

# Adsorption behavior of Cr(VI) on modified natural zeolite by a new bolaform *N,N,N',N',N',N'*-hexamethyl-1,9-nonanediammonium dibromide reagent

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## Abstract

The demand for effective adsorbents is to increase in response to the widespread recognition of the deleterious health effects of Cr(VI)–oxyanions exposure through drinking water. In this study, Cr(VI)–oxyanions uptake from aqueous solutions by a new bolaform *N,N,N',N',N',N'*-hexamethyl-1,9-nonanediammonium dibromide reagent-modified natural zeolitic materials from Zahedan, Iran, was investigated using batch technique. Spectrophotometry method was used for Cr determination. The Cr(VI)-solution concentration varied between 2 and 104 mg L<sup>-1</sup>. It was shown that the Cr(VI) uptake strongly depended on pH. The maximum removal of Cr(VI) occurred in acidic media at pH < 1.5. The amounts of Cr(VI) adsorbed increased with increase in dose of both adsorbents and their contact time. Based on results an adsorption mechanism has been suggested. The adsorption data for modified zeolite using the amine was consistent with Langmuir isotherm equation and the equilibrium data was analyzed using the Langmuir isotherm.

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## 1. Introduction

It is suggested that Cr(III) and Cr(VI) are these most abundant oxidation states in natural and industrial waters. The former is considered to be essential to mammals for the maintenance of glucose, lipid and protein metabolism, while Cr(VI) is thought to be toxic and carcinogenic [1–4]. Low-level exposure to chromate ion is known to be toxic to mammals, capable of permeating cell membranes, a powerful mutagen for mammals and a potential carcinogen [5].

A number of treatment methods for the removal of metal ions from aqueous solutions have been reported, mainly ion exchange, electrochemical reduction, evaporation, solvent extraction, reverse osmosis, chemical precipitation, membrane filtration and adsorption [6]. Most of these methods involve high capital cost and are not suitable for small-scale industries. The adsorption processes are generally known to be one of the most effective techniques for removal of environmentally hazardous

metals. As it is easy to remove the adsorbent from aqueous media after treatment, adsorption technique is generally considered to be a promising method and has been studied for chromate removal as well. Adsorbents with strong affinity and high loading capacity for targeted metal ions have been developed by modifications of the surface of various substrates, such as polymers and clays with metal complexing groups [7,8].

Natural zeolites normally possess a negatively charged surface and therefore only cation exchange properties [9]. However, zeolite surfaces can be modified with substances possessing positively charged groups, which can provide these inexpensive and readily available materials with anion sorption properties [10,11]. Natural zeolites modified by different reagents have already been tested as sorbents for inorganic anions and organic contaminant [12–19] removal from environmental matrices as well as for the sorption of different toxins in the veterinary sciences [20].

Natrolite, Na<sub>2</sub>[Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>]·2H<sub>2</sub>O, is one of the fibrous zeolites with the framework constructed from the chains of corner-sharing Al and Si oxygen tetrahedral. The main structural unit is Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub> consisting of five tetrahedral, of which four are bound into the ring and the fifth, the SiO<sub>4</sub> tetrahedron, links

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the rings to form the chain extended along the *c*-axis. The adjacent chains are connected by outer oxygen ions O<sub>2</sub> of the rings, forming a three-dimensional framework. Ordered Na<sup>+</sup> ions and H<sub>2</sub>O molecules fill the voids of the framework. By the use of a wide range of different methods including Raman spectroscopy and NMR in ref. [21] it was found that the change in chemical composition of the nonframework ions and/or water content is followed by orientational changes (tilting and rotating) of the framework tetrahedral. The flexibility of the Natrolite framework also allows partial disorder in (Al, Si) distribution [22]. Natrolite, due to its physical and chemical properties, i.e., cation exchange capacity, large specific area and adsorptive affinity for organic and inorganic ions, is considered one of the most promising candidates for use in decontamination and disposal of high-level heavy metal wastes.

In the present study for first time, the capacity of natural zeolite (Natrolite) modified by *N,N,N,N',N',N'*-hexamethyl-1,9-nonanediammonium dibromide (HMNA-Br<sub>2</sub>) to remove Cr(VI)-oxyanions from aqueous media was investigated under various conditions. The sorption and desorption of chromate from aqueous solution on the original zeolite and modified zeolites were studied. It was shown that adsorption data for modified zeolite was consistent with Langmuir isotherm equation.

## 2. Experimental

### 2.1. Reagents and materials

All reagents were prepared from analytical reagent grade chemicals unless specified otherwise and purchased from Merck Company. All aqueous solutions were prepared with double-distilled water (DDW). A Cr(VI) solution stock containing 0.2 g L<sup>-1</sup> Cr(VI) was prepared by dissolving pure potassium dichromate, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. The Cr(VI) sorption experiments were performed using solutions of initial chromium concentration between 0.038 and 2.0 mmol L<sup>-1</sup> (2 and 104 mg Cr/L). A suitable volume of acid (hydrochloride acid) or base (sodium hydroxide) solution was added to adjust pH that was measured with pH meter.

A bolaform reagent, *N,N,N,N',N',N'*-hexamethyl-1,9-nonanediammonium dibromide (HMNA-Br<sub>2</sub>) was prepared as described by Menger and Wrenn [23] from reaction between 1,4-dibromononane and trimethylamine. Natural Iranian Natrolite zeolite from the Hormak area (Zahedan city, Sistan & Baluchestan province, Iran) was used in this work.

### 2.2. Surface modification

The treatment of the zeolite with NaCl caused an almost seven-fold increase of its sodium content at the expense of K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Fe<sup>2+</sup>. On the other hand, the treatment of the Na-form of the zeolite by the quaternary amine solutions leads only to partial removal of Na, suggesting that the organic amino groups containing cations are sorbed via ion-exchange but only to places easily accessible to molecules of big dimensions. Thus, this process is limited to the external surface of the zeolite grains. However, the sorption of a cationic surfactant

onto a negatively charged zeolite surface is a complex process involving both cation exchange and hydrophobic bonding [24]. The grain size of the material used for the experimental work was 0.5–1.0 mm. The zeolites were washed with 1 mol L<sup>-1</sup> HCl with agitation at 50 °C for 2 h, keeping them for 24 h in the acid solution, decanted and washed with water until a pH of 6 was obtained. The stability of zeolite in acidic media was checked by XRD, and there is no change in XRD pattern of zeolite before and after washing with acid. The Na-form of the zeolitic material was prepared prior to modification. For this purpose the zeolitic material was agitated for 48 h in a 1 mol L<sup>-1</sup> NaCl solution at 25 °C, washed using distilled water until free of chloride ions (AgNO<sub>3</sub> test) and dried at 105 °C to constant weight. The chemical modification was performed by mixing of the bromide salts of *N,N,N,N',N',N'*-hexamethyl-1,9-nonanediammonium dibromide (HMNA-Br<sub>2</sub>) and natural zeolite. For this purpose 5 g of the zeolite in Na-form were mixed for 12 h with 50 mL of surfactant solution in the rotary evaporator and shaken at 150 rpm. Solutions of HMNA-Br<sub>2</sub> concentrations = 0.01 mol L<sup>-1</sup> was utilized for the modification at 40 °C. A mixture of 75% ethanol and 25% water was used as a solvent due to relatively low solubility of HMNA-Br<sub>2</sub> in water. The concentration of the surfactant in the resultant solution was determined using reagent absorbance at λ<sub>max</sub> = 237 nm. The amount of surfactant adsorbed on the zeolite surface was determined by difference of initial concentration and the concentration of surfactant in the filtrate solution. The suspension was cooled in air and filtered off and then washed several times with double-distilled water and dried in an oven at 120 °C for 12 h prior to use.

### 2.3. General procedure

For the individual experiments 0.2–2 g of organo-modified zeolitic materials were shaken for 24 h with 20–50 mL of the individual solutions of Cr(VI) in polypropylene centrifuge tubes at ambient temperature. The concentration of the Cr(VI) in the resultant solution was determined using oxyanions absorbance at λ<sub>max</sub> = 372 nm for direct determination of Cr(VI) or λ<sub>max</sub> = 541 nm after complexation with sym-diphenylcarbazide (DPC) (0.002 mol L<sup>-1</sup> DPC in ethanol) for low concentration of Cr(VI). The amount of Cr(VI) adsorbed on the zeolite surface was determined by difference of initial concentration and the concentration of surfactant in the filtrate solution. The parallel tests on blank samples have been used for comparison. The pH of the solutions was checked before beginning and at the end of the sorption experiments. Duplicate samples were prepared for all experimental conditions.

### 2.4. Instrumentation

The characterization of the Zeolitic materials took place in the Spectrum Kansaran Binaluod Mine Material Research Company (SKBMMRC), Mashhad, Iran. XRF experiments and XRD experiments were recorded on Phillips PW-1480 and Phillips XPERT spectrometers and were performed with computer via the X40 and Apdw software's, respectively. UV-vis spectra were recorded on an analytikjena SPECORD S100 spectrometer with

photodiode array detector. IR spectra were recorded as KBr disks on a Shimadzu IR instrument. A Metrohm 632 pH-meter with a Metrohm double junction glass electrode was used for pH monitoring.

### 3. Results and discussion

#### 3.1. Characterizations of zeolitic material

The raw as well as the Na- and surface-modified forms of the zeolitic material were characterized. The Natrolite zeolite crystals were separated by hand. The analysis of the natural zeolite material used for the experimental work obtained by XRF is given in Table 1. The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the material is 1.77 corresponding to a Natrolite zeolite [25]. XRD pattern of the zeolite was shown a Natrolite pattern using Apdw software. The mineral content of the zeolitic material from quarry face, based on the XRF technique, was Natrolite 99.63% (w/w) (see Table 1). Also, some samples were Natrolite more than 92% (w/w) accompanied by small amounts of accessory minerals such as Celestine (SrSO<sub>4</sub>). Water content was 9.47% (w/w) using loss on ignition (LOI) study in 1050 °C for Na-form zeolite (Table 1, column 4). Also, the LOI method has been used to estimate organic matter in modified Natrolite zeolite. An accurate and stable weight loss 15.47% was achieved after 2 and 5 h of burning modified zeolite at 1050 °C for organic matter and water (see Table 1, column 5), whereas LOI of Na-form zeolite was 9.47.

The modification of the zeolitic material after treatment with the HMNA-Br<sub>2</sub> solution was verified by the IR spectra examination of the material. The IR spectrum of the Na-form zeolite contains bands due to Si–O–Si and Si–O–Al vibrations (1200–950 cm<sup>-1</sup>), the presence of zeolitic water (3619, 3440 and 1640 cm<sup>-1</sup>) and pseudo-lattice vibrations (800–500 cm<sup>-1</sup>). The IR spectrum of the modified zeolite by HMNA-Br<sub>2</sub> had additionally two intense bands in the region 3000–2800 cm<sup>-1</sup> assigned to the asymmetric and symmetric stretching of the C–CH<sub>2</sub> group of the alkyl chain. Also, the expected scissoring oscillations due to the methylene groups of the aliphatic chain (1460 cm<sup>-1</sup>) were not observed. These bands could be covered by the wide band due to Si–O or shifted according to the structural order of the methylene chain group [26]. Similarly, the vibrations associated

with the symmetric and asymmetric CH<sub>3</sub>–N stretching were not observed in the IR spectra of organo-zeolitic material. According to Sullivan et al. this behavior indicates lower hydration of the sorbed head-groups (quaternary ammonium) than of those in solution [27].

The pH measurement as a function of solution pH was studied with following method. 10 mg of the zeolite in different forms were mixed for 24 h with 10 mL of deionized water in 15-mL centrifuge tubes placed in the rotary evaporator. The pH range of deionized water (with pH 6.5) for the Na-form zeolite was 7.1; and for the HMNA-Br<sub>2</sub>-form zeolite, 9.4.

#### 3.2. The sorption experiments

For experiments using Natrolite, 0.5 g of zeolite was added to a vial and 20 mL of HMNA-Br<sub>2</sub> solution at concentrations from 0.2 to 10 mmol L<sup>-1</sup> was put into the each of them. Then, the sample was placed into a shaker and was shaken at room temperature for 24 h to obtain maximum adsorption of HMNA-Br<sub>2</sub>. After this time, the Natrolite mixture was centrifuged and the mixture was filtered. Then, the extracted solution was analyzed in order to obtain the HMNA-Br<sub>2</sub> concentration.

Adsorption of HMNA-Br<sub>2</sub> as a cationic surfactant from solution onto zeolite surface can be explained by the Langmuir isotherm. The Langmuir adsorption isotherm equation, applied in ion exchange study is:

$$S = \frac{K_1 S_m C}{1 + K_1 C} \quad (1)$$

where  $S$  is the amount adsorbed on solid at equilibrium (mmol kg<sup>-1</sup>),  $C$  the equilibrium liquid concentration (mmol L<sup>-1</sup>),  $S_m$  the adsorption capacity or adsorption maximum (mmol kg<sup>-1</sup>), and  $K_1$  is the Langmuir coefficient or adsorption intensity (L mmol<sup>-1</sup>). The Langmuir equation can be rearranged to the following linear form:

$$\frac{C}{S} = \frac{1}{K_1 S_m} + \frac{C}{S_m} \quad (2)$$

The adsorption isotherm of HMNA-Br<sub>2</sub> on Natrolite is presented in Fig. 1 (up) and the corresponding Langmuir adsorption isotherms of HMNA-Br<sub>2</sub> are shown in Fig. 1 (down). The maximum HMNA-Br<sub>2</sub> adsorption and Langmuir coefficient from

Table 1  
Analysis of the zeolitic materials utilized (all data expressed as oxides, %, w/w)

Element	Natrolite zeolite composition [25]	Natural Natrolite zeolite <sup>b</sup>	Na-form zeolite (%) <sup>b</sup>	Modified zeolite with 70 mg/L HMNA-Br <sub>2</sub> <sup>b</sup> (%)
SiO <sub>2</sub>	47.4	49.44	47.46	44.60
Al <sub>2</sub> O <sub>3</sub>	26.8	26.07	26.70	25.23
Na <sub>2</sub> O	16.3	14.68	16.37	14.70
MgO	–	0.03	0.00	0.00
K <sub>2</sub> O	–	0.01	0.00	0.00
CaO	–	0.11	0.00	0.00
Fe <sub>2</sub> O <sub>3</sub>	–	0.22	0.00	0.00
LOI <sup>a</sup>	9.5	9.44	9.47	15.47

<sup>a</sup> Loss on ignition (this method has been used to estimate of water and organic matter).

<sup>b</sup> From XRF study.

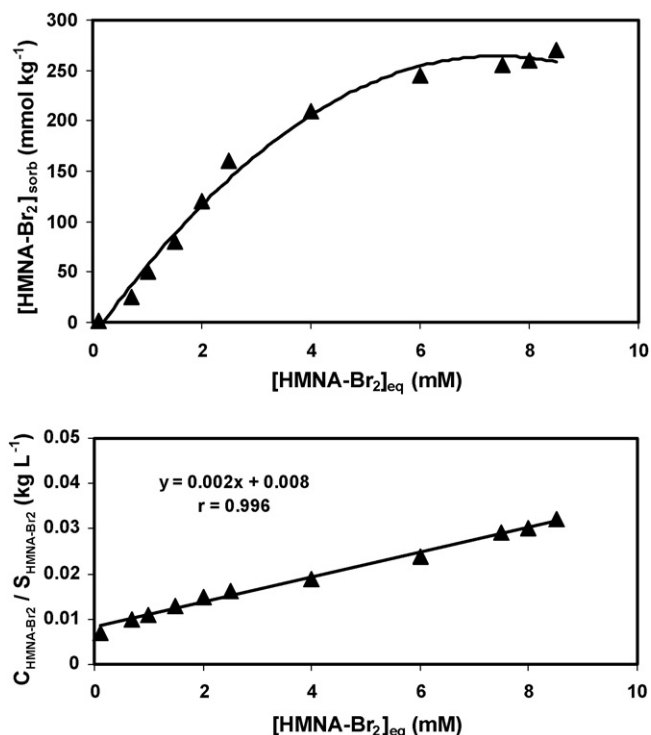


Fig. 1. (Up) adsorption isotherm of HMNA-Br<sub>2</sub>, (down) Langmuir isotherm of HMNA-Br<sub>2</sub> adsorbed on natural Natrolite zeolite.

Fig. 1 (down) are 500 mmol kg<sup>-1</sup> and 0.25 L mmol<sup>-1</sup>, respectively.

Chromate ions exist in an aqueous solution in different ionic forms. The pH and concentrations dictate which particular chromate species will predominate. The dichromate ions (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) dominate in acidic environments for chromium concentrations higher than 500 mg L<sup>-1</sup>, while the HCrO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup> oxyanions dominate at concentrations below 500 mg L<sup>-1</sup>. The ratio of HCrO<sub>4</sub><sup>-</sup> to CrO<sub>4</sub><sup>2-</sup> depends on the pH of the solution [28]. HCr<sub>2</sub>O<sub>7</sub><sup>-</sup> is present at low pH values (pH < 1). At slightly acidic pH (below 7) Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> is the most predominant Cr(VI) species with small quantities of HCrO<sub>4</sub><sup>-</sup>, the share of which decreases as pH increases. At neutral and slightly alkaline pH, CrO<sub>4</sub><sup>2-</sup> is the predominant chromate species in the aqueous phase. Beyond pH 8 the removal of CrO<sub>4</sub><sup>2-</sup> by organo-modified zeolite is not favored. This results from the competition between the chromate and hydroxide ion and the formation of hydroxyl complexes of chromium [29]. So, the effect of the pH was then evaluated between 1 and 7 for sorption of anionic chromate species using modified Natrolite zeolite. For the sorption experiments 1 g of the modified Natrolite zeolite were shaken in polypropylene tubes for 24 h with 50 mL of 0.1 mmol L<sup>-1</sup> Cr(VI) solution. The initial pH of the solutions was adjusted at different values using dilute nitric acid. The dependence of removal percentage for Cr(VI) upon pH of the aqueous solution is shown in Fig. 2. The adsorptions of chromate were constant in pH from 1 to 1.5 and decreased with an increase in pH up to 3.5 and then were constant. So, pH 1.5 was chosen as the optimum pH. The acidic

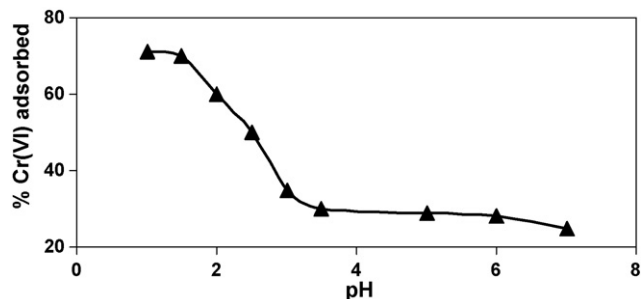


Fig. 2. Influence of the initial solution pH on adsorption of chromate using modified natural Natrolite zeolite, 1 g modified Natrolite zeolite, 50 mL Cr(VI) 0.1 mmol L<sup>-1</sup>.

media have been used for Cr(VI) extraction using quaternary amine (tetra-butylamine bromide, TBA-Br) in our laboratory [30,31].

Also, the removing of Cr(VI) was studied by varying the amount of modified zeolite. The results are shown in Fig. 3. The adsorption of Cr(VI) increased with an increasing in the amount of modified zeolite. Also, The experiment of adsorption as a function of contact time was conducted at known initial Cr(VI) concentration (0.1 mmol L<sup>-1</sup>), dose of 1 g modified zeolite in 50 mL. The removal was 70, 89 and 93% after 60, 90 and 120 min, respectively. Adsorption slowed down in later stages because initially a large number of vacant surface sites may be available for adsorption and after some time, the remaining vacant surface sites may be difficult to occupy due to repulsive forces between solute molecules of the solid and bulk phase. These results indicate that the modified zeolite has a very good adsorption capacity for Cr(VI)-oxyanions in solution.

The Cr(VI)-oxyanions adsorption isotherm and the corresponding Langmuir isotherm for modified zeolite are presented in Fig. 4. The experimental data can be fitted well to Langmuir adsorption isotherm. The Langmuir isotherm parameters, maximum Cr(VI)-oxyanions adsorption and Langmuir coefficient are 44.6 mmol kg<sup>-1</sup> and 3.5 L mmol<sup>-1</sup>, respectively.

To study efficiency of proposed method, removing of Cr(VI) ions from different syntactic natural water from Sistan & Baluchestan province have been investigated. For this experi-

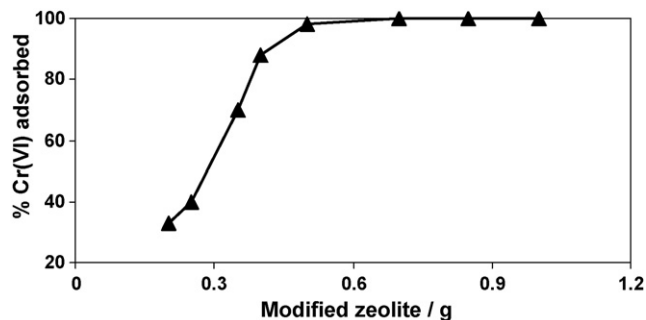


Fig. 3. The effect of amount of modified zeolite on adsorption of Cr(VI), pH 1.5 and 20 mL Cr(VI) 0.1 mmol L<sup>-1</sup>.

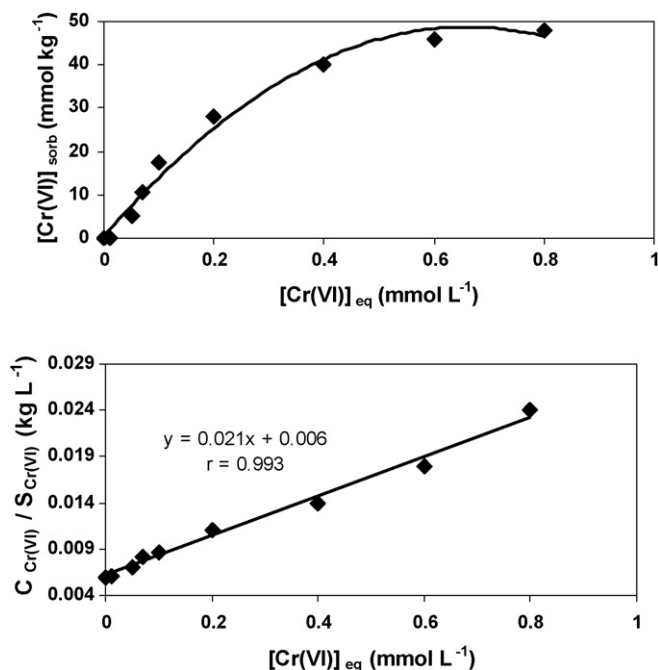


Fig. 4. (Up) Adsorption of Cr(VI)-oxyanions to HMNA-Br<sub>2</sub> natural zeolite treated, (down) Langmuir isotherm of Cr(VI) oxyanions adsorbed on modified zeolite.

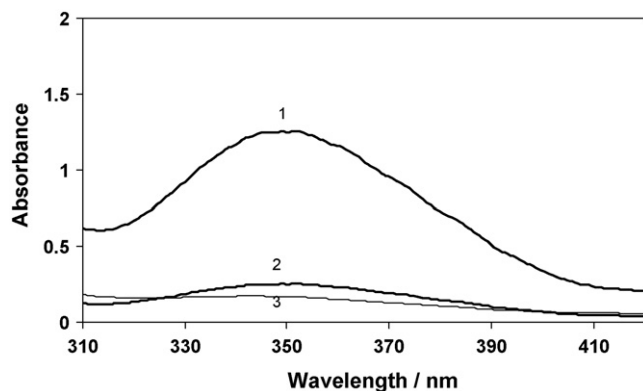


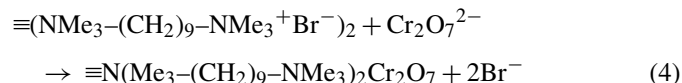
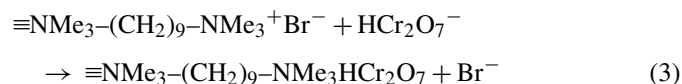
Fig. 5. UV-vis spectrum for removing of Cr(VI)-oxyanions in two syntactic natural water from Khash city in Sistan & Baluchestan province, before 1 (0.001 mol L<sup>-1</sup> Cr(VI)) and 2 (0.0001 mol L<sup>-1</sup> Cr(VI)) and 3 after contacted with modified natural Natrolite zeolite by HMNA-Br<sub>2</sub>, contact time 2 h, pH<sub>init</sub> 1.5.

ment 1 g of modified zeolitic materials were shaken for 2 h with 30 mL of syntactic natural water Khash city of Cr(VI) at ambient temperature. A sample UV-vis spectrum for removing of Cr(VI)-oxyanions in two syntactic natural water from Khash city in Sistan & Baluchestan province is shown in Fig. 5. As it can seem, the modified natural zeolite can be removed the polluted ion from the natural water.

### 3.3. Adsorption mechanism

The prevalent forms of Cr(VI)-oxyanions at pH 1.5 are HCr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. The adsorption of these oxyanions on modified zeolites can be described by the anionic exchange

reactions [31]:



The  $\equiv$  shown in Eqs. (3) and (4) is the anionic zeolite bead. This mechanism was well supported by the observations significantly increasing adsorption process with decreasing the pH of solutions. During the experiment, it was necessary to adjust the pH under 1.5. It is also concluded from Eqs. (3) and (4) that the terminal ammonium groups present on modified zeolite are reactive sites for oxyanions sorption. Finally, the formation of  $\equiv \text{NMe}_3-(\text{CH}_2)_9-\text{NMe}_3\text{HCr}_2\text{O}_7$  salt is more favored than the other chromate complexes. This result from the fact that the organic coat on the zeolite surface holds oxyanion chromate ions in the salt forms that possess lower solubility products in acidic pH. The same result has been obtained by other group [29].

## 4. Conclusions

From this research, it is concluded that Natrolite zeolite modified by a new bolaform *N,N,N,N',N',N'*-hexamethyl-1,9-nonanedi ammonium dibromide reagent for Cr(VI)-oxyanions sorption from water. The sorption of Cr(VI)-oxyanions in the pH employed (pH < 1.5) was constant but the Cr(VI) sorption significantly affected by pH value and decreased with increasing of pH from 1.5 to 7.0. The variation in adsorption can be attributed to the presence of deferent hexavalent chromium anionic species. The adsorption of the prevalent forms of dichromate ions, HCr<sub>2</sub>O<sub>7</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, in optimum pH range on modified zeolites can be described by the anion exchange. The sorption of HMNABr<sub>2</sub> from solution onto Natrolite zeolite surface and Cr(VI)-oxyanions from solution onto modified Natrolite zeolite with HMNABr<sub>2</sub> surface were fitted well by Langmuir isotherm. Easy synthesis procedure of modified zeolite, high chromium adsorption and good recovery make it one of the potential alternatives for removal of toxic chromium ion from water samples.

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