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EVALUATION OF SYNTHETIC CRYPTOMELANE AS AN ADSORBENT FOR SELECTIVE REMOVAL OF STRONTIUM IONS FROM WATER EFFLUENTS

Abstract. *^{90}Sr is a fission product of uranium, which has become a component of the environment due to nuclear weapon tests, the operation of nuclear fuel cycle enterprises and nuclear power plants, or radiation accidents. The chemical properties of strontium ions are similar to calcium, so the development of techniques for selective removal of strontium radionuclides from water effluents assumed greater importance in recent years. Manganese dioxide mineral species are considered promising adsorption materials for selective removal of strontium radionuclides from water effluents. Synthetic cryptomelane (manganese dioxide mineral with tunnel structure) was prepared by the hydrothermal method in an acidic solution. The results of X-ray diffraction and Fourier transform infrared spectroscopy confirmed the tunnel structure of the synthesized material. Results of scanning electron microscopy revealed that cryptomelane is formed as micron-sized rounded particles of cocoon-shaped morphology composed of nanofibers. To determine the efficiency of the as-synthesized cryptomelane in the selective removal of strontium ions from multicomponent solutions, the effect of contact time, foreign cations (Na, K, Ca), and pH on strontium ions adsorption was investigated in detail. The as-synthesized cryptomelan demonstrated fast adsorption kinetics and enhanced adsorption in an alkaline medium, as well as high adsorption efficiency in diluted multicomponent solutions. The desorption experiments demonstrated that strontium ions adsorbed by the synthesized cryptomelane cannot be easily desorbed. The obtained results allow considering synthetic cryptomelane as a promising material for selective removal of strontium ions from multicomponent solutions and further retention by the crystals.*

Key words: *Manganese dioxide, cryptomelane, selective adsorption, strontium radionuclides, water decontamination.*

Introduction

^{90}Sr (half-life ~ 28 years) is a fission product of uranium, which has become a component of the environment due to nuclear weapon tests, operation of nuclear fuel cycle enterprises and nuclear power plants or radiation accidents. The chemical properties of ^{90}Sr are similar to calcium ones, so when entering the human body, strontium radionuclides can easily replace calcium and cause damage to human health. Therefore, the development of techniques for selective removal of strontium radionuclides from contaminated waters become important in recent years.

Adsorption is the most effective and economical method used for purification of natural and technological waters contaminated by strontium radionuclides [1]. Synthetic inorganic adsorbents are the preferred materials due to their efficiency, radiation, and thermal stability. The highest selectivity to strontium ions was demonstrated by crystalline titanates, silicotitanates, oxides/hydrated oxides of titanium (IV), manganese (IV), zirconium (IV), and various composites [1–4].

High selectivity to strontium ions of some manganese dioxide-based adsorbents have been discussed in many publications [1-5]. The term “manganese dioxide” in most cases refers to a number of mineral species with layered (busserite, birnessite, etc.) or tunnel (cryptomelane, todorokite, etc.) structure. They are composed of MnO_6 octahedra (where Mn is represented predominantly by Mn^{4+} and Mn^{3+}) as the main building blocks [6].

There are several publications that show the high efficiency of synthetic cryptomelane for strontium and cesium ions removal from multicomponent solutions with inactive metal cations (Na, K, Ca, Mg) [5, 7]. According to these data, the adsorption of cesium and strontium radionuclides on synthetic cryptomelane is substantially governed by a cation-exchange reaction. The selectivity coefficients were estimated as $K_{Cs/K} = 0.6$ and $K_{Sr/K} = 1.0$.

Despite the fact that the synthetic cryptomelene is considered a promising adsorbent for strontium ions, the published information is not sufficient for practical application. Particularly, the adsorption kinetics of strontium ions, adsorption capacity, and the desorption procedure of strontium ions have not been investigated.

In this study, the synthetic cryptomelane was prepared by a hydrothermal method via the reaction between Mn(II) and Mn(VII) ions in an acidic medium. The synthesized cryptomelane was used for the removal of Sr ions from the model solutions in batch mode to evaluate the adsorption process.

Experimental

Synthesis of cryptomelane. Cryptomelane (α-MnO_2,) was prepared by the hydrothermal method under acidic conditions as described in [8]. Briefly, $KMnO_4$ solution (0.37M, 100 mL) was added to $MnCl_2$ solution (0.52 M, 30 ml) containing HNO_3 (65%, 3mL). The resulting suspension was then transferred into a Teflon-lined stainless steel autoclave, sealed and maintained at 100 °C for 24 h without shaking or stirring. The obtained black precipitate was filtered, washed several times with distilled water, and then dried at 120 °C for 12 h in air.

All chemicals were of analytical grade and were used as received without additional purification. Nonradioactive $SrCl_2{\times}6H_2O$ was used as a surrogate for ^{90}Sr because of its identical chemical characteristics.

Characterization procedure and ***adsorption experiments*** are well described in [9]. All the experiments were performed in duplicate.

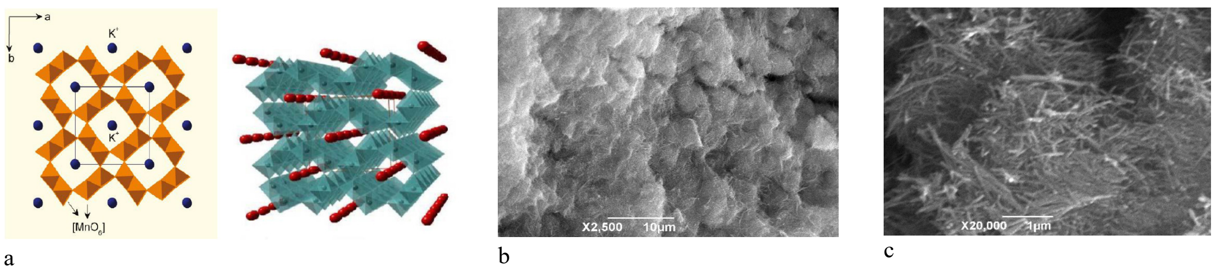
Results and discussion

Cryptomelane belongs to the hollandite-type minerals with a well-defined one-dimensional tunnel structure (Fig. 1a). Cryptomelane structure is composed of double chains of edge-shared MnO_6 octahedra linked at vertices to form (1 × 1) + (2 × 2) tunnels. The small (1 x 1) tunnels in the cryptomelane phase are empty, and the larger ones (2 × 2) with a pore size of 4.6 Å are filled with potassium ions and water molecules to stabilize the structure. A general formula of cryptomelane is $A_xMn_8O_{16}$ (A denotes the cations in the (2 x 2) tunnels; $0 \leq x \leq 2$, in most cases A is potassium cation) [6, 8]. Although in natural cryptomelane the tunnel sites are occupied primarily by K^+, variable amounts of other cations (Ca, Na, Ba, Ag, Sr, Pb, Zn, Co, etc.) and water molecules can be also present [10, 11].

The synthesized product is micron-sized rounded particles of black color. SEM images show that particles have cocoon-shaped morphology (Fig.1 b) and they are composed of nanofibres. At higher magnification (Fig.1 c), the individual nanofibers with an average width of ~ 50 nm and a length of ~ 1 µm can be seen. The nanofibers are dense, with a uniform uniform diameter along the entire length. The EDS spectrum of the outer surface (Fig.1 d, e) demonstrates the presence of peaks corresponding to K, Mn, and O elements. The average atomic ratio of K/Mn is about 0.115.

The X-ray diffractogram of the synthesized sample (Fig. 2 a) exhibits several well-defined and symmetrical peaks pointing on well crystallized material. The peaks observed at 2θ =12.8° (110), 18.1° (200), 25.8 (220), 28.8° (310), 37.7° (211), 42.2° (301), 49.8° (411), 56.0 (600) match the pattern of the standard cryptomelane with tetragonal symmetry corresponding to KMn_8O_{16}, (JCPDS 29-1020).

The FTIR spectrum of the synthesized sample (Fig. 2 b) displays absorption bands similar to those previously reported for cryptomelane [12, 13]. The broad band at 3300 cm^{-1} is attributed to the stretching vibration of hydroxyl groups. The absorption band at 1635 cm^{-1} is attributed to the hydroxyl groups bending vibration of water molecules. An intensive peak at 720 cm^{-1} has been mentioned in many publications describing the FTIR cryptomelane spectra



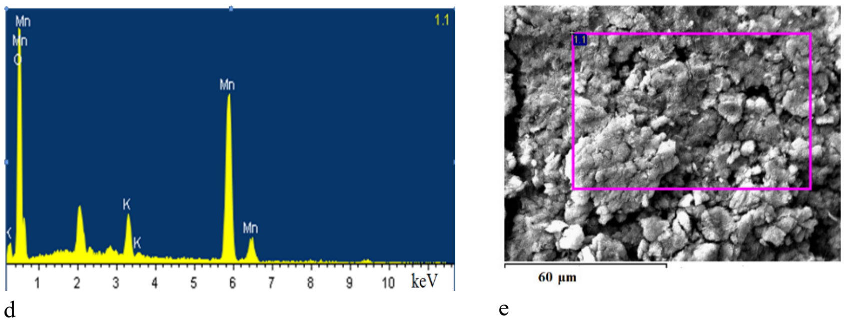


Fig. 1. Schematic structure of cryptomelane (a); Representative SEM images of the synthesized cryptomelane (b, c); EDS spectrum of the surface part of the synthesized cryptomelane (d, e)

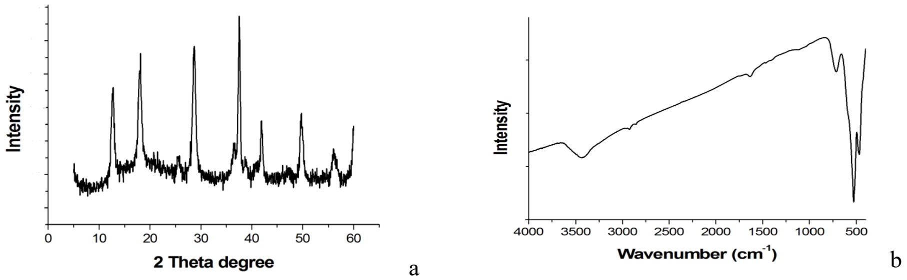


Fig. 2. Diffraction pattern (a) and FTIR spectra (b) of the synthesized cryptomelane

(variations from 708 to 720 cm^{-1}), and obviously, it is among the main characteristic vibrations of the MnO_6 octahedral framework of cryptomelane [13].

Strontium ions adsorption studies. To determine the efficiency of the synthesized cryptomelane for the selective strontium ions removal from multicomponent solutions, the effect of contact duration, pH, and competitive ions (Na, K, Ca) on strontium ions adsorption was carefully investigated (Fig.3).

The effect of contact time on the amount of strontium ions adsorbed by the synthesized cryptomelane (Q_{Sr}, mg/g) from the monocomponent solution with Sr ions concentration of 40 mg l^{-1} (Fig. 3 a) demonstrates that strontium ions adsorption is a fast process; it has reached equilibrium within 60 min.

The effect of pH on strontium ions adsorption on the synthesized cryptomelane was studied in a model monocomponent solution with Sr ions concentration of 40 mg l^{-1} (Fig. 3b). The adsorption capacity increases almost linearly from 2.4 to ~ 11 mg g^{-1} with increasing pH from 3 to 11. Thus, the experimental studies have revealed that the alkaline medium is preferable for the effective removal of strontium ions from multicomponent solutions using cryptomelane as an adsorbent.

The effect of foreign ions concentration on strontium ion adsorption was studied using four sets of model solutions with neutral pH, equal concentration of strontium ions (40 mg l^{-1} or ~ 0.46 mmol l^{-1}), and various concentrations of foreign ions. One of them contained only strontium ions. Other set of the solutions along with strontium contained sodium ions (0.01, 0.13, and 0.26 mol l^{-1}). The third set of the solutions along with strontium contained potassium ions (0.01, 0.07, and 0.17 mol l^{-1}, respectively). And the fourth set of the solutions contained strontium and calcium (0.01, 0.03, and 0.06 mol l^{-1}) ions. The adsorption capacity of the synthesized cryptomelane was examined, and the obtained results are presented in Fig. 3 c. The obtained results testify that the occurrence of sodium and potassium ions in the model solutions leads to a reduction of the Q_{Sr} values. The most notable decrease in strontium ions adsorption on the synthesized cryptomelane occurs in the model solutions with calcium ions. The obtained results are in a good agreement with those presented for the as-synthesized cryptomelane [5], where a decrease of ^{89}Sr distribution coefficient with increasing of foreign ions concentration (Na, K, Ca, and Mg) was demonstrated.

However, it should be noted that the model solutions presented here can be considered "rigid experimental conditions". The sodium ion concentration, for example, in one of the model solution (0.26 mol l^{-1} or about 6,000 mg l^{-1}; Sr:Na= 1:560) is several hundred times higher than that in tap water (2-20 mg l^{-1}) and only one and a half times lower than sodium ion concentration in typical seawater (10000 mg l^{-1}). The calcium ion concentration in other model solutions (0.03 mol l^{-1}, or 1200 mg l^{-1}; Sr:Ca= 1:65) is also much higher than that in tap water (2–85 mg l^{-1}) [14] and even higher than that in seawater (~ 470 mg l^{-1}) [15].

Desorption of strontium ions. There is no available information on the desorptin of strontium ions from Sr-loaded cryptomelane. Earlier it was shown that Sr-loaded birnessite (manganese dioxide with a layered structure) could be completely regenerated in 0.1 M HCl and 1 M NH_4NO_3 solutions [9]. The desorption of Sr ions from the Sr-loaded cryptomelane was also carried out using 0.1 M HCl and 1 M NH_4NO_3 solutions as desorbing agents. The obtained results have shown that after 24-h treatment the desorption efficiency of the first solution was 4.6 % and the second one – 5.2 %. These results suggest that strontium ions adsorbed by the cryptomelane have been stabilized there and cannot be easily desorbed.

Conclusions

Synthetic cryptomelane was prepared by the hydrothermal method via the reaction between Mn(II)

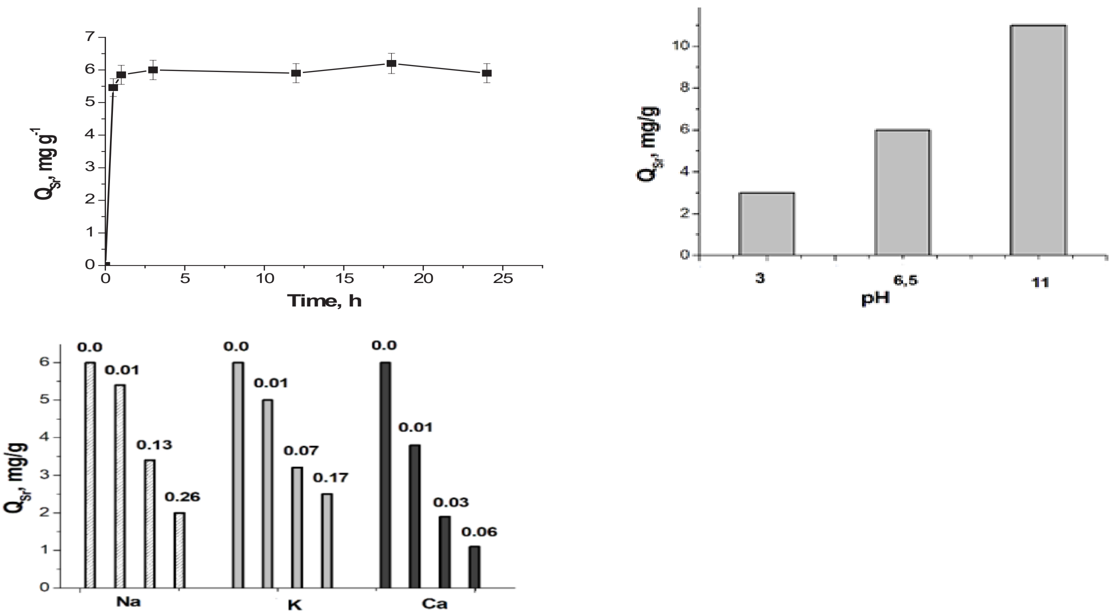


Fig. 3. The influence of the experimental conditions on the amount of Sr ions adsorbed by the synthesized cryptomelane.
Initial strontium concentration - 40 mg l^{-1}; adsorbent dose - 3.33 g l^{-1}; pH ~ 6.5; T - 298 K.
Effect of contact time (a); Effect of pH (b); Effect of foreign ions concentration (c).

and Mn(VII) ions in the acidic solution. The results of X-ray diffraction and FTIR analysis confirmed the tunnel structure of the synthesized material.

Results of SEM analysis revealed that cryptomelane is formed as black-colored micron-sized rounded particles of cocoon-shaped morphology composed of nanofibres with an average width of ~ 50 nm and a length of ~ 1 μm.

The strontium ions adsorption on the synthesized cryptomelan was studied as a function of contact time, pH, and presence of foreign cations (Na, Ca, K) in the model solutions. The as-synthesized cryptomelan demonstrated fast adsorption kinetics, enhanced adsorption in an alkaline medium, and high adsorption efficiency in diluted multicomponent solutions.

Although the cryptomelane adsorption capacity decreases with the increase in the foreign ions concentration the synthesized cryptomelane can be considered as an adsorbent with rather high selectivity to strontium ions, taking into account the sufficiently high adsorption parameters obtained when sorbing from the model solutions with a significant excess of foreign ions over strontium ions.

The currently presented results demonstrated that cryptomelane is a promising material for the removal of strontium ions from multicomponent solutions and further retention of them inside the crystals. However, before being suitable for industrial application, cryptomelane should be transformed from finely dispersed powder form to nanocomposite materials.

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ОЦІНКА СИНТЕТИЧНОГО КРИПТОМЕЛАНУ ЯК АДСОРБЕНТУ ДЛЯ СЕЛЕКТИВНОГО ВИЛУЧЕННЯ ІОНІВ СТРОНЦІЮ ЗІ СТІЧНИХ ВОД

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Анотація. *У результаті випробувань ядерної зброї, роботи підприємств ядерного паливного циклу, атомних електростанції та радіаційних аварій радіостронцій, як продукт поділу урану, став компонентом навколишнього середовища. Цей радіонуклід є аналогом кальцію, тому розвиток методів селективного видалення радіостронцію зі стічних вод є актуальною проблемою. Мінерали діоксиду мангану розглядаються як перспективні адсорбційні матеріали для селективного видалення радіостронцію з водних розчинів. Синтетичний криптомелан (мінерал з тунельною структурою) був синтезований в кислому розчині з використанням гідротермального методу. Результати рентгенівської дифракції та інфрачервоної спектроскопії Фур'є підтвердили тунельну структуру синтезованого матеріалу. Результати сканувальної електронної мікроскопії показали, що криптомелан утворюється у вигляді округлих частинок мікронного розміру, які складаються з нановолокон. З метою визначення селективних властивостей синтезованого мінералу з багатокомпонентних розчинів проведено детальні дослідження впливу часу реакції, концентрації катіонів що конкурують (Na, K, Ca), та pH розчину на адсорбційну поведінку іонів стронцію. Синтетичний криптомелан продемонстрував швидку кінетику і підвищену адсорбцію в лужному середовищі, а також високу ефективність адсорбції з багатокомпонентних розчинів. Десорбційні експерименти показали, що іони стронцію, які вилучаються синтетичним криптомеланом, не можуть бути легко десорбовані. Отримані результати дозволяють розглядати синтетичний криптомелан як перспективний матеріал для селективного вилучення іонів стронцію з багатокомпонентних розчинів.*

Ключові слова: *діоксид мангану, криптомелан, селективна адсорбція, радіостронцій, дезактивація водних розчинів.*