanochemical activation of montmorillonite during different times (0.5–4 h) leads to certain changes in its structure. First of all, the gradual destruction of the crystalline phase occurred during long-term grinding. Secondly, the morphology of the mechanochemical-activated sample (MCA MMT 2 h) becomes more uniform, with the dominance of spherical and (quasi)regular particles. Thirdly, MCA made it possible to achieve a fairly high degree of increase in the specific surface area, by almost two times (from 80.3 m<sup>2</sup>/g to 146.8 m<sup>2</sup>/g). A gradual increase in the total pore volume and an increase in the pore radius with increasing activation time were observed.

As a result of structural changes, the sorption properties of natural MMT improve primarily due to the increase in the equilibrium values of sorption and  $K_d$  in the region of low equilibrium concentrations of Cs, Sr, and U ions in the solution. The filling of the surface of natural montmorillonite and mechanochemical-activated montmorillonite occurs in various ways for the radionuclides uranium (VI), strontium (II), and cesium (I). The obtained sorbents can be effectively used to remove trace amounts of radionuclides of different chemical natures (uranium, cesium, and strontium) from polluted surface and underground waters. The noted fixation of radionuclides on the surface of mechanoactivated montmorillonite makes it possible to use it as a matrix for burying radioactive waste during heat treatment. The mechanochemically activated clays can be applied to the environmental protection technology in the engineered clay barriers in multibarrier systems for the control of radioactive contamination [18,19].

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