

Proceeding Paper

# Clay-Based Sorbents for Environmental Protection from Inorganic Pollutants <sup>†</sup>

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**Abstract:** Natural clay minerals are widely used in various environmental protection technologies as cheap, accessible, and effective sorbents. Considering the tasks and conditions for purification of polluted waters the different methods of surface modification of clay minerals were used. The surface modification of the montmorillonite by cationic surfactants (hexadecyltrimethylammonium bromide); the method of surface modification of montmorillonite by large-sized inorganic cations of Fe, Al, Zr, Ti; applying nanoscale zero-valent iron powder to the montmorillonite surface were used for increasing of efficiency of water purification from chromium (VI) and uranium (VI).

**Keywords:** contaminated water; heavy metals; radionuclides; clay minerals; surface modification

## 1. Introduction

Heavy metals and radionuclide compounds are among the ones of all the standard pollutants of surface and underground waters. They have increased toxicity for living organisms and humans even at very low concentrations in water [1,2]. The main sources of environmental pollution with uranium compounds are nuclear fuel cycle enterprises. In Ukraine, nuclear fuel cycle enterprises are located in the Kryvyi Rih Basin [3]. To a much lesser extent, environmental pollution is associated with the use of depleted uranium munitions, which take place in places of armed conflicts [4]. Chromium occupies a special place among heavy metals due to its high toxicity. Chromium compounds are found in the effluents of electrochemical industries and wastes of the hydrometallurgical industry. The maximum allowable limits in water according to World Health Organization are low: 0.03 mg/L for uranium compounds and 0.05 mg/L for chromium compounds [5]. Therefore, problems of environmental protection from inorganic pollutants are becoming more and more relevant.

To remove trace amounts of toxicants, the most effective are sorption methods that combine high selectivity to the target compounds with sufficient productivity. The special attention is paid to the development of sufficiently cheap sorbents. Natural clay minerals are widely used in various environmental protection technologies. However, their significant drawback is insufficient sorption capacity, especially to anionic forms of pollutants. Thus, the maximum sorption of Cr(VI) ions on kaolinite with a specific surface of 15.54 m<sup>2</sup>/g is only 3.33·10<sup>-7</sup> mol/g [6]. Therefore, various methods of surface modification to increase the effectiveness of clay minerals are used. There is the use of surfactants, hydroxo complex of inorganic cations, nanoparticles of active metals, etc. These methods make it possible to obtain cheap “low cost” sorbents with improved sorption properties for their application in environmental protection technologies.

Modification of the surface of layered silicates with organic substances quaternary ammonium bases [7] allows for a significant increase in their sorption properties to nonionic organic compounds and anionic forms of dangerous inorganic toxicants

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(chromium, arsenic, uranium, etc.). Both negatively and positively charged areas are formed on the surface of particles-active centers of sorption processes. Thus, organobentonite with different degrees of surface modification shows high efficiency to U(VI) ions in a wide pH range [8,9]. The maximum values of sorption on organobentonite modified with hexadecyltrimethylammonium bromide (HDTMA,  $(C_{16}H_{33})N(CH_3)_3Br$ ) are 17.39 and 12.44 mg/g at medium pH of 7 and 9, respectively [10]. Significant amounts of sorption of anionic forms of U(VI) in the alkaline pH region are also achieved for the modified HDTMA fibrous silicate sepiolite [11]. For samples modified by hexadecyltrimethylammonium bromide, hexavalent chromium sorption values are 30 mmol/kg for kaolinite and 795 mmol/kg for montmorillonite at  $pH < 1$  [12]. When modifying the surface of kaolinite, illite, and smectite using HDTMA in quantities sufficient to form a monolayer, the removal of chromate, arsenate, and nitrate ions from aqueous solutions were recorded [13,14].

The intercalation of large inorganic cations into the interlayer space of clays of smectite groups is the perspective method of modification. The inorganic cations migrate into the interlayer space of clay minerals, fixed, and create two-dimensional zeolite-like materials. These materials-pillared interlayered clays (PILC)-have adjustable flat micropore sizes and high heat resistance [15,16]. For modification of montmorillonite Fe, Zr, and Fe/Zr ions were used; the maximum sorption capacity for chromium (VI) ions was 16.24; 19.24, and 22.34 mg/g [17].

The use of nano-sized powders of zero-valent iron in nature protection technologies is associated with significant difficulties due to their high tendency to rapid oxidation and aggregation. An effective method of solving this problem is the immobilization of nanoparticles of zero-valent iron on the surface of organic and inorganic materials: activated carbon, silica gel, diatomite, cellulose, graphene, and clay minerals [18,19]. Montmorillonite-supported zero-valent iron allows for significantly higher removal efficiency of U (VI) compounds from water (99.2%) than using zero-valent iron (48.3%) [20]. For an iron-containing sorbent based on fibrous silicate-sepiolite, the maximum value of sorption of Cr (VI) is 43.86 mg/g, which is one of the highest values obtained during the sorption of hexavalent chromium compounds [21,22].

The aim of our article was the comparison of the purification efficiency the contaminated of uranium and chromium compounds water with the sorbents on the base of montmorillonite modified by the different methods.

## 2. Materials and Methods

The most common mineral of the smectite group of ones-montmorillonite (MMT) was taken from the Cherkasy deposit (Ukraine). The 2:1 structure of montmorillonite is composed of one octahedral sheet that is contained between two tetrahedral sheets. Large amounts of water can be accommodated between the layers of MMT [23]. The general structural formula of montmorillonite is  $(Ca_{0.12}Na_{0.03}K_{0.03})_{0.18}(Al_{1.39}Mg_{0.13}Fe_{0.44})_{1.96}(Si_{3.88}Al_{0.12})_{4.0}O_{10}(OH)_2 \cdot nH_2O$ , the cation exchange capacity (CEC) is 1.0 mmol/g.

Modification of the surface of MMT was carried out by (i) cationic surfactant HDTMA [9]; (ii) the salts of inorganic cations Al, Zr, Ti, Fe [24,25]; (iii) zero-valent iron by reduction of ions  $Fe^{3+}$  with a solution of sodium borohydride in a nitrogen atmosphere [20,26]. The synthesized samples of sorbents were named MMT-HDTMA; MMT-PILC; MMT-ZVI.

Low-temperature nitrogen adsorption isotherms were determined on a volumetric automatic apparatus (Quantachrome, Nova 2200e) at  $-196$  °C. The surface morphology of MMT was studied by scanning electron microscopy SEM on a Jeol JSM-6060 instrument.

Sorption experiments on the removal of uranium (VI) and chromium (VI) ions from water were performed from a solution prepared from uranyl trihydrosulfate salt ( $UO_2SO_4 \cdot 3H_2O$ ) and potassium dichromate  $K_2Cr_2O_7$ . The ionic strength was created with a solution of NaCl. Experimental studies on the effect of pH were performed at initial

concentrations of each of the heavy metals 100  $\mu\text{mol/L}$ . Sorption isotherms were obtained at pH 6. The sorption values from the solutions were determined under static conditions in a thermostated cell at 25  $^{\circ}\text{C}$  with continuous shaking of the samples for 1 h (volume of the aqueous phase-50 mL, the mass of sorbent-0.1 g). After establishing the adsorption equilibrium, the liquid phase was separated by centrifugation (6000 rpm). The equilibrium metal concentration was determined spectrophotometrically (UNICO 2100UV) using an Arsenazo III reagent at a wavelength of 665 nm for U (VI) and a diphenylcarbazide at a wavelength of 546 nm for Cr (VI). The sorption U(VI) and Cr (VI)  $a$ ,  $\mu\text{mol/g}$ , was calculated by the formula:

$$a = (C_{\text{in}} - C_{\text{eq}}) \cdot V/m,$$

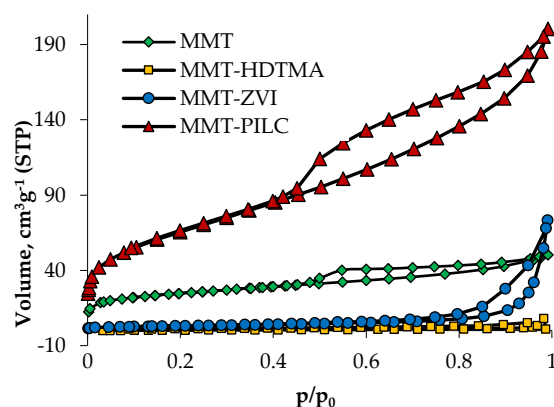
where  $C_{\text{in}}$ ,  $C_{\text{eq}}$ -the initial and equilibrium concentration of the metal,  $\mu\text{mol/L}$ ;  $V$ -volume of solution, L;  $m$ -mass of the sample of sorbent, g.

### 3. Results and Discussion

The modification of the surface of MMT by cationic surfactant HDTMA was confirmed (i) the increase in the basal reflex on the MMT-HDTMA diffractograms from 1.23 nm to 2.81 nm, (ii) the change in the  $\xi$ -potential of the particles from -65 to 55 mV, and (iii) the appearance of characteristic bands at 2920  $\text{cm}^{-1}$  and 2850  $\text{cm}^{-1}$  in the IR spectra of surfactant modified samples [9]. An increase in the values of the basal reflex on the diffractograms from 1.261 for MMT to 1.736 nm for A1-PILC, 1.81 for Zr-PILC, and 1.55 for Ti-Fe-PILC samples indicate an increase in the interlayer space of the mineral. This is the main characteristic of the successful intercalation process that is judged [24,25]. The appearance of peaks 0.252 and 0.202 nm of iron compounds ( $\alpha$ -Fe, FeO, FeOOH) in the diffractograms of the synthesized samples MMT-ZVI indicates the modification of the MMT surface with nanoscale zero-valent iron [26].

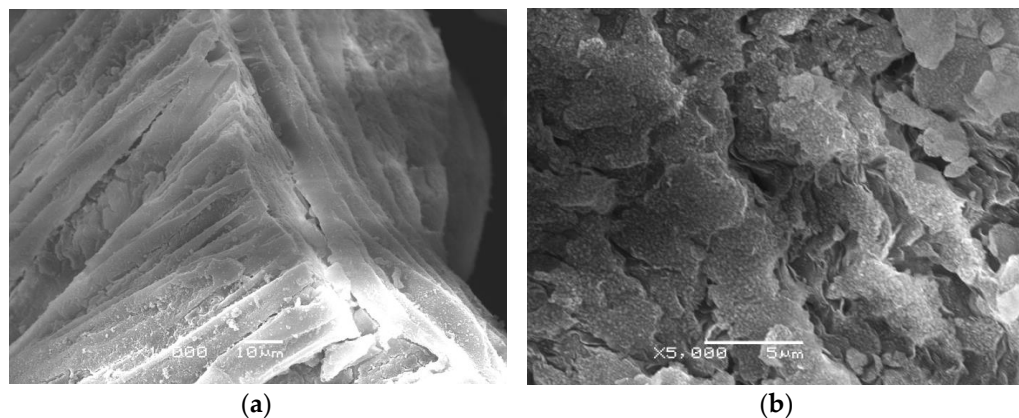
The nitrogen sorption isotherm on the natural montmorillonite (Figure 1), according to the modified de Boer classification, belongs to type II isotherms and is typical for non-porous sorbents with a small macroporous component [27]. The nature of the nitrogen adsorption curves on the samples of MMT-HDTMA, MMT-ZVI, and MMT-PILC are similar to MMT. In the range of values  $p/p_0 > 0.4$ , the pronounced hysteresis loops can be observed on isotherms (MMT, MMT-ZVI, MMT-PILC) indicating the presence of a well-developed structure of H3 type meso and macropores typical for such samples.

The specific surface area of MMT (89.1  $\text{m}^2/\text{g}$ ) sharply decreases after the surface modification and consists of 2.3  $\text{m}^2/\text{g}$  for MMT-HDTMA and of 24.7  $\text{m}^2/\text{g}$  for MMT-ZVI. Such reduction is stipulated by practically complete filling of micropores with surfactant molecules or iron nanoparticles the resultant blocking of the access of nitrogen molecules to these pores. The sample of MMT-PILC has an increased specific surface area of 236.2  $\text{m}^2/\text{g}$ . This is due to the formation of stable two-dimensional porous structures in the interlayer space of the mineral.



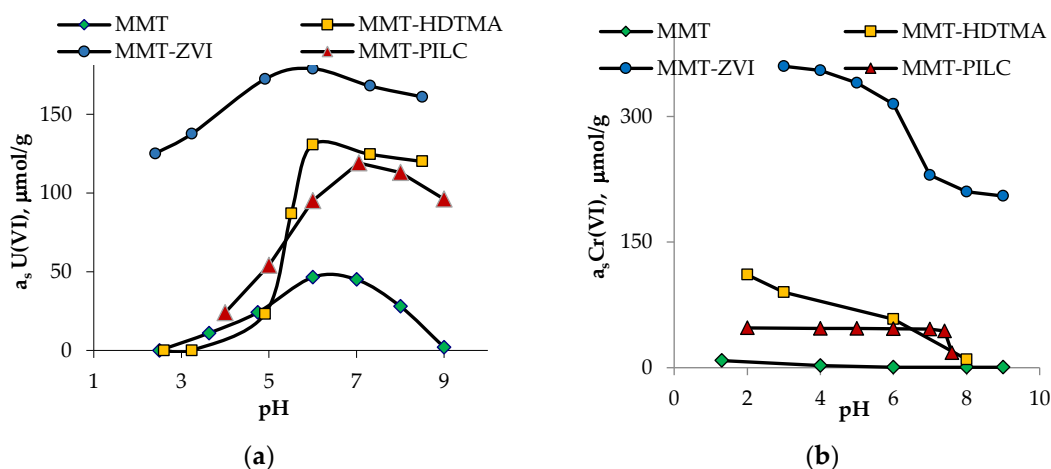
**Figure 1.** Nitrogen adsorption-desorption isotherms of natural and modified montmorillonites.

The layered structure of montmorillonite is shown in Figure 2a. As it is shown in Figure 2b, in the sample MMT-HDTMA the montmorillonite surface is covered by cluster forms of the surfactant mainly. The total organic carbon content of MMT-HDTMA was 9.29% (*w/w*) which corresponds to 11.14% (*w/w*) of the HDTMA-ions.



**Figure 2.** SEM microphotographs of the particles of natural (a) and HDTMA modified (b) montmorillonite.

The dependence of the sorption values of uranium and chromium ions on the surface of natural and modified montmorillonite from pH is presented in Figure 3. The curve MMT for U(VI) (Figure 3a) has a characteristic form with a marked minimum in the acidic and alkaline pH areas. In the neutral pH area, the charge of the MMT surface and the charge of uranium ions have opposite signs. It influences the proceedings of sorption processes and the appearance of the maximum on the curve [26]. Natural MMT practically does not remove chromium anions due to the negative surface charge in a wide pH range (Figure 3b). The forms of heavy metals in the solution affect the sorption values [28]. Uranium in the acidic pH area exists in the uranyl cation  $UO_2^{2+}$  while in the neutral and alkaline area in solution, uranium exists mainly in the form of neutral  $UO_2(OH)_2$ ,  $UO_2CO_3$  and negatively charged species  $(UO_2)_2CO_3(OH)^{-}$ . In natural waters under aerobic conditions, chromium is in the form of  $HCrO_4^-$  and  $CrO_4^{2-}$  depending on the pH of the environment.

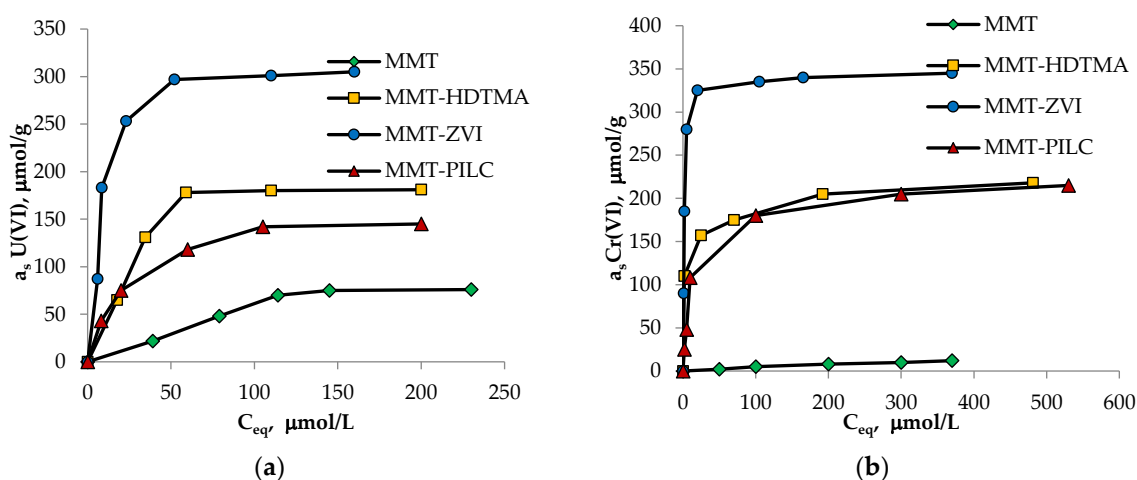


**Figure 3.** Effect pH on U(VI) (a) and Cr(VI) (b) sorption by the natural and modified MMT.

The surface modification of MMT by organic and inorganic compounds leads to exchange its sorption characteristics and expanding the pH range of sorbents. The values of uranium sorption on MMT-HDTMA and MMT-PILC samples increase in the alkaline pH

region (Figure 3a). The values of chromium sorption on MMT-HDTMA and MMT-PILC samples increase in the acidic and neutral pH region (Figure 3b). MMT-ZVI samples significantly improve the sorption of uranium (VI) and chromium (VI) in the all range of pH, with a maximum for uranium at pH 4–7, for chromium at pH 3–5.

Sorption isotherms of uranium and chromium ions show that the sorption characteristics of samples of montmorillonite (Figure 4) modified with surfactant or salts of inorganic cations or zero-valent iron are much higher as compared to those for natural mineral MMT (76  $\mu\text{mol/g}$  U(VI) and 12  $\mu\text{mol/g}$  Cr(VI)). The maximum sorption capacity of modified montmorillonite were for MMT-HDTMA 181  $\mu\text{mol/g}$  U(VI) and 218  $\mu\text{mol/g}$  Cr(VI); for MMT-PILC 145  $\mu\text{mol/g}$  U(VI) and 215  $\mu\text{mol/g}$  Cr(VI); for MMT-ZVI 305  $\mu\text{mol/g}$  U(VI) and 345  $\mu\text{mol/g}$  Cr(VI).



**Figure 4.** Isotherms of sorption of U(VI) (a) and Cr(VI) (b) by the natural and modified MMT.

Organoclays MMT-HDTMA can retain harmful substances due to the formation of surface sorption complexes with uranium and chromium compounds. Active sorption centers of MMT-PILC samples are hydroxyl groups of the metals in the interlayer space. Removal of U(VI) and Cr(VI) from water on the MMT-ZVI samples occurs primarily due to the exchange of hydroxyl ions of the hydroxide film on the surface of nanoscale iron particles by uranium or chromium complexes. In addition, for the samples MMT-ZVI the reduction of U(VI) to U(IV) and Cr(VI) to Cr(III) can occur with the next immobilization of uranium or chromium compounds on the surface of the sorbent.

#### 4. Conclusions

Sorption materials on the base of montmorillonite (organoclays, pillared clays, clay-supported zero-valent iron) were used for the removal of inorganic pollutants uranium (VI) and chromium (VI) from contaminated water. A significant increase in the sorption characteristics of the synthesized materials was shown. The obtained sorbents can be widely used in water purification technologies and modern environmental protection technologies. It is advisable to carry out organophilization of clays when underground reaction barriers are created in the soil along the path of movement of polluted waters. The use of pillared clays is effective for the deep cleaning of small volumes of water from heavy metals and radionuclides. Sorbents based on zero-valent iron and clay minerals can be widely used both in the mode of water purification on underground permeated reactive barriers and on traditional sorption technological equipment.

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