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## SORPTION OF Cr(VI) ONTO HDTMA MODIFIED ZEOLITIC TUFFS

### SORPCJA Cr(VI) NA TUFACH ZEOLITOWYCH MODYFIKOWANYCH HDTMA

**Abstract:** The removal of Cr(VI) from aqueous solutions was investigated using clinoptilolite and phillipsite-chabazite rich tuffs. These minerals were modified using hexadecyltrimethyl – ammonium bromide (HDTMA-Br) and used for Cr(VI) ions removal. The physicochemical characteristics of zeolitic minerals were revealed by XRD, XRF, BET and FT-IR techniques. The uptake capacities of modified zeolites were compared in batch sorption experiments. To predict the sorption isotherms and to determine the characteristic parameters for process design, three isotherm models the Freundlich, the Langmuir, and the Bilangmuir, were applied to experimental data. The data obtained reveal homogeneous Cr(VI) sorption on one kind of active sites on PC-HDTMA surface and heterogeneous sorption on two kinds of active sites on CL-HDTMA surface.

**Keywords:** hexavalent chromium, HDTMA-Br modified zeolites, clinoptilolite, phillipsite, sorption equilibrium

## 1. Introduction

Cr(VI) is one of dangerous heavy metal ions and is a major pollutant. As for human being, long term exposure to Cr(VI) may cause liver, kidney and lung damage as well as skin ulceration [1]. It is introduced into environment through effluents of electroplating, leather tanning, dyeing and metal cleaning industries with an average concentration of 50 mg L<sup>-1</sup>.

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During the past three decades, several physical, chemical, and biological methods have been used to remove Cr(VI) and dyes from leather effluents. Among them, adsorption of Cr(VI) on low-cost materials is a commonly employed purification technique due to its simplicity, the cost of design and operation [2]. Because of widespread occurrence natural zeolites have gained great interest for their utilization in water/wastewater treatment. These crystalline microporous aluminosilicates constitute a major group with unique physical properties. The tetrahedral framework of zeolites, composed of  $\text{SiO}_4$  and  $\text{AlO}_4$ , possesses a net negative structural charge that promotes the exchange of cations while hindering the adsorption of anions and organic pollutants. However, the negative charge can be tuned by a surface modification with an aliphatic hydrocarbon which consists of a hydrophobic alkyl long tail and a hydrophilic quaternary ammonium cation charged part. The most common used surfactant is hexadecyltrimethyl – ammonium bromide (HDTMA-Br). Its molecules are too large to enter the Angstrom-scale internal zeolite channels and thus have access only to the external surface area of zeolite [3]. Their sorption is attributed to both cation exchange and hydrophobic bonding, which results in positive surface charge. The external zeolite surface is never completely sealed by an organic sheet. Therefore, such a treatment enables zeolites for sorption of cations, anions and non-polar organics, and offers zeolite potential for soil remediation and separation of differently charged chemical species [4, 5]. It is well known that different zeolitic minerals exhibit different sorption properties. Thus, the goal of this work was to study the adsorption properties of two different zeolitic materials modified with a cationic surfactant to be used for the effective sorption of Cr(VI) anionic species.

## 2. Experimental

### 2.1. Materials and analysis

The zeolitic-rich tuffs used in the present study were: clinoptilolite CL from Slovakia (Nižný Hrabovec) and phillipsite-chabazite PC from Italy (Phlegraean). The samples of CL had particles size 0.25–0.50 mm, while the particles of PC were smaller than 0.25 mm. The mineralogical composition of zeolites was determined by X-ray powder diffraction (XRD) using Philips X'pert ADP and Thermo XTRA. The identification of phases was based on ICDD PDF-2 database and the collection of patterns recommended by International Zeolite Association. CL: clinoptilolite 74 %, cristobalite 11 %, plagioclase 6 %, illite and smectite 4 %, tridymite 3 %, kaolinite 1 %, quartz 1 %. PC: phillipsite 27 %, chabazite 27 %, plagioclase 15 %, K-feldspar 13 %, illite and smectite 8 %, calcite, 6 %, alunite 2 %, quartz 2 %. The X-ray fluorescence analysis (XRF) was employed to determine the chemical compositions of the sorbent (after the sample was homogenized and pelleted) with an Axios mAX PANalytical, Netherlands. The data obtained are depicted in Table 1. It is observed that the major constituents in the raw zeolites are  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in a descending order. The higher  $\text{SiO}_2$  and lower  $\text{Al}_2\text{O}_3$  in clinoptilolite rich tuff (CL: Si/Al = 5.11, PC Si/Al = 2.71) results mainly from

the predominance of zeolitic mineral content (CL: clinoptilolite 74 %; PC: phillipsite 27 % + chabazite 27 %).

Table 1

Chemical analysis of zeolitic rich tuffs

Zeolite	Si	Al	O	Fe	Mg	Ca	Na	K	Cl
CL	33.1	6.48	53.5	0.92	0.45	1.99	0.27	2.97	0.009
PC	25.4	9.38	49.4	2.64	0.69	3.38	1.08	5.86	0.032

The surface area, average pore diameter, and pore volume of the natural zeolites were determined by the  $N_2$ -BET method using a surface area and porosimetry analyzer, Micromeritics, ASAP 2420. Both minerals have negatively charged surfaces due to the isomorphous replacement of  $Si^{4+}$  by  $Al^{3+}$ , which is neutralized by easily exchangeable cations such as  $Na^+$ ,  $K^+$  and  $Ca^{2+}$ . To determine cation exchange capacity (CEC), all exchangeable cations were leached by  $Ca^{2+}$  ions ( $CaCl_2$ ) according to procedure described by Gillman [6]. The concentrations of relieved ions were determined by atomic absorption spectroscopy (AAS). The external cation exchange capacity (ECEC) of zeolitic tuffs were measured by ion exchange with hexaammine cobalt(III) chloride ( $[Co(NH_3)_6]Cl_3$ ) according to procedure described by Orsini and Remy [7]. The results of the after mentioned measurements are displayed in Table 2. As evidence from ten times larger micropore volume ( $V_{p\ micro}$ ), PC has more porous texture than CL and consequently larger surface area ( $A_{BET}$  and  $A_{micro}$ ). This evident big difference does not differentiate greatly CEC and ECEC values. A little higher CEC of PC relates to higher Al content (Table 1) in the zeolite framework [8] but it does not relate directly to the amount of exhalable cations present on PC external surface.

Table 2

Physical parameters of zeolitic rich tuffs

Zeolite	ECEC [mval 100 g <sup>-1</sup> ]	CEC [mval 100 g <sup>-1</sup> ]	$A_{BET}$ [m <sup>2</sup> g <sup>-1</sup> ]	$A_{micro}$ [m <sup>2</sup> g <sup>-1</sup> ]	$V_{p\ tot}$ [cm <sup>3</sup> g <sup>-1</sup> ]	$V_{p\ micro}$ [cm <sup>3</sup> g <sup>-1</sup> ]
CL	12.11	93.80	29.47	8.15	0.11	0.004
PC	11.74	101.48	111.73	97.28	0.07	0.047

Infrared spectra of unloaded and Cr(VI) loaded HDTMA modified zeolites were obtained using a Fourier transform infrared spectrometer (Bruker Vertex 70) using the KBr pressed disk technique. Spectra were collected in the mid infrared (MIR) region (4000–400 cm<sup>-1</sup>) with a resolution of 2 cm<sup>-1</sup>.

## 2.2 Zeolite modification

Prior to the modification the zeolites were converted to their Na forms by suspending of zeolitic material in a 3 % NaCl solution at 25 °C for 48 h. This procedure was

repeated three times. Then samples were washed with distilled water (0.1  $\mu\text{S}$ ) until a reaction with 1 %  $\text{AgNO}_3$  solution was negative and next dried at 105  $^\circ\text{C}$  to constant weight. The Na-forms of zeolitic materials were modified by hexadecyltrimethyl-ammonium bromide (0.98 %, Sigma, Lot SLBC8213). The amount of surfactant [g] equals to the 2.0 ECEC [ $\text{mmol g}^{-1}$ ] was calculated from the following formula:

$$m_{\text{HDTMA-Br}} = \left( \frac{M_{\text{HDTMA-Br}}}{A} \right) \cdot \text{ECEC} \cdot m \quad (1)$$

where:  $m$  is mass of zeolitic material [g],  $M$  is molar mass of HDTMA-Br [ $\text{g mmol}^{-1}$ ],  $A$  is the chemical purity of HDTMA-Br. Mixtures of 2.0 g of a zeolitic sample and 0.1 L of surfactant solution were mixed in an ultrasonic cleaner (POLSONIC Sonic-2) at 40  $^\circ\text{C}$ . After 24 h, the zeolite was washed with deionized water and dried at 105  $^\circ\text{C}$  to constant weight. The obtained modified zeolites were called CL-HDTMA and PC-HDTMA for clinoptilolite rich tuff and phillipsite-chabazite rich tuff, respectively.

### 2.3. Cr(VI) sorption on modified zeolite

The Cr(VI) sorption experiments on modified zeolites were performed in 50 mL screw top polyethylene tubes with 0.1 g of modified zeolite and 10 mL Cr(VI) solution inside. A stock solution containing 250  $\text{mg L}^{-1}$  of Cr (VI) was prepared by dissolution of  $\text{K}_2\text{CrO}_4$  (Chempur, analytical grade) in distilled water at  $\text{pH}_{\text{init}}$  adjusted to the value of 3.0 or 4.0 or 5.0 (pHmeter CP-401 ELMETRON) by using  $\text{HNO}_3$ . The concentration of Cr(VI) working solutions,  $C_{\text{init}}$  ranged between 0.6–180  $\text{mg L}^{-1}$ , were prepared by dilution of the stock solution with distilled water with  $\text{pH}_{\text{init}}$  adjusted to given value. The samples were placed into an end-over-end tumbling shaker (POL-EKO APARATURA) refitted at 140 rpm and shaken for 24 h (time sufficient to attain equilibrium). Next, the sorbent was separated from aqueous solution using a 0.2  $\mu\text{m}$  polyethersulfone syringe filter (Whatman), and the residual concentrations of chromium in the liquid samples were analyzed by the inductively coupled plasma optical atomic emission spectrometer ICP-OES (Integra XL, GBC Scientific Equipment). The amount of metal ions adsorbed per unit mass of modified zeolite [ $\text{mg g}^{-1}$ ] was calculated as follows:

$$q_e = \frac{(C_{\text{init}} - C_e)}{M} V \quad (2)$$

where  $C_{\text{init}}$  and  $C_e$  [ $\text{mg L}^{-1}$ ] are the initial and the equilibrium ion concentrations, respectively,  $M$  [g] represent the weight of the adsorbent, and  $V$  [L] is the volume of the solution.

## 3. Results and discussion

The infrared spectra of CL-HDTMA and PC-HDTMA, before and after Cr(VI) sorption, are shown in Fig. 1 and 2, respectively. There are three groups of bands, which

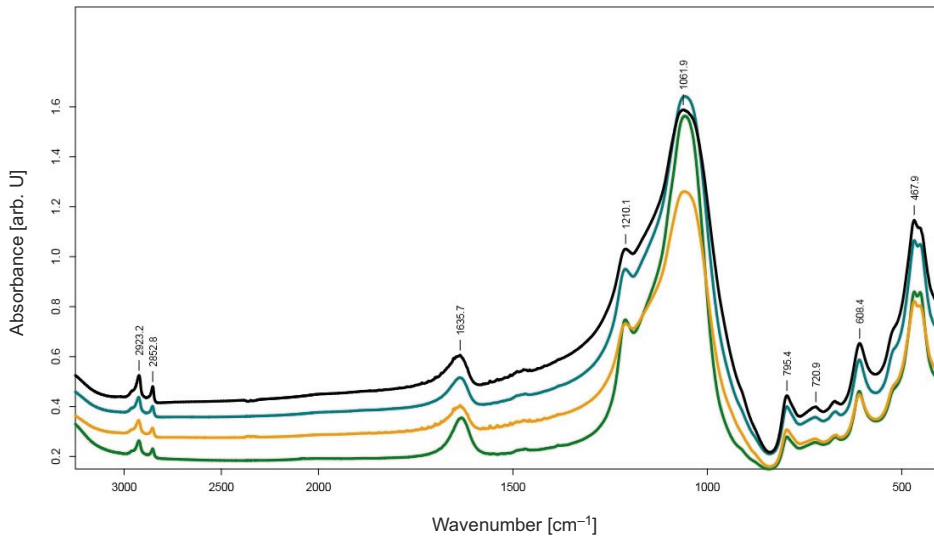


Fig. 1. FTIR spectra of HDTMA modified clinoptilolite before (black line) and after Cr(VI) from solution at:  $\text{pH}_{\text{init}} = 3$  (yellow line),  $\text{pH}_{\text{init}} = 4$  (green line),  $\text{pH}_{\text{init}} = 5$  (blue line)

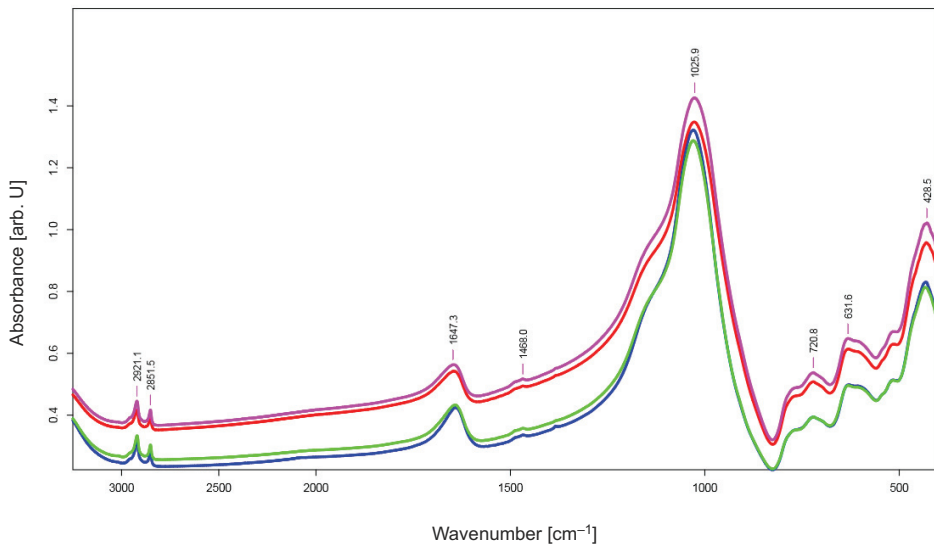


Fig. 2. FTIR spectra of HDTMA modified phillipsite before (green line) and after Cr(VI) from solution at:  $\text{pH}_{\text{init}} = 3$  (blue line),  $\text{pH}_{\text{init}} = 4$  (red line),  $\text{pH}_{\text{init}} = 5$  (pink line)

appear in the spectrum of all the samples: 600–1200, 1450–1650 and 2700–3000  $\text{cm}^{-1}$ . The first group of bands comes from pseudolattice vibrations of aluminosilicate structure and vibrations characteristic for HDTMA. The second and third groups of bands appear as a consequence of deformation and stretching vibrations in water

molecules [8]. They are owing to surfactant molecules as well. The weak spectra at  $1468\text{ cm}^{-1}$  are related to the banding vibration of C-CH<sub>3</sub>. For crystalline HDTMA, the positions of the CH<sub>2</sub> symmetric and asymmetric stretching modes are around 2850 and 2918  $\text{cm}^{-1}$ , respectively [9]. These bands shifted to 2852.8 and 2923.2  $\text{cm}^{-1}$  for CL-HDTMA (black line), and to 2851.5 and 2921.1  $\text{cm}^{-1}$  for PC-HDTMA (green line), indicating the formation of admicel on the zeolite surface. Furthermore, their intensity decreased after Cr(VI) sorption, which can result from reduction of the packing density of amine chains.

To determine the effect of pH on the sorption of Cr(VI) onto modified zeolites, batch equilibrium studies at different  $\text{pH}_{\text{init}}$  values (3, 4, 5) were carried out. The gained results are depicted in Fig. 3. The maximum values of sorption capacity ( $q_m$  [ $\text{mg g}^{-1}$ ]) obtained for PC-HDTMA revealed that efficiency of Cr(VI) sorption increases with lowering of solution pH. The predominant anionic forms of Cr(VI) in the solution of concentration  $C_{\text{init}} 180\text{ mg L}^{-1}$  and  $\text{pH}_{\text{init}} = 3$ , are  $\text{HCrO}_4^-$  (75 %) and  $\text{Cr}_2\text{O}_7^{2-}$  (25 %). Their amounts slightly reduce with increasing of pH and at  $\text{pH}_{\text{init}} 5$  a  $\text{CrO}_4^{2-}$  anion appears (10 %) [10]. According to Thanos et al. the preferential sorption of univalent anions over bivalent once results from the less amount of active sites required for their attachment [11]. Figure 3 also proves that more than twice bigger sorption efficiency was obtained for CL-HDTMA than for PC-HDTMA at the same Cr(VI) solution  $\text{pH}_{\text{init}} = 4$ . It stems directly from different efficiency of zeolites modification. The amount of HDTMA sorbed depends above all on the amount of zeolitic fraction in the tuff (74 % CL and 54 % PC). Other important factors are the geological origin of the zeolites, their cation and framework composition (see Table 1), and the amount of impurities such as forms of silica, feldspars, clay minerals, metal oxide/hydroxide nanoparticles, clusters, microcrystals, or agglomerates on the external zeolite surface [9].

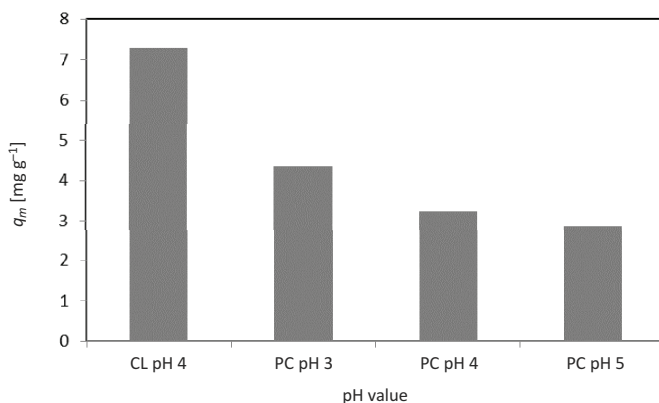


Fig. 3. Effect of the pH value of the adsorption solution on Cr(VI) adsorption capacity

The equilibrium uptakes and the adsorption yields obtained for Cr(VI) sorption at  $\text{pH}_{\text{init}} = 4$  onto CL-HDTMA and PC-HDTMA are shown in Fig. 4. As can be seen, an increase in the  $C_{\text{init}}$  enhances the adsorption uptake of Cr(VI) despite the maximum

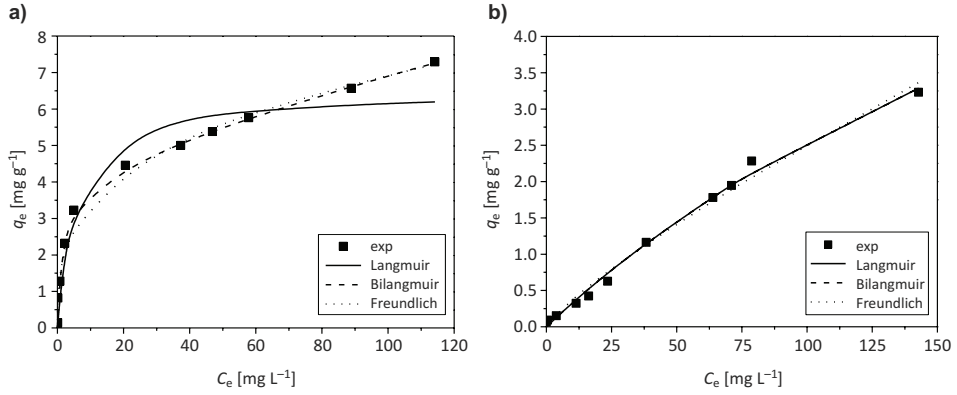


Fig. 4. Equilibrium adsorption isotherms for adsorption of Cr(VI) onto HDTMA-zeolite,  $\text{pH}_{\text{init}} = 4$ ; a) CL-HDTMA, b) PC-HDTMA

chromium saturation was not achieved (lack of plateau on both equilibrium graphs). Nevertheless, the obtained sorption effectiveness for modified CL was almost twice bigger than for modified PC. One could suppose that PC due to its smaller particle size ( $\approx 0.25 \text{ mm}$ ) should have sorbed greater amount of HDTMA than CL. However, due to specific structure of phillipsite-chabazite, the attachment of HDTMA can partially occur into cylindrical caves. The trapped HDTMA molecules are probably not available for Cr(VI) ions sorption [10].

To examine the relationship between sorbed and aqueous concentration of Cr(VI) at equilibrium three empirical models were used for fitting the experimental data. The Langmuir and the Freundlich models are commonly used for analysis the sorbent surface to be monolayer or multilayer, respectively. The Langmuir model is based on an assumption that the sorption takes place at specific homogeneous sites:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where:  $q_e$  is the amount of Cr(VI) adsorbed onto the sorbent [ $\text{mg g}^{-1}$ ];  $C_e$  is the Cr(VI) concentration at equilibrium [ $\text{mg L}^{-1}$ ];  $q_m$  is maximum adsorption capacity [ $\text{mg g}^{-1}$ ]; and  $K_L$  [ $\text{L mg}^{-1}$ ] is the Langmuir equilibrium constant. In opposite to the previous model, the Freundlich one assumes that sorption takes place on heterogeneous surface or surfaces supporting sites of varied affinities:

$$q_e = K C_e^{1/n} \quad (4)$$

where:  $n$  is parameter characterizing the system heterogeneity. The Bilangmuir model is the simplest case of heterogeneous model. It assumes the coexistence of two kinds of active sites which behave independently but are associated with monolayer adsorption ( $q_{m1}$  and  $q_{m2}$ ):

$$q_e = \frac{q_{m1}K_1C_e}{1 + K_1C_e} + \frac{q_{m2}K_2C_e}{1 + K_2C_e} \quad (5)$$

where:  $K_1$  and  $K_2$  are energies of the adsorption related to adsorption sites 1 and 2, respectively. The isotherm equations applied to the experimental data were fitted using MAPLE 15. A non-linear regression analysis was performed using the Levenberg-Marquardt algorithm. The Fisher's test (FT), the mean error (ME), and the approximation of the standard deviation ( $\sigma$ ) were used to measure the goodness-of-fit [12]. Fig. 4 shows  $q_e$  as a function of  $C_e$  under equilibrium with the application of the above isotherm equations for Cr(VI) solution at  $\text{pH}_{\text{mit}} = 4$ . The value of isotherm parameters and statistical tests are summarized in Table 3. Upon comparing the depicted values, the isotherm curve for CL-HDTMA predicted by the four-parameters Bilangmuir model coincides with the experimental curve with the highest FT and the lowest  $\sigma$  and ME values. According to Li and Bowman, the coexisted two different active sites can be assigned to the hydrophobic environment of the loosely packed organic pseudophase and to ion-exchange sites on a densely packed bilayer [13]. It is worth to notice that the equilibrium relationship  $q_e = f(C_e)$  obtained for CL represents smooth distribution of experimental points covering the linear and nonlinear range of equilibrium curve ( $q_e = 0 - 7.5 \text{ mg g}^{-1}$ ). In case of PC-HDTMA, the modeling calculation was done for experimental data representing twice shorter equilibrium range ( $q_e = 0 - 3.5 \text{ mg g}^{-1}$ , linear range). Here, the best approximation was obtained for the two-parameter Langmuir model (FT = 156). The obtained value of maximum sorption capacity equals to the value obtained for the Bilangmuir model ( $q_{mL} = q_{m1BL} + q_{m2BL}$ ). Moreover, the homogeneity of Cr(VI) sorption on PC-HDTMA was further confirmed by equal energy of chromium binding ( $K_{1BL} = K_{2BL}$ ) into both Bilangmuir active sites.

Table 3

Isotherm parameter values and statistical tests for Cr(VI) sorption onto CL-HDTMA and PC-HDTMA,  $\text{pH}_{\text{mit}} = 4$

Model	$K$	$q_m/n$	$K_2$	$q_{m2}$	FT	ME	$\sigma$
CL-HDTMA							
Langmuir	0.19	6.48	—	—	19.39	27.37	0.58
Bilangmuir	0.67	3.91	0.0022	16.72	195.04	18.25	0.18
Freundlich	1.66	3.23	—	—	79.09	50.71	0.29
PC-HDTMA							
Langmuir	0.0033	10.23	—	—	156.46	24.20	0.08
Bilangmuir	0.0033	4.24	0.0033	5.99	121.69	24.20	0.09
Freundlich	0.0561	1.21	—	—	80.71	25.95	0.12

## 4. Conclusion

The analysis of infrared spectra revealed that characteristics for HDTMA vibrations were shifted after adsorption onto zeolitic structure and the intensity of characteristics



peaks decreased after Cr(VI) sorption. The efficiency of Cr(VI) sorption depends on the quantity and type of the zeolitic material presents in a zeolitic tuff. The increase of Cr(VI) sorption with decreasing of solution pH indicates higher affinity of HDTMA modified zeolites for univalent chromium anions. The modeling calculation reveals homogenous Cr(VI) sorption onto modified PC-zeolite and heterogeneous sorption onto modified CL-zeolite. The sites heterogeneity relates to coexistence of two different active sites, which can represent different surfactant density.

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