

Effect of the pH on the Cr(VI) Sorption on HDTMA-zeolites

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Abstract: The uptake of Cr(VI) from aqueous solutions was investigated using clinoptilolite and phillipsite 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 concentration of Cr(VI) working solutions, C_{init} ranged between 5-100 mg·L⁻¹, were prepared by dilution of the stock solution with distilled water with pH_{init} adjusted to the value of 3.0 or 4.0 or 5.0. The residual concentrations of chromium in the liquid samples were analyzed by ICP-OES. The uptake capacities of modified zeolites were compared in batch sorption experiments. The comparison of the obtained data identified that efficiency of Cr(VI) sorption onto clinoptilolite is always higher than in phillipsite case. The analysis of the infrared spectra revealed that after adsorption of Cr(VI) the characteristics for HDTMA vibrations were shifted in PHI-HDTMA case, while for CLI-HDTMA the intensity of characteristics peaks decreased.

Key words: Hexavalent chromium, HDTMA-Br modified zeolites, sorption, FTIR spectra.

1. Introduction

Chromium is an active metal that has several oxidation states. Hexavalent chromium is extremely toxic, causing severe clinical problems. It is introduced into environment through various industrial processes like electroplating, leather tanning, dyeing and metal cleaning. Over recent years, numerous research work has been carried out towards removal of Cr(VI) contaminant from aqueous solutions. None of the standard unit processes of water treatment technology ensure complete removal of chromium. The sorption techniques seems to be the most relevant as they allow for a selective removal of simple ions present in liquid streams even in relatively low concentrations. In the last decade there has been a growing effort to evaluate the feasibility and suitability of using natural minerals (e.g. zeolites) as effective, low-cost sorbent. Their usage for anionic

contaminates removal requires a modification of their sorption surface [1]. It is well known, that the hexadecyltrimethyl-ammonium (HDTMA) modified zeolites are effective sorbents of Cr anions [2]. Among the important factors, controlling the chromium uptake is the initial pH of the solution, which defines Cr(VI) hydrolysis products and the chromium concentration in the solution. Thus, the aim of this research was to investigate the effect of the pH on the Cr(VI) sorption on two different zeolitic materials modified with HDTMA.

2. Materials and Methods

The zeolitic-rich tuffs used in the present study were: clinoptilolite CLI from Slovakia (Nižný Hrabovec) and phillipsite PHI from Italy (Phlegraean). The samples of CLI had particles size 0.25-0.5 mm, while the particles of PHI were smaller than 0.25 mm. The mineralogical composition of zeolites was determined by X-ray powder diffraction (XRD) using Philips Xpert ADP and Thermo XTRA. The

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identification of phases was based on ICDD PDF-2 database and the collection of patterns recommended by International Zeolite Association. CLI: clinoptilolite 74%, cristobalite 11%, plagioclase 6%, illite and smectite 4%, tridymite 3%, kaolinite 1%, quartz 1%. PHI: 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 SiO₂, Al₂O₃ and Fe₂O₃ in a descending order. The higher SiO₂ and lower Al₂O₃ in clinoptilolite rich tuff (CLI: Si/Al = 5.11, PHI: Si/Al = 2.71) results mainly from the predominance of zeolitic mineral content (CLI: clinoptilolite 74%; PHI: phillipsite 27% + chabazite 27%).

The surface area, average pore diameter, and pore volume of the natural zeolites were determined by the N₂-BET method using a surface area and porosimetry analyzer, Micromeritics, ASAP 2420. In order to determine cation exchange capacity (CEC), all exchangeable cations were leached by Ca²⁺ ions (CaCl₂) according to procedure described by Gillman [3]. The concentrations of relieved ions were determined by atomic absorption spectroscopy (AAS). The external cation exchange capacity (ECEC) of zeolitic tuffs were measured according to procedure described by Orsini and Remy [4]. The results of the after mentioned measurements are displayed in Table

2. As evidence, from ten times larger micropore volume ($V_{p\ micro}$), PHI has more porous texture than CLI 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 PHI relates to higher Al content (Table 1) in the zeolite framework [5] but it does not relate directly to the amount of exhalable cations present on PHI external surface.

2.1 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 μS) until a reaction with 1% AgNO₃ solution was negative and next dried at 105 °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 was calculated from the Eq. (1):

$$m_{HDTMA-Br} = \left(\frac{M_{HDTMA-Br} [g/mmol]}{A} \right) \cdot ECEC [mmol/g] \cdot m [g] \quad (1)$$

where: m is mass of zeolitic material, M is molar mass of HDTMA-Br, 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 °C.

Table 1 Chemical analysis of zeolitic rich tuffs.

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

Table 2 Physical parameters of zeolitic rich tuffs.

Zeolite	ECEC mval/100g	CEC mval/100g	A_{BET} m ² /g	A_{micro} m ² /g	$V_{p\ tot}$ cm ³ /g	$V_{p\ micro}$ cm ³ /g
CLI	12.11	93.80	29.47	8.15	0.11	0.004
PHI	11.74	101.48	111.73	97.28	0.07	0.047

After 24 h, the zeolite was washed with deionized water and dried at 105 °C to constant weight. The obtained modified zeolites were called CLI-HDTMA and PHI-HDTMA for clinoptilolite rich tuff and phillipsite-chabazite rich tuff, respectively.

2.2 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 mg·L⁻¹ of Cr(VI) was prepared by dissolution of K₂CrO₄ (Chempur, analytical grade) in distilled water at pH_{init} adjusted to the value of 3.0 or 4.0 or 5.0 (pHmeter CP-401 ELMETRON) by using HNO₃. The concentration of Cr(VI) working solutions, C_{init} ranged between 5-100 mg·L⁻¹, were prepared by dilution of the stock solution with distilled water with pH_{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 μm 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 (mg·g⁻¹) was calculated as Eq. (2):

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

where C_{init} and C_e (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.

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 (4,000-400 cm⁻¹) with a resolution of 2 cm⁻¹.

3. Results and Discussion

The efficiency of Cr(VI) removal from solutions at different pH_{init} values (3, 4, 5) are depicted in Fig. 1 and Fig. 2, respectively. The comparison of the obtained data identified that efficiency of Cr(VI)

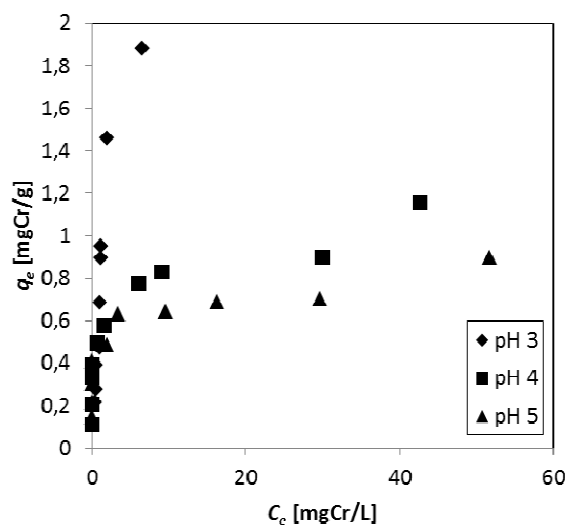


Fig. 1 Sorption isotherms for the removal of chromates from aqueous solutions on the CLI-HDTMA for different pH_{init}.

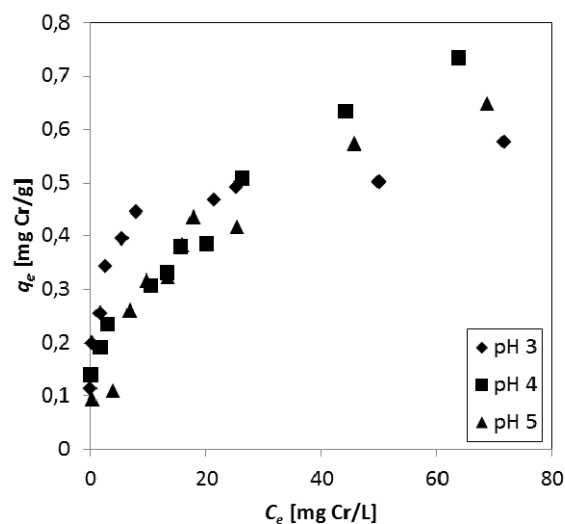


Fig. 2 Sorption isotherms for the removal of chromates from aqueous solutions on the PHI-HDTMA for different pH_{init}.

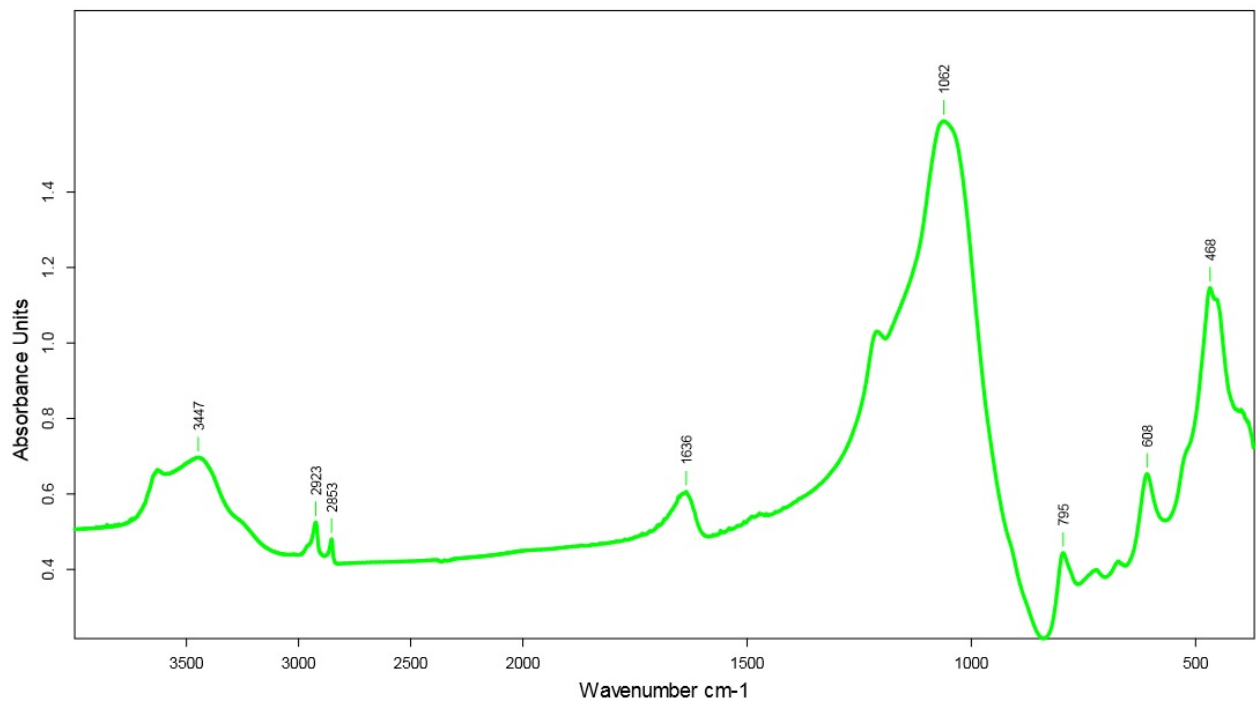


Fig. 3 FTIR spectra of CLI-HDTMA before sorption of chromate anions.

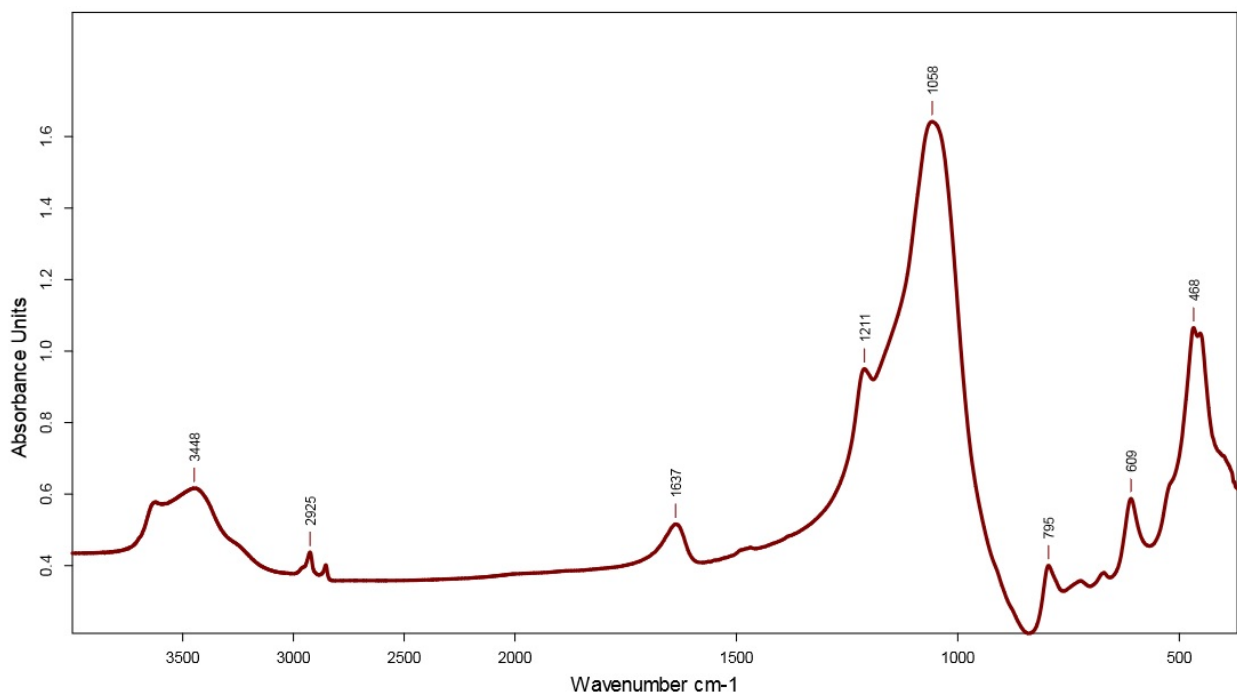


Fig. 4 FTIR spectra of CLI-HDTMA after sorption of chromate anions.

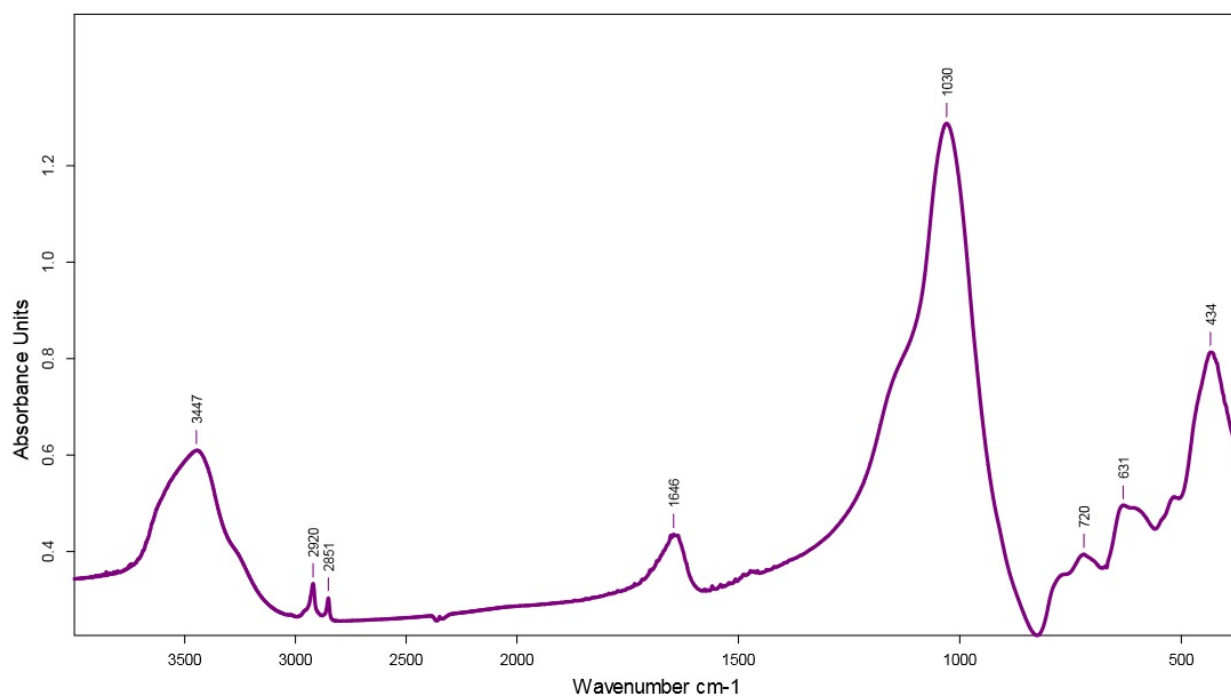


Fig. 5 FTIR spectra of PHI-HDTMA before sorption of chromate anions.

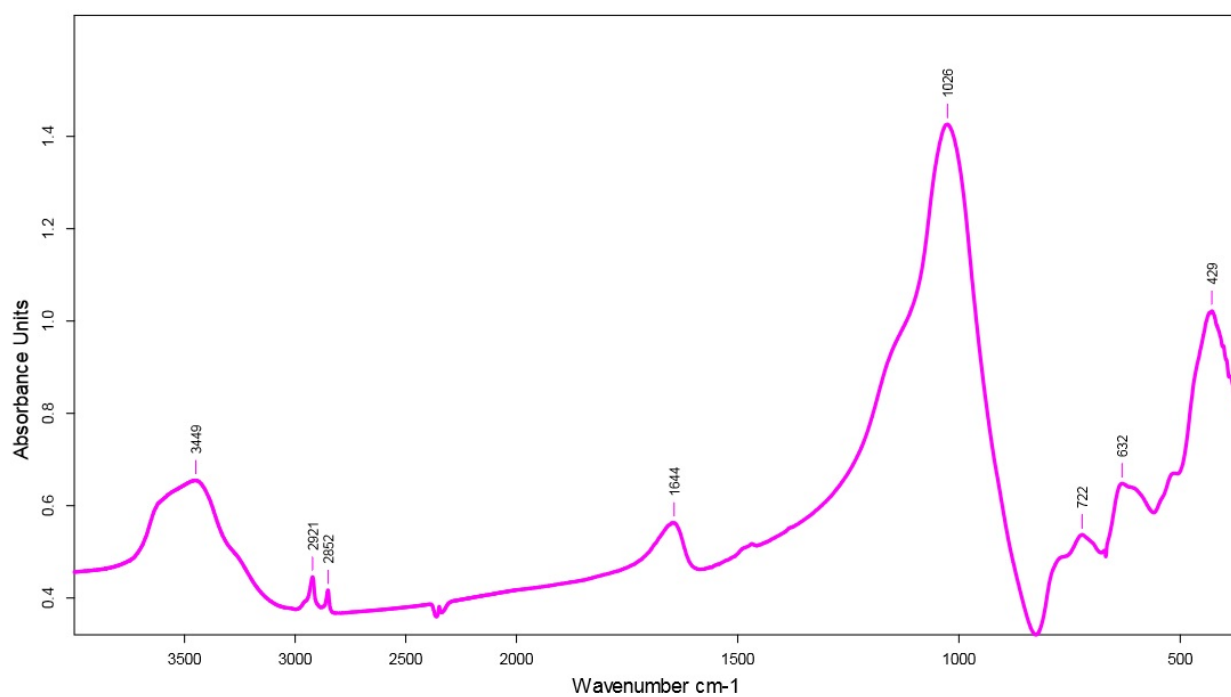


Fig. 6 FTIR spectra of PHI-HDTMA after sorption of chromate anions.

sorption onto CLI-HDTMA is always higher than in PHI-HDTMA case. Due to the smaller particle size (≤ 0.25 mm) of PHI, it was expected that PHI sorbed more HDTMA than CLI on its external surface and consequently had higher capacity towards Cr anions than CLI. However, due to specific structure of phillipsite tuff, the attachment of HDTMA can partially occur also into cylindrical caves. The trapped HDTMA molecules are probably not available for Cr(VI) ions sorption [5].

FTIR spectra of CLI-HDTMA before and after sorption of chromate anions are depicted in Fig. 3 and Fig. 4, respectively, while the corresponding FTIR spectra of PHI-HDTMA are depicted in Fig. 5 and Fig. 6. There are three groups of bands, which appear in spectrum of all the samples: 600-1,200, 1,450-1,650 and 2,700-3,000 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 of water molecules [6]. They own to surfactant molecules as well. The weak spectra at 1,468 cm^{-1} are related to the banding vibration of C-CH₃. For crystalline HDTMA, the positions of the CH₂ symmetric and asymmetric stretching modes are around 2,850 and 2,918 cm^{-1} , respectively [7]. The comparison of FTIR spectra on Fig. 3 and Fig. 4 identified that after chromium sorption onto CLI-HDTMA, the bands in the 800-400 cm^{-1} region remain unchanged. Similar data was obtained by other authors [8, 9]. On the other hand, the corresponding comparison of PHI-HDTMA spectra identified the shift of band from 434 cm^{-1} (Fig. 5) to 429 cm^{-1} after sorption of Cr(VI) (Fig. 6). Furthermore, in the region of 1,300-800 cm^{-1} two bands at ca. 1,211 and 1,060 cm^{-1} are visible for CLI-HDTMA. In contrary, only one band at ca. 1,030 cm^{-1} for the PHI-HDTMA is observed. The band was shifted to 1,026 cm^{-1} after sorption of Cr(VI) (Fig. 6). The analysis of the infrared spectra in the 2,700-3,000 cm^{-1} revealed that

after adsorption of Cr(VI) the intensity of peaks characteristics for HDTMA vibrations decreased for CLI-HDTMA, which was not the case for PHI-HDTMA.

4. Conclusions

The efficiency of Cr(VI) removal from solutions at different pH_{init} values (3, 4, 5) onto CLI-HDTMA is always higher than in PHI-HDTMA case. The comparison of FTIR spectra identified that after chromium sorption onto CLI-HDTMA, the bands in the 800-400 cm^{-1} region remain unchanged. On the other hand, the corresponding comparison of PHI-HDTMA spectra identified the shift of band from 434 cm^{-1} to 429 cm^{-1} after sorption of Cr(VI). In the region of 1,300-800 cm^{-1} two bands at ca. 1,211 and 1,060 cm^{-1} are visible for CLI-HDTMA. In contrary, only one band at ca. 1,030 cm^{-1} for the PHI-HDTMA is observed. The band was shifted to 1,026 cm^{-1} after sorption of Cr(VI). The analysis of the infrared spectra in the 2,700-3,000 cm^{-1} revealed that after adsorption of Cr(VI) the intensity of peaks characteristics for HDTMA vibrations decreased for CLI-HDTMA, which was not the case for PHI-HDTMA.

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