Kinetics of Cr(VI) adsorption from aqueous medium onto bentonite

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INTRODUCTION

Chromium is not naturally found in watercourses. However, its presence was found in wastewaters of various industries, such as leather processing, textile, photographic and glass industries, ceramics, metal and wood processing industries, pigment production, inorganic chemicals, electrical and electronic equipment, etc. (Hu et al., 2009; Gupta et al., 2010). Although there are few different oxidation states of chromium, contaminated soil and water contain trivalent (Cr(III)) and hexavalent (Cr(VI)) chromium. While trivalent chromium is important for glucose, lipids and proteins metabolism, hexavalent chromium is highly toxic, and has carcinogenic and mutagenic effect on people and environment (Haney et al., 2014; Dupont & Guillon, 2003). Acute exposure to hexavalent chromium compounds causes nausea, diarrhea, lung cancer, leads to liver, kidney and stomach damage, respiratory problems and internal bleeding (Bhattacharyya & Gupta, 2006; Costa & Klein, 2006;

Because of its abundance and toxicity, heavy metals have become a serious environmental problem. The presence of heavy metals, such as Cr(VI), in the watercourses leads to numerous health problems in humans and animals. Cr(VI) is highly toxic, even in low concentrations. Because of its carcinogenic, mutagenic and teratogenic effects on human beings, Cr(VI) is considered one of the most critical pollutants. Due to this, it is necessary to remove Cr(VI) from wastewater prior to its discharge into the recipient.

This paper studied the possibility for application of bentonite as an adsorbent for Cr(VI) from aqueous medium. The characterization of bentonite was determined with chemical composition, specific surface, XRD method and FTIR. Optimal parameters such as pH of solution, adsorbent weight, time of adsorption and temperature were examined. Values of those parameters were: initial pH value of solution pH=2, adsorbent weight 2 g, time of adsorption 60 min, temperature 308 K. Experimental data were obtained by Freundlich and Langmuir isotherm adsorption models as well as pseudo-first and pseudo-second order kinetics. Results were best described with Freundlich isotherm adsorption model and pseudo-second order kinetics.

Shouman et al., 2013; Shekhawat et al., 2015). Due to the toxic, mutagenic and cancerogenic effect of Cr(VI), American Environment Protection Agency (U.S. EPA., 2010) announced this oxidation form of chromium as a high risk pollutant.

According to the recommendation of the World Health Agency (WHO, 2019), the maximum permissible concentration of chromium in drinking water is 0.05 mg/L. According to the order of hygienic safety of drinking water of the Republic of Srpska, the maximum concentration of total chromium is 0.05 mg/L (Official Gazette of the Republic of Srpska, Nos. 16/02 and 10/98).

Among the numerous physical, chemical and biological methods for the removal of Cr(VI) compounds from aqueous solutions, the adsorption method is the applicable method based on its simplicity and cost-effectiveness. Various numbers of different materials such as natural clays (Zachara et al., 1988; Ajouyed et al., 2011; Li et al., 2016; Algamal et al., 2018), natural zeolites (Faghihian & Bowman, 2005; Jorfi et al., 2017), agricultural and industrial waste material (Šciban & Klašnja, 2002), different carbon materials, activated carbon (Mohan & Pittman, 2006) etc. were tested as an adsorbent for Cr(VI) compounds from aqueous medium.

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Great specific surface, layered structure, high ion exchange capacity, as well as chemical and mechanical stability are the properties of clays, which are specified as good adsorbents for cationic, anionic and neutral metal forms. Bentonite is natural clay. Main component of bentonite is mineral montmorillonite (over 60 %). Montmorillonite is the type of smectite clay minerals, layered silicate structure type 2:1, where one octahedral layer (AlO₄ octahedral) is positioned between two tetrahedral layers (SiO₄ tetrahedral).

This paper studied the possibility of natural clay bentonite application as an adsorbent for Cr(VI) from aqueous medium. Experimental data were obtained by Freundlich and Langmuir adsorption isotherms and pseudo-first and pseudo-second kinetic models.

MATERIALS AND METODS

Natural clay bentonite, product of "Bentoprodukt" d.o.o., Šipovo, Republic of Srpska, was used in this study. Physicochemical properties of bentonite were determined with chemical composition method, X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and specific surface method.

Chemical composition of bentonite was specified with different experimental methods: gravimetric (content of SiO_2), volumetric (content of Fe_2O_3 and Na_2O), spectrophotometric (content of TiO_2 and CaO) and potentiometric titration (content of AI_2O_3).

Mineralogical analysis of bentonite was performed by X-ray diffraction analysis on a powder sample at instrument PHILIPS PW-1710 with CuK α radiation (voltage 40 kV, current strength 50 mA, 20 range 5-60°). XRD spectrum was indentified in ASTM standard base.

Specific surface of bentonite was determined with BET method, by adsorption of nitrogen at 77 K at instrument Flowsorb II 2300. FTIR analysis was performed on FTIR-spectrophotometer Bruker "Tensor 27" in range from 4000 to 400 cm⁻¹.

Batch adsorption experiments were processed in Erlenmayer flasks in thermostat (WiseCircu WCR, model WCR-P22, Witeg, Wertheim, Germany). The effect of the initial pH of the solution, the weight of the adorbent, the contact time and temperature of the adsorption process were examined. For adsorption experiments, volume of 50 mL of Cr(VI) solution (concentration 10 mg/L) was always taken, while the other parameters varied from experiment to experiment. When the adsorption equilibrium was established, the suspensions were centrifuged for 20 minutes at 13 000 rpm (Alresa Mod, Digicen) and the content of Cr(VI) in supernatant was determined by spectrophotometric method. All the experiments were performed twice.

Stock solution of $K_2Cr_2O_7$, concentration 100 mg/L, was prepared by dissolving 0.2828 g of K₂Cr₂O₇ p.a. in 1000 mL of distilled water. Solutions for adsorption study (2; 4; 6; 8 and 10 mg/L) were prepared by diluting the stock solution. Concentration of chromium, which is at the pH=2 in the form of hydrogen chromate ion $(HCrO_{A}^{-})$ was determined by spectrophotometer (Perkin Elmer Lambda 25) with 1,5 diphenylcarbazide method (DPC). DPC forms with Cr(VI) red-violet complex in acid sulfate media (pH=2). Intensity of color is proportional to the concentration of Cr(VI) in the aqueous solution and was measured at λ_{max} =541.17 nm. 2.5 mL of the solutions was taken and diluted for spectrophotometric measurements, pH of the solution was adjusted to 2 and 2 mL od DPC was added. 0.25 % DPC solution was prepared by dissolving 0.2590 g DPC, a.p. in 100 mL acetone. For pH adjusting sulfuric acid was used (H₂SO₂:H₂O=1:1). pH of the solution was adjusted wih Jenway 3520 pH meter with accuracy ±0.1. The amount of adsorbed Cr(VI) per gram of bentonite, q (mg/g) and efficiency of adsorption, E (%), was calculated by using the following equations:

$$q_e = \frac{\left(c_0 - c_e\right) \cdot V}{m} \tag{1}$$

$$E(\%) = \frac{(c_0 - c_g)}{c_0} \cdot 100$$
 (2)

 c_{0} and c_{e} are initial and equilibrium concentration of Cr(VI) (mg/L) in solution, respectively, V is the volume of solution for adsorption (L) and *m* is weight of adsorbent (g).

The adsorption kinetics and batch adsorption study of Cr(VI) from aqueous medium onto bentonite was performed at initial Cr(VI) concentration 10.0 mg/L, volume 50 mL and optimal parameters (pH=2.0; m=2.0g; t=60 min. and T= 308 K). Kinetics of adsorption was studied during 180 min. Reaction times were 10, 20, 30, 40, 50, 60, 90, 120, 150 and 180 min. After that, suspensions were centrifuged and content of Cr(VI) in supernatant was measured spectrophotometrically.

RESULTS AND DISCUSSION

Characterization of adsorbent

The chemical composition of bentonite in mass % is presented in Table 1. The results showed that the main components of bentonite are SiO_2 and Al_2O_3 . Of the other constituents, Fe_2O_3 and trace of CaO, Na₂O and TiO₂ are detected.

Adsorbent	Chemical composition (mass %)									
	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	GŽ	H_2O
Bentonite	52.88	23.72	6.80	1.80	-	0.02	-	0.83	12.62	-

Table 1. The chemical composition of adsorbent (bentonite)

The bentonite diffractogram (Figure 1. left) showed that this clay is the mixture of different mineral phases, the most represented mineral is montmorillonite and mixture illite-montmorillonite, as well as quartz and calcium silicates.



Figure 1. XRD pattern of bentonite (left) and FTIR spectrum of bentonite (right)

FTIR spectrum provides the information about the structure and type of functional groups at the surface of the material. Figure 1. (right) shows FTIR spectrum of bentonite. According to the literature data (Madejova, 2003; Ikhtiyarova et al., 2012), a group of peaks with wave number 3750-3500 cm⁻¹ correspond to vibrational bands of -OH groups from adsorbed water onto bentonite. A peak with wave number 3624 cm⁻¹ is typical for smectite with large amount of Al in octahedral layer, while peak with wave number of 1634.33 cm⁻¹ corresponds to -OH deformations in water. Minerals from carbonate group showed peak at 1431 cm⁻¹ and quartz at 796 and 690 cm⁻¹. The characteristic peaks in the range of wave numbers 1200-900 cm⁻¹ (995 and 912 cm⁻¹) are the result of the stretching vibrations of the various Si-O groups and bending vibrations of the AI-O-AI groups, while the peaks with the wave numbers 600-400 cm⁻¹ (519 and 459 cm⁻¹), attributed to the bending vibration bands of Si-AI-O and Si-O groups, respectively.

Adsorption potential of adsorbent depends on specific surface, and those parameters are proportional. Specific surface of bentonite was determined by BET method and the value is 88.80 m²/g.

Influence of the initial pH of the solution on the adsorption of Cr(VI)

One of the most important parameters of adsorption process is the pH value of aqueous media in which adsorption is carried out, because this parameter affects the ionization state of functional groups on the surface of the adsorbent and the state of ionic groups of metal in solution (Özcan et al., 2004). The effect of the initial pH of the solution was examined in these conditions: 1.0000 g/ 50 mL of solution, concentration of Cr(VI) 10 mg/L, contact time of 2 hours and at the temperature of 293 K. Depending on the pH value in the medium and concentration, chromium exists in different species, such as oxianion dichromate $Cr_2O_2^{-2}$, hydrogen chromates $HCrO_{4}^{-}$, chromates CrO_{4}^{-2} . In the solution concentrations bellow 1 g/L hydrogen chromate $HCrO_{4}^{-}$ is dominant species, while in the range above 1 g/L dichromate $Cr_2O_7^2$ species exists. Based on this literature data, pH values for these experiments were 2, 3, 4 and 5 and the obtained results are shown in Figure 2a.



Figure 2. a) The efficiency of chromium Cr (VI) adsorption in function of initial pH (conditions: m = 1.0000 g; V = 50 mL; $c_0 = 10 \text{ mg} / \text{L}$; T = 293 K; t = 2 h); b) The effect of the adsorbent weight on the adsorption of Cr(VI) (conditions: V = 50 mL; T = 293 K; $c_0 = 10 \text{ mg} / \text{L}$; t = 2 h; pH=2.0)

Figure 2a. shows that adsorption efficiency onto bentonite increases when pH value of the solution decreases. The highest adsorption efficiency was obtained for the lowest initial pH= 2 (E=45.85 %), which is in good correlation with literature data (Ajouyed et al., 2011; Tichapondwa & Van Biljon, 2019). At this pH value of the solution, the surface of bentonite is protonated (due to excess of H⁺ ions) and positively charged. In these conditions, hydrogen chromate HCrO₄⁻ dominates, and the process of the adsorption is the consequence of electrostatic attraction between the positively charged bentonite surface and negatively charged HCrO₄⁻ ions (Akar et al., 2009; Brum et al., 2010). pH=2 value was chosen as an optimal parameter for further studies.

Effect of the adsorbent weight on adsorption of Cr(VI)

Adsorbent weight is an important parameter in the adsorption process, because it determines the capacity of the adsorbent for a different initial concentration of adsorbate. The efficiency of Cr(VI) adsorption onto bentonite was studied on different weights of adsorbent (0.5; 1.0; 1.5 and 2.0), while the other parameters were constant: initial Cr(VI) concentration 10.0 mg/L, pH of the solution was 2, volume 50 mL, contact time 2 hours and temperature was 293 K. The obtained results are shown in Figure 2b. The results showed that adsorption efficiency increases with bentonite weight and reaches maximum (53.60 %) at weight of 2.0 g. This is explained by the fact that when the weight of adsorbent increases, total surface for the binding metal ions increases as well as the number of the adsorption sites (Wanees et al., 2013). Optimal weight of bentonite for further studies was 2.0 g. Suspensions with higher weights than 2 g were dense and contact between adsorbate and adsorbent was aggravated and they were not studied.

Effect of contact time on adsorption of Cr(VI)

The effect of contact time on the adsorption of Cr(VI) onto bentonite was studied at an initial concentration 10 mg/L, volume 50 mL, pH=2 and temperature 293 K. Adsorption was examined through a period of 120 min. The effect of contact time on adsorption process is presented in figure 3a. Based on the obtained results, it can be concluded that adsorption of Cr(VI) onto bentonite takes place in two phases. The first phase is very fast and occurs in the first 60 min of the interaction of the bentonite with Cr(VI) solution, when the maximum adsorption efficiency is reached (56.32 %). This phase took place fast, due to high concentration of active sites onto bentonite surface and high concentration of metal ions. The second phase is slower and during this phase the adsorption efficiency decreases slightly, as the number of free active sites as well as the initial Cr(VI) concentration decreases. Electrostatic repulsion can take place between bonded $HCrO_4^{-1}$ ions and $HCrO_4^{-1}$ species, which are remaining in the solution (Algamal et al., 2018). Contact time t=60 min was chosen as an optimal parameter for further experiments.

Effect of temperature on adsorption of Cr(VI)

Figure 3b. shows the effect of temperature on the adsorption efficiency of Cr(VI) from aqueous solution onto bentonite. Three different temperatures (293; 298 and 308 K) were considered, while the other parameters were constant: V=50 mL; $c_0=10$ mg/L; t=60 min; m=2.0000 g and pH=2.0). Increasing the temperature in this adsorption study positively affected the efficiency of this process and the maximum was reached at the temperature 308 K (41.60 %). These results showed that adsorption of Cr(VI) onto bentonite is of chemical nature and has endothermic character. For further studies, temperature of 308 K was selected as optimal.



Figure 3. a) The efficiency of chromium Cr (VI) adsorption in function of time (conditions: m = 2.0000 g; V = 50 mL; pH=2.0; $c_0 = 10 \text{ mg} / \text{L}$; T = 293 K); b) The effect of temperature on adsorption of Cr(VI) (conditions: m = 2.0000 g; V = 50 mL; $c_0 = 10 \text{ mg} / \text{L}$; t = 60 min; pH=2.0)

Kinetic study

Kinetic adsorption models provide insights into the rate of adsorption process and its mechanism, involving mass transfer, diffusion (external and internal) and the interaction of adsorbates particles with active sites onto adsorbent surface. The most commonly used kinetic adsorption models are pseudo-first and pseudo-second order kinetic models.

The pseudo-first order kinetic model, as well known as Lagergren's kinetic model, is one of the most commonly used models. In this model, adsorbate reacts with active center and forms an adsorption complex. The pseudofirst order model is represented by the equation:

$$\frac{dq_t}{dt} = k_1(q_s - q_t) \tag{3}$$

 $q_{\rm e}$ is the amount of adsorbed particles at the equilibrium (mg/g), $q_{\rm t}$ is the amount of adsorbed particles at the time *t* (mg/g), $k_{\rm 1}$ is the pseudo-first order adsorption rate constant (min⁻¹). After integration from *t*=0 to *t*=*t* and $q_{\rm r}$ =0 to q= $q_{\rm r}$, equation (3) takes the following form:

$$q_t = q_e (1 - e^{k_1 t}) \tag{4}$$

For practical reasons, equation (4) goes to linear form:

$$ln(q_e - q_t) = lnq_e - k_1 t \tag{5}$$

The constant k_1 is obtained from the graph of the dependence $\ln(q_2 - q_1) = f(t)$.

The pseudo-second order kinetic can be represented by the equation:

$$\frac{dq_t}{dt} = k_2 (q_s - q_t)^2 \tag{6}$$

Integration equation (6) from t=0 to t=t and $q_t=0$ to $q_t=q_t$, equation gets the following form:

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \tag{7}$$

where k_2 is the pseudo-second order adsorption rate constant (g mg⁻¹ min⁻¹), while the other quantities have the same content as in the previous model. The linear form of equation (7) is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_g^2} + \frac{1}{q_g} t \tag{8}$$

 q_{e} and k_{2} can be obtained from the graph of dependence $t/q_{t}=f(t)$. The pseudo-second order model describes the chemisorptions on solid adsorbents.

The kinetic of Cr(VI) adsorption from aqueous solution onto bentonite was studied at optimal parameters: V=50 mL; c_0 =10 mg/L; pH=2.0; m=2.0000 g and T=308 K and different adsorption times. The values of the kinetic parameters for applied kinetic models are presented in Table 2. The consistency between the experimental data and proposed kinetic models was determinated by the value of correlation coefficient R². The greater value of this coefficient, gives more information about the proposed theoretical model. Results showed (Table 2) that adsorption of Cr(VI) onto bentonite follows pseudo-second order kinetic (R²=0.9917). Pseudo-second order kinetics indicates that the adsorption and ion exchange occurs on the adsorbent surface and that the limiting factor of adsorption rate is chemical binding to active sites (Wanees et al., 2013).

Table 2. Kinetic parameters for adsorption of Cr(VI) onto bentonite

Pse k	udo-first o inetic mod	rder el	Pseudo-second order kinetic model			
k ₁ (min ⁻¹)	q _e (mg g ⁻¹)	R ²	k ₂ (g mg ⁻¹ min ⁻¹)	q _e (mg g ⁻¹)	R ²	
0.0021	1.4827	0.4681	0.9807	0.1748	0.9917	

Adsorption istoherms

Adsorption isotherms are important for determination of maximum adsorption capacity of adsorbents as well as for describing the interactions between adsorbates and adsorbents. Freundlich and Langmuir adsorption isotherms are the most commonly used isotherms for the characterization of adsorption process.

Freundlich adsorption model describes adsorption on energetically heterogeneous surface with interactions between adsorbents and adsorbed molecules. This model confirms multilayered adsorption. This isotherm is presented by the equation:

$$q_e = K_F \cdot c_e^{\frac{1}{n}} \tag{9}$$

where q_e is the equilibrium adsorption capacity (mg/g), c_e is the equilibrium concentration of adsorbate in solution (mg/L) and K_F and n are constants of the Freundlich adsorption isotherm. The Freundlich constant K_F (mg g⁻¹)(L mg⁻¹)^{1/n} indicates the adsorption capacity of the adsorbent while the constant n describes the affinity of the adsorbent to the adsorbate and to the heterogeneity of the surface. The logarithmic form of the equation (9) is:

$$lnq_{s} = lnK_{F} + \frac{1}{n}lnc_{s} \tag{10}$$

The constant $K_{\rm F}$ and *n* are obtained from dependence of $\ln q_{\rm e}$ on $\ln c_{\rm e}$, as the intercept and slope on the graph, respectively.

Langmuir's model of adsorption isotherm refers to the adsorption on an energy uniform surface without any interactions between adsorbed molecules. Only one molecule can bind to one adsorption site and the maximum amount of adsorption is the formation of a monomolecular layer on the surface of the adsorbent. The Langmuir adsorption isotherm is described in the equation:

$$q_{\varepsilon} = \frac{q_{m} \cdot K_{L} \cdot c_{\varepsilon}}{1 + K_{L} \cdot c_{\varepsilon}} \tag{11}$$

where $q_{\rm e}$ is the equilibrium adsorption capacity (mg/g), $c_{\rm e}$ is the equilibrium concentration of adsorbate in solution (mg/L), $K_{\rm L}$ is the Langmuir adsorption energy constant (L/mg), related to the adsorption energy and $q_{\rm m}$ is the maximum adsorption capacity (mg/g). The linear form of this isotherm is:

$$\frac{c_e}{q_e} = \frac{1}{q_m} c_e + \frac{1}{K_L q_m}$$
(12)

Graph dependence c_e/q_e vs. c_e determines constant values $1/(K_1q_m)$ from intercept and $1/q_m$ from slope.

The adsorption of Cr(VI) from aqueous solution onto bentonite was studied at the optimal parameters: V=50 mL; pH=2.0; m=2.0000 g; t=60 min, T=308 K and different initial concentrations of Cr(VI) (2; 4; 6; 8 and 10 mg/L). The values of Freundlich and Langmuir isotherm parameters are presented in Table 3. Based on the value of the correlation coefficients, the Freundlich isotherm model (R²=0.913) is more suitable for describing adsorption of Cr(VI) onto bentonite than Langmuir's (R²=0.795). The obtained results were in accordance with the previously presented data (Bentchikou et al., 2017; Tsafam et al., 2019). The Freundlich model assumes an energetically heterogeneous surface of adsorbents and Cr(VI) can bind to multiple types of active sites (Šćiban et al., 2014).

Table 3. Parameters of the adsorption isotherms

Langi	nuir adsor isotherm	ption	Freundlich adsorption isotherm			
K _L (L mg ⁻¹)	q _m (mg g ⁻¹)	R ²	K_{F} (mg g ⁻¹)(mg L ⁻¹) ^{1/n}	n	R ²	
0.2994	0.2982	0.7950	0.0665	1.4206	0.9130	

The Freundlich constant n is related to the intensity of adsorption and the heterogeneity of the surface. When the parameter value is n=1, adsorption follows a linear function, for n < 1 adsorption is unfavorable and when n > 1 adsorption is favored (Güzel et al., 2012). The value of parameter n in this adsorption process is 1.4206 and suggests that adsorption of Cr(VI) onto benotnite is favored.

CONCLUSIONS

The results of this study showed that bentonite has a potential to remove Cr(VI) from aqueous solution. Although, the maximum adsorption efficiency was obtained at pH=2.0 (E=45.85 %), the experimental data showed that even at pH=5.0 bentonite binds a certain amount of Cr(VI). The pseudo-second order kinetic model best describes adsorption process in this study. Analysis of adsorption data indicates that the adsorption of Cr(VI) onto bentonite obeys the Freundlich isotherm model.

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Kinetika adsorpcije Cr(VI) jona iz vodene sredine na bentonitu

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Ključne riječi: bentonit, adsorpcija, Cr(VI), kinetika, izoterme.

Zbog svoje brojnosti i toksičnosti teški metali su postali ozbiljan ekološki problem. Prisutnost teških metala, kao što je Cr(VI) u vodenim tokovima dovodi do brojnih zdravstvenih problema kod ljudi i životinja. Cr(VI) je veoma toksičan, čak i u malim koncentracijama. Zbog svojih kancerogenih, teratogenih i mutagenih dejstava na ljude Cr(VI) se smatra jednim od najkritičnijih zagađivača. Stoga je potrebno ukloniti Cr(VI) iz otpadnih voda prije njihovog ispuštanja u recipijent.

U radu je ispitana mogućnost upotrebe prirodnog bentonita kao adsorbensa Cr(VI) iz vodenog rastvora. Karakterizacija bentonita obuhvatala je određivanje hemijskog sastava, specifične površine, XDR-analizu i FTIR analizu. Ispitani su osnovni parametri koji utiču na proces adsorpcije kao što su: inicijalna pH vrijednost rastvora, masa adsorbensa, vrijeme kontakta i temperatura. Nađeni optimalni parametri adsorpcije su: inicijalna pH vrijednost rastvora pH=2,0; masa adsorbensa 2 g; vrijeme kontakta 60 min.; temperatura 308 K. Eksperimentalno dobijeni rezultati analizirani su upotrebom Frojndlihovog i Lengmirovog modela adsorpcionih izotermi i kinetičkih modela pseudo-prvog i pseudo-drugog reda. Utvrđeno je da se eksperimentalni podaci pokoravaju Frojndlihovom modelu adsorpcione izoterme i kinetičkom modelu pseudo-drugog reda.