

DETERMINATION OF THERMODYNAMIC PARAMETERS OF CHROMIUM(VI) ADSORPTIONS ON ORGANOSILANIZED SEPIOLITES

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Abstract: *The adsorption of anionic species of chromium(VI) on the organosilanized sepiolites from aqueous solution at 298 K for different initial solution pH values was investigated. Natural, acid activated and thermo-acid activated sepiolites were functionalized by covalent grafting mercapto-silane and amine-silane to the silanol groups onto the sepiolite surface. It was examined applicability of three models of adsorption isotherms to the process of adsorption of Cr(VI). Adsorption equilibrium data for all amine-silane functionalized sepiolites fitted well to the Freundlich model, and Dubinin-Radushkevich model can successfully describe the equilibrium data for all mercapto-silane functionalized sepiolites. By determining the thermodynamic parameters it is possible to predict the nature and possible mechanisms of the adsorption process. The values of the thermodynamic parameters indicate a spontaneous adsorption process of a prevalently physical nature. Understanding of adsorption Cr(VI) by functionalized sepiolites has a major impact on a variety of industrial applications and environmental protection.*

Keywords: *Chromium(VI), Adsorption, Sepiolite, Thermodynamic parameters*

1. INTRODUCTION

Several methods for removing chromium(VI) from aqueous solutions have been perfected. The most commonly used methods are: chemical deposition, ion exchange, ultrafiltration, flotation, electrocoagulation, extraction, electrochemical deposition, reverse osmosis, electrodialysis, adsorption, evaporation, cementation, blowing air, blowing water vapor and flocculation. Chemical precipitation is traditionally the most widely used method. Of the chemical precipitation processes, which include the precipitation of hydroxides, sulfides, carbonates and phosphates, the most commonly used method for the removal of chromium is the reduction of Cr(VI) to Cr(III) in an acidic medium with a pH of approximately 2.0 and subsequent precipitation of chromium hydroxide Cr(III) by increasing the pH of the medium to 9.0 - 10.0 using lime [1]. The disadvantage of the precipitation process is the formation of sediment, and sediment deposition is a problem for the environment. The best results are achieved by applying ion exchange, reverse osmosis, filtration and electrocoagulation, but these methods are uneconomical due to high operating costs [2 – 5].

Adsorption on appropriate adsorbents has proven to be a practical, efficient and economically viable method for removing contaminants from aqueous solutions and for separating adsorbed species for further analysis or regeneration. By properly designing and managing the adsorption process, it is possible to obtain purified water of high quality. In recent years, the method of removing chromium(VI) from aqueous solutions by adsorption on solid adsorbents of mineral, organic or biological origin, the most important of which are activated carbon, zeolites, clays, industrial by-products, agricultural waste, biomass, polymeric organic resins and macroporous polymers [6 – 8].

Due to their high prevalence in soil and sediments, low prices and large specific surface area, clay minerals were investigated as possible adsorbents of hexavalent chromium. However, research has shown that anionic species of hexavalent chromium from aqueous solutions are very poorly adsorbed on clay minerals, primarily due to the negative charge on the surface of clay minerals in a very wide range of pH values of the aqueous medium. In order to increase the

affinity for hexavalent chromium anions, clay minerals were functionalized in different ways, which significantly increased their adsorption capacity towards hexavalent chromium.

2. EXPERIMENTAL

Sepiolites, natural, acid-activated and thermo-acid-activated are functionalized with 99.99% pure organosilanes, manufactured by "Sigma" Aldrich: (3-mercaptopropyl)trimethoxysilane, $(\text{OCH}_3)_3\text{Si}-(\text{CH}_2)_3-\text{SH}$ or mercapto-silane and [3-(2-aminoethylamino)propyl]trimethoxysilane, $(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$ or amino-silane. Mercaptosilanized samples of natural, acid-activated, and thermoacid-activated sepiolite were designated MSEP, MASEP, and MTASEP, respectively. Aminosilanized samples of natural, acid-activated, and thermoacid-activated sepiolite were designated APT-SEP, APT-ASEP, and APT-TASEP, respectively. Functionalization was proven by scanning electron microscopy, X-ray diffraction analysis, infrared spectroscopic analysis, differential thermal analysis, adsorption-desorption nitrogen isotherms and determination of the point of zero charge, pH_{pzc} . It was determined that the structure of the starting material was preserved during the functionalization. The adsorption of Cr(VI) on organosilanized sepiolites was examined at different initial concentrations of Cr(VI) solution from 5 to 205 mg/dm³ and at different initial pH values: 4.5; 3.0 and 2.0 ± 0.1 . The adsorbent/solution ratio was 0.10 g/25 cm³ for mercaptosilanized sepiolites and 0.05 g/25 cm³ for aminosilanized sepiolites. The amounts of Cr(VI) ions adsorbed per unit mass of functionalized sepiolites were calculated using equation [9]:

$$q_e = \frac{c_i - c_e}{m} V \quad (1)$$

where: c_i - initial concentration of Cr(VI) solution (mg/dm³); c_e - equilibrium concentration of Cr(VI) solution (mg/dm³); m - mass of adsorbent (g); V - volume of Cr(VI) solution (dm³).

3. BASICS OF THE ADSORPTION PROCESS AS A METHOD OF REMOVING CHROME(VI) FROM AQUEOUS SOLUTIONS

Adsorption is based on the physical or chemical interactions of particles (adsorbate and adsorbent) belonging to different phases, at the interface of the phases. Table 1 gives some criteria on the basis of which it is possible to determine the type of adsorption, although none of them is reliable enough to be applied in all cases [10].

Physical adsorption is based on nonspecific electrostatic interactions, the establishment of specific interactions, the action of weak van der Waals forces, and the construction of hydrogen bonds between the adsorbate and the adsorbent. Of all nonspecific electrostatic interactions, only Coulomb's long-range electrostatic attractive forces between oppositely charged particles that are directly proportional to the product of their charges and inversely proportional to the square of the distance between their centers are taken into account [11]. Specific adsorption involves the formation of ion pairs and the construction of surface complexes between adsorbate particles and active sites on the surface of the solid adsorbent. Four types of van der Waals forces participate in the realization of van der Waals connections: (1) electrostatic attraction of molecules having a permanent dipole and which are oriented towards each other so that the oppositely charged ends of the molecules are opposite to each other; (2) the interaction between the permanent dipole of a polar molecule and the induced dipole of a non-polar molecule, which occurs when a permanent dipole moves an electron cloud of a nonpolar molecule relative to its nucleus, resulting in a dipole that disappears when the electric field ceases; (3) dispersion's or London forces between a temporarily formed dipole in one molecule and an induced dipole in another molecule; (4) repulsive intermolecular forces due to mutual repulsion of filled molecular orbitals. The energy of van der Waals bonds ranges from 1 to 40 kJ/mol. Hydrogen bonds also contribute to physical adsorption, as electrostatic attraction bonds between oppositely charged ends of polar molecules in which a hydrogen atom is covalently bound to an atom of an element that exhibits high electronegativity (fluorine, oxygen, nitrogen, chlorine, sulfur, carbon), so the electron pair that forms the bond, almost entirely belongs to the atom of high electronegativity, while the hydrogen atom almost like a naked proton represents the positively charged pole of a polar molecule. The energies of the hydrogen bond range from 20 to 40 kJ/mol, but unlike van der Waals bonds, the hydrogen bond has a certain orientation [12].

The energy released during physical adsorption is small. It is released through the vibrations of the adsorbent lattice and is dissipated as heat received by the adsorbate particles. Thanks to this energy, the adsorbate particles move on the surface of the adsorbent, gradually losing energy to eventually be adsorbed to a degree called accommodation. Physical adsorption can be a reversible process.

Hemisorption involves the transfer of electrons between the adsorbent and the adsorbate and the construction of chemical bonds on the surface layer itself, so these processes are often irreversible. Due to the specificity of chemical bonds, hemisorption takes place only until the formation of a monolayer of adsorbates, in contrast to physical adsorption where the formation of more layers is possible. If the adsorption takes place in several layers, the first can be bound to the surface by either physical or chemical bonds, and the second and other layers must be physically bound [13].

When the adsorption takes place from the multicomponent liquid phase (solution), the correct choice of solvent and adsorbent can accelerate the adsorption of the dissolved component on the surface of the solid adsorbent. The adsorption process on the solid surface of the adsorbent from the solution is influenced by: (1) the nature of the adsorbate and the nature of the adsorbent, (2) development of the adsorbent surface, (3) structure, shape, size, polarity and dissociation ability of adsorbate particles, (4) pH value of the solution and (5) temperature [13]. According to the nature of the adsorbate, adsorption from the solution can be: (1) adsorption of neutral molecules (nonelectrolytes) and (2) adsorption of ions (electrolytes) [14].

Table 1. Conventional criteria for distinguishing between physical and chemical adsorption [10].

Criterion	Physical adsorption	Hemisorption
Standard enthalpy of the adsorption process	Low value; typical values are about 20 kJ/mol	High value; typical values of about 200 kJ/mol
Temperature dependence	It is significant only at low temperatures (lower than the boiling point of the adsorbate)	It takes place in a wide range of temperatures (and at temperatures significantly higher than the boiling point of the adsorbate)
Layer thickness	Single-layer and multi-layer are possible	Only single layer is possible
Dissociation of adsorbed molecules	No dissociation	Dissociation may occur
Speed of establishing balance and process reversibility	Fast reversible process	Speed of hemisorption is less than that of physical adsorption; irreversible process
Activation energy	Low value	High value; depends on the degree of surface coverage
Chemical similarity of adsorbate and adsorbent	Not necessary	Necessary
Electron participation	There is no electron transfer, although adsorbate polarization can occur	Electron transfer leads to the formation of bonds between the adsorbate and the surface of the adsorbent

4. APPLICABILITY OF VARIOUS ADSORPTION ISOTHERM MODELS ON ADSORPTION OF CHROME(VI) ON ORGANOSILANIZED SEPIOLITES

When the adsorption equilibrium of the adsorbate-solid adsorbent system is established, at a constant system temperature, the adsorption isotherm gives the dependence between the amount of substance adsorbed on the adsorbent, q_e and its equilibrium concentration in the solution, c_e :

$$q_e = f(c_e) \quad (2)$$

Figures 1 to 6 show the isotherms for adsorption of Cr(VI) from solutions of different initial pH values on mercaptosilanized sepiolites (MSEP, MASEP and MTASEP) and on aminosilanized sepiolites (APT-SEP, APT-ASEP and APT-TASEP) on constant temperature (25°C) when in adsorption systems (Cr(VI) solution - organosilanized sepiolite) an equilibrium is established between the adsorbed amount of Cr(VI), q_e and the concentration of Cr(VI) in the solution, c_e .

According to Figures 1, 2 and 3, the MASEP sample has a higher Cr(VI) adsorption capacity than the MSEP and MTASEP samples at all tested initial pH values of the Cr(VI) solution. The adsorption capacity of the MSEP sample increases with decreasing initial pH of the solution (Figure 1). On the MASEP sample the maximum adsorption capacity was recorded at the initial pH value of the solution 3.0 (Figure 2), and at the initial pH values of the solution 2.0 and 4.5, the adsorption capacity of this sample is approximately the same. The adsorption capacity of the MTASEP sample increases with decreasing initial pH of the solution, but has approximately the same value at initial pH values of 2.0 and 3.0 (Figure 3). When adsorbing Cr(VI) from solution on aminosilanized sepiolites, it is observed that APT-ASEP (Fig. 5) has a higher adsorption capacity than APT-SEP (Fig. 4) and APT-TASEP (Fig. 6), at the investigated initial pH values of the solution. At lower initial pH values of Cr(VI) solution, a larger amount of Cr(VI) was adsorbed on all three aminosilanized sepiolites. Based on Figures 4, 5 and 6, it is observed that the adsorption capacity of all three aminosilanized sepiolites at the initial pH of the solution 2.0 was significantly higher than at the initial pH values of 3.0 and 4.5.

Langmuir's and Freundlich's [13 – 21] as well as Dubinin-Radushkevick's (D-R) [17, 22] models of the adsorption isotherm were used to describe the adsorption processes of Cr(VI) from solution on organosilanized sepiolites. The models are very simple and can interpret experimental results in a wide range of adsorbate concentrations. Their isotherms can be easily transformed into a linear form and the parameters are calculated by linear regression analysis.

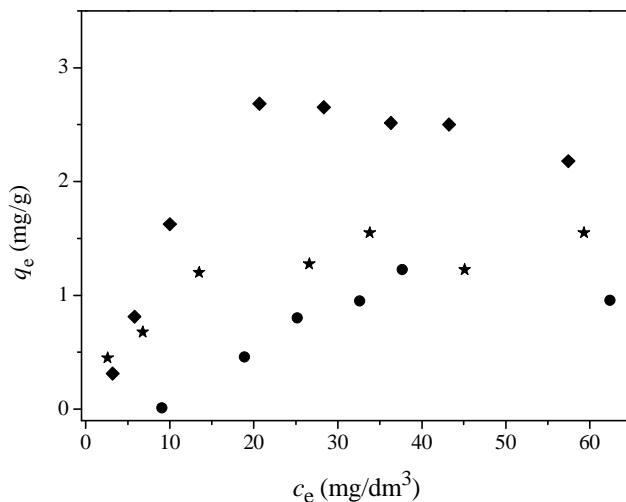


Figure 1. Adsorption isotherms for Cr(VI) adsorption on MSEP at different initial pH values of the solution: 2,0 (◆), 3,0 (★) and 4,5 (●); at 25 °C, in a relationship MSEP/Cr(VI)-solution = 0,1 g : 25 cm³.

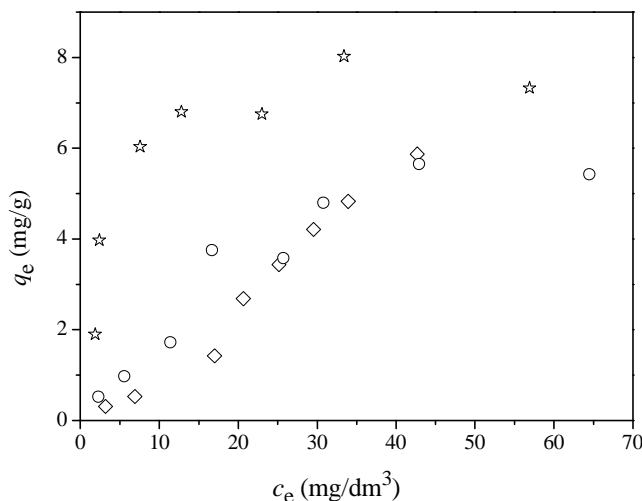


Figure 2. Adsorption isotherms for Cr(VI) adsorption on MASEP at different initial pH values of the solution: 2,0 (◇), 3,0 (☆) and 4,5 (○); at 25 °C, in a relationship MASEP/Cr(VI)-solution = 0,1 g : 25 cm³.

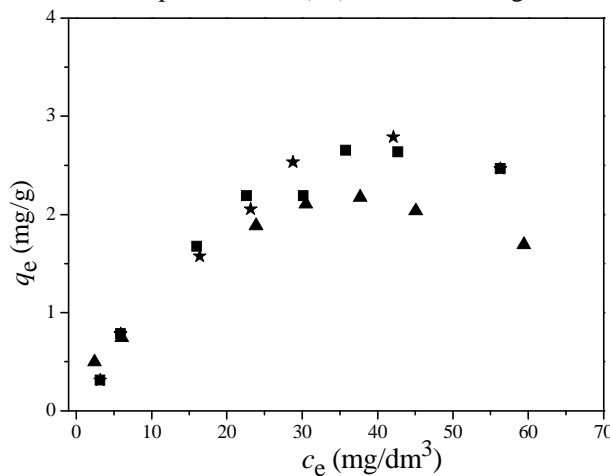


Figure 3. Adsorption isotherms for Cr(VI) adsorption on MTASEP at different initial pH values of the solution: 2,0 (■), 3,0 (★) and 4,5 (▲); at 25 °C, in a relationship MTASEP/Cr(VI)-solution = 0,1 g : 25 cm³.

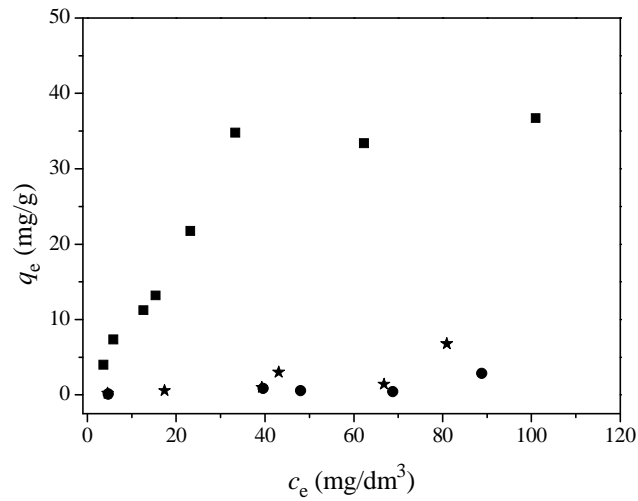


Figure 4. Adsorption isotherms for Cr(VI) adsorption on APT-SEP at different initial pH values of the solution: 2,0 (■), 3,0 (★) and 4,5 (●); at 25 °C, in a relationship APT-SEP/Cr(VI)-solution = 0,05 g : 25 cm³.

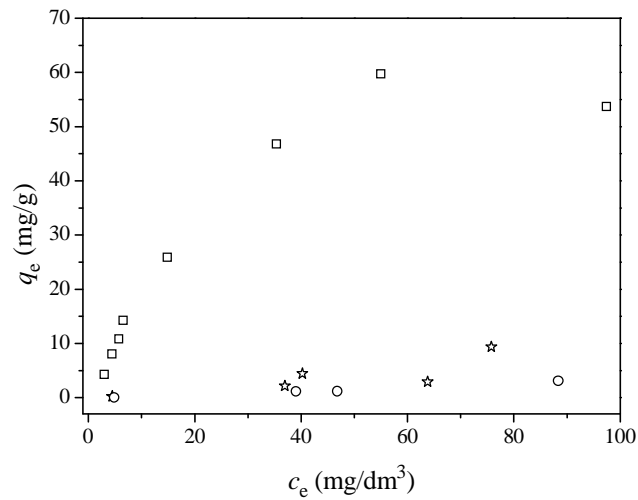


Figure 5. Adsorption isotherms for Cr(VI) adsorption on APT-ASEP at different initial pH values of the solution: 2,0 (□), 3,0 (☆) and 4,5 (○); at 25 °C, in a relationship APT-ASEP/Cr(VI)-solution = 0,05 g : 25 cm³.

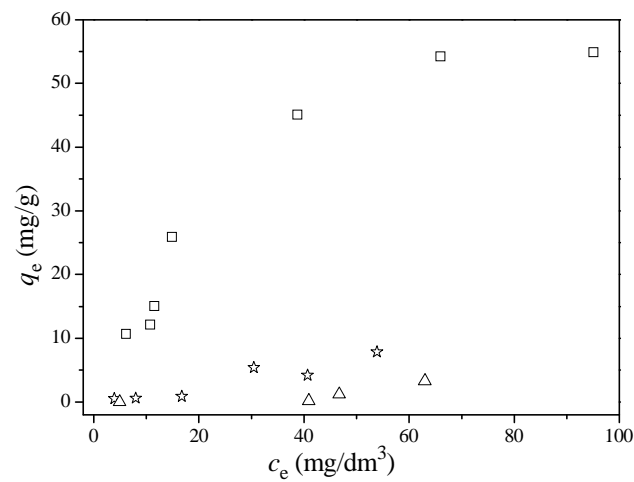


Figure 6. Adsorption isotherms for Cr(VI) adsorption on APT-TASEP at different initial pH values of the solution: 2,0 (□), 3,0 (☆) and 4,5 (△); at 25 °C, in a relationship APT-TASEP/Cr(VI)-solution = 0,05 g : 25 cm³.

Freundlich's isotherm model successfully describes the adsorption of Cr(VI) ions on all three aminosilanized sepiolites, at all investigated initial pH values of the solution, as well as on some mercaptosilanized samples for certain initial pH values of the solution (MASEP, at $\text{pH}_{\text{initial}} = 2, 0$ and MTASEP, at $\text{pH}_{\text{initial}} = 3.0$). The fact that the adsorption of Cr(VI) on most samples of organosilanized sepiolites can be successfully described by the Freundlich adsorption isotherm model indicates multilayer adsorption of Cr(VI), with lateral interactions between the adsorbed Cr(VI) anions. The fact that the adsorption of Cr(VI) on most samples of organosilanized sepiolites can be successfully described by the Freundlich adsorption isotherm model indicates multilayer adsorption of Cr(VI), with lateral interactions between the adsorbed Cr(VI) anions. The surface of the sepiolite sample is energetically heterogeneous and the adsorption energy of Cr(VI) depends on the degree of coverage of the surface of the sepiolite sample by adsorbed Cr(VI) [23].

The adsorption of Cr(VI) on all mercaptosilanized sepiolites can be well described using the D-R isotherm model, with the exception of the adsorption of Cr(VI) on MTASEP at $\text{pH}_{\text{initial}} = 4.5$. According to the D-R model, the adsorption of Cr(VI) takes place by forming a series of equipotential surfaces near the surface of the adsorbent, which have the same adsorption potential.

5. THERMODYNAMICS OF CHROME(VI) ADSORPTION ON ORGANOSILANIZED SEPIOLITES

By determining the thermodynamic parameters of adsorption processes, it is possible to predict the nature and possible mechanisms of the adsorption process. The standard Gibbs energy (so-called free energy) of the adsorption process, ΔG^{θ} is determined by applying the equation [17, 19 – 21]:

$$\Delta G^{\theta} = -RT \ln K_C \quad (3)$$

wherein R (8,314 J/(mol K)) gas constant and T (K) absolute temperature, and K_C the thermodynamic equilibrium

constant. K_C can be determined from the dependence of $\ln \frac{q_e}{c_e}$ on q_e . K_C is determined as $\lim_{q_e \rightarrow 0} \frac{q_e}{c_e}$ by drawing the

dependence of $\ln \frac{q_e}{c_e}$ on q_e and by extrapolation for $q_e = 0$. The section of rectilinear dependence on the ordinate gives the value of K_C .

A negative sign of the standard free energy of the adsorption process, ΔG^{θ} indicates that adsorption is a spontaneous process, while its values for physical adsorption are from -20 to 0 kJ/mol and for hemisorption from -80 to -400 kJ/mol [17 – 19].

Hemisorption processes take place at temperatures higher than those characteristic of physical adsorption. High activation energy, E_a (40 to 800 kJ/mol) indicates chemical adsorption, while low activation energy (5 to 40 kJ/mol) is characteristic of physical adsorption [17]. Since hemisorption requires higher activation energy, it takes place at lower temperatures at a limited rate, which increases with increasing temperature. In contrast, the rate of physical adsorption is high at lower temperatures and decreases with increasing temperature.

The negative, *ie* positive value of the standard enthalpy of adsorption, ΔH^{θ} indicates that adsorption is an exothermic or endothermic process. The values of enthalpy of physical adsorption are from 20 to 80 kJ/mol [17 – 19]. Such a small change in the enthalpy of adsorption is insufficient to break the chemical bonds, so that the particle that is physically adsorbed retains its identity, although it can be deformed as a result of binding to active sites on the surface of the adsorbent. Since adsorbate particles bind to the adsorbent by covalent chemical bonds during hemisorption, the enthalpy of hemisorption values, depending on the nature of the adsorbent, is from 100 to 400 kJ/mol, which is comparable to the covalent bond energies of 460 to 490 kJ/mol in some compounds [17 – 19].

The negative value of the standard entropy of the adsorption process, ΔS^{θ} indicates a decrease in the disorder on the contact surface of the phases, due to the loss degrees of freedom of the translation of adsorbate on the surface of the adsorbent. Exceptionally, positive values of standard entropy are possible if the adsorbate dissociates during adsorption or if it retains high surface mobility [20, 21].

Table 2 shows the values of the standard Gibbs energy, ΔG^{θ} adsorption of Cr(VI) on organosilanized sepiolites determined using the equation 3 [17, 19–21]. The values of ΔG^{θ} shown in Table 2 are in the range of -20.019 kJ/mol $\leq \Delta G^{\theta} \leq -2.457$ kJ/mol. Negative values of ΔG^{θ} indicate that the process of Cr(VI) adsorption on organosilanized sepiolites takes place spontaneously [19, 20].

Table 2. Standard Gibbs energies of the Cr(VI) adsorption process from a solution of initial pH values of 2.0, 3.0 and 4.5 on organosilanized sepiolites at 25 °C.

Adsorbent	ΔG^{θ} (kJ/mol)		
	$\text{pH}_{\text{initial}} = 2.0$	$\text{pH}_{\text{initial}} = 3,0$	$\text{pH}_{\text{initial}} = 4,5$
MSEP	-12.067	-14.079	-2.457

MASEP	-10.995	-20.019	-13.318
MTASEP	-12.193	-12.091	-13.437
APT-SEP	-17.733	-8.210	-6.002
APT-ASEP	-18.958	-7.289	-4.056
APT-TASEP	-17.937	-10.729	-5.435

Based on the results shown in Table 2, with a decrease in the initial pH values from 4.5 over 3.0 to 2.0, the absolute value of the free energy of Cr(VI) adsorption on aminosilanzed sepiolites increases, which indicates that the spontaneity of the process increases. At the initial pH value of 2.0, the highest negative values of ΔG^0 were obtained (Table 2) and the highest adsorption capacities of Cr(VI) on aminosilanzed sepiolites (Figures 4, 5 and 6). Of all three aminosilanzed sepiolites, the largest amount of Cr(VI) is adsorbed on APT-ASEP (Fig. 5) during adsorption for which ΔG^0 has the largest negative value (Table 2). Thus, for aminosilanzed sepiolites the values of ΔG^0 (Table 2) and the maximum adsorption capacities of Cr(VI) (Figures 4, 5 and 6) agree with the description of the Cr(VI) adsorption process using the Freundlich model. Based on that, it is concluded that Cr(VI) is adsorbed in several layers on the surface of aminosilanzed sepiolites and with the decrease of the initial pH value of the solution the affinity of aminosilanzed sepiolites towards Cr(VI) increases [24], ie the spontaneity of adsorption process increases [19, 20]. By nature, adsorption of Cr(VI) on aminosilanzed sepiolites is a physical process, indicated by the formation of multiple layers on the surface of aminosilanzed sepiolites (according to the Freundlich model), as well as the values of ΔG^0 shown in Table 2 in the range of $-18.958 \text{ kJ/mol} \leq \Delta G^0 \leq -4.056 \text{ kJ/mol}$.

Unlike aminosilanzed, for mercaptosilanzed sepiolites are not obtained in all cases the highest negative values of free energy of Cr(VI) adsorption for the highest adsorption capacities Cr(VI). For MASEP, the highest absolute value of ΔG^0 was obtained for the adsorption of Cr(VI) at an initial pH of 3.0 (Table 2), although the highest adsorption capacity of Cr(VI) on MASEP was at an initial pH of 2.0 (Figure 1). At an initial pH of 4.5, the absolute value of ΔG^0 of adsorption of Cr(VI) on MASEP is $\approx 83\%$ lower than at an initial pH of 3.0, although at an initial pH of 4.5 the adsorption capacity of Cr(VI) on MASEP 20% lower than at initial pH 3.0. Also, with MTASEP, the highest absolute value of ΔG^0 was obtained for Cr(VI) adsorption at the initial pH value of 4.5 (Table 2), although the highest Cr(VI) adsorption capacity on MTASEP was at the initial pH value of 3.0 (Figure 3). For MASEP, the highest negative value of ΔG^0 adsorption of Cr(VI) (Table 2) and the highest adsorption capacity of Cr(VI) (Figure 2) are at the same initial pH value (3.0), however, at the initial pH value of 2.0, higher adsorption capacity on MASEP corresponds to a lower absolute value of ΔG^0 and at an initial pH value of 4.5, lower adsorption capacity on MASEP corresponds to a higher absolute value of ΔG^0 . The discrepancy between the values of the highest adsorption capacities of Cr(VI) on mercaptosilanzed sepiolites (Figures 1 to 3) and the values of ΔG^0 (Table 2) of Cr(VI) adsorption as well as the facts that the adsorption process on all three mercaptosilanzed sepiolites, at the same initial pH, can be very well described using different models of adsorption isotherms indicate that the adsorption of Cr(VI) from aqueous solutions can take place according to different mechanisms, whose presence in the total removal of Cr(VI) changes with the change of pH value of the solution. The values of ΔG^0 adsorption of Cr(VI) on mercaptosilanzed sepiolites shown in Table 2 are in the range of $-20,019 \text{ kJ/mol} \leq \Delta G^0 \leq -2,457 \text{ kJ/mol}$, which indicates the predominantly physical nature of the adsorption process [17 – 19]. However, based on the value of $|\Delta G^0| = 20,019 \text{ kJ/mol}$, for the adsorption of Cr(VI) on MASEP, at the initial pH value of the solution of 3.0, it can be concluded that in addition to the physical mechanisms of adsorption, chemical mechanisms of adsorption are also possible [17 – 19].

6. CONCLUSION

The subject of this paper is the removal of anionic species of chromium(VI) from aqueous solutions using natural, acid-activated and functionalized sepiolites as sorbents. Natural sepiolite (SEP), acid-activated sepiolite at room temperature (ASEP) and acid-activated sepiolite with heating (TASEP) were functionalized by covalent binding of mercaptosilane and aminosilane to surface silanol groups of sepiolite. The results of investigation showed that the adsorption of Cr(VI) on natural and acid-activated sepiolite is negligibly small and that it is significantly increased by the functionalization of sepiolite with organosilanes. The Dubinin-Radushkevich isotherm model describes Cr(VI) adsorption well on mercaptosilanzed sepiolites, while the Freundlich model best describes the adsorption process on aminosilanzed sepiolites. The standard Gibbs energy of the adsorption process indicates that the adsorption of Cr(VI) on functionalized sepiolites is a spontaneous process based mainly on the physical interactions of chromate anions and the adsorbent surface.

7. LITERATURE

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