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Original Research

Efficient Removal of Hexavalent Chromium in Aqueous Solution by Cationic Surfactant-Treated Natural Anatolian Clinoptilolite

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Abstract

Sodium clinoptilolite-rich tuff from the Western Anatolia, Bigadic region was modified with octadecyltrimethylammonium bromide(ODTMA-Br) and hexadecyltrimethylammonium bromide (HDTMA-Br), and used for the first time to remove chromium(VI) from aqueous solution in a series of batch adsorption experiments. Various physico-chemical parameters affecting the adsorption process such as the contact time, pH, the optimum sorbent dosage and the initial concentration of chromium were studied. The Cr(VI) adsorption capacity of ODTMA- and HDTMA-treated clinoptilolite (Cp) was highly pH-dependent, and was found to be 3.65 mg/g and 2.85 mg/g at pH 2.0 and 3.0, and 0.25 g/50 mL sorbent dosage, 3 h equilibrium time and 25ºC, respectively. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were applied to describe the adsorption isotherms. Langmuir's model fitted the equilibrium data better than the Freundlich isotherm. From the D-R isotherm model, the mean adsorption energy (E) calculated as 15.075 and 14.744 kJ/mol for ODTMA-Cp and HDTMA-Cp sorbents showed that the adsorption of chromium occurred by chemisorption. The kinetic data indicated that the sorption of hexavalent chromium onto modified Cp followed well the pseudo-first-order kinetics. The current study considers that further developments in this line of research should continue

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to grow in the coming years, i.e., regarding water treatment, heavy metal and chromate removal using easily-available, low-cost microporous natural materials such as clinoptilolite.

Keywords: chromium (VI), clinoptilolite, adsorption, HDTMA-Br, ODTMA-Br

Introduction

Chromium(VI) is one of the most toxic pollutants, which is readily leached into groundwater or surface waters via wastewater discharges derived from intense and rapid industrial activities over the years like leather tanning, electroplating, and corrosion protection [1]. Currently, the legislation involving liquid industrial waste is getting more rigid, particularly in the more developed countries, and requires any wastewater to be treated before it is released into the environment [2]. Indeed, chromium is a naturally occurring element found in rocks, animals, plants, and soil, mainly in its insoluble trivalent form, Cr(III). A substantial increase of Cr(VI) due to human activities is much more toxic than Cr(III) because of its solubility in almost all pH ranges and greater mobility than Cr(III) [3]. Additionally, at low concentrations, while Cr(III) is an essential micronutrient for animals and humans as it plays a significant role in the normal metabolism of carbohydrates, lipids, and proteins [4, 5], chromium(VI) is regarded as one of the most carcinogenic and teratogenic pollutants [1]. Furthermore, chromium compounds are non-biodegradable and tend to accumulate in living organisms [6]. Therefore, using an efficient and easily applicable treatment agent or undergoing a process of disposing of Cr(VI)-contaminated wastewater prior to the discharge into the aquatic environment has gained great importance [7]. Several conventional chemical and physicochemical methods such as chemical precipitation, oxidation, ultrafiltration, reverse osmosis, membrane filtration, adsorption, and ion exchange have been developed to remediate Cr(VI)-contaminated wastewater and water [8-10]. Concerning those Cr(VI) removal methods, ion exchange and membrane separation have some drawbacks, such as a relatively high cost, a long production cycle, large pH changes in the production process, scarce target resin, sometimes poor product quality, and additionally, the mechanical fragility of membranes has hindered their widespread use. On the other hand, chemical precipitation creates large amounts of solid sludge [11]. Each treatment certainly has its own restrictions such as efficiency, environmental friendliness, operation difficulty, availability as well as the high cost. Hussain et al., in their review article reported that, studies on the use of easily obtainable low-cost alternative adsorbents for the treatment of wastewaters with a high metal concentration have remarkably increased in recent years [12]. Today, modified sorbents are still effectively utilized to remove Cr(VI). For example, the effect of various natural clay-based sorbents modified with the cationic surfactant cetyltrimethylammonium bromide on the migration behavior of chromium (VI) has been currently investigated by Sun et al. [13]. A new method for the magnetic solid-phase separation of Cr(VI) from aqueous solution using the modified melamine-formaldehyde adsorbent has been applied by Avan et al. [14].

Zeolites have gained prominence as excellent sorbents in removing heavy metal cations from wastewaters as they have higher ion-selective capabilities than many other adsorbents. They can be used in the treatment of industrial wastewater since they are abundant in nature and can be obtained locally with ease. Furthermore, they have a high chemical stability and a specific surface area, which brings huge advantages in wastewater treatment. Zeolites are crystal-shaped aqueous aluminum silicates of alkaline and alkaline-earth elements. One of the most widespread natural zeolites is clinoptilolite with unique crystal structures consisting of a three-dimensional framework of SiO_4 and AlO_4 tetrahedral that leads to a net permanent negative charge density in the zeolite lattice [15, 16]. Thanks to their physico-chemical and rich negatively-charged surface characteristics, clinoptilolite minerals like other zeolites act as excellent molecular sieves besides good exchangers of cations [17]. Zeolite tuffs usually contain more than 70 % of clinoptilolite. Clinoptilolite, naturally abundant in Turkey, belongs to the heulandite family and has the property of removing trace amounts of various heavy metal cations from aqueous solutions using ion exchange and adsorption [18, 19]. The selectivity order of the natural clinoptilolite for heavy metals has been determined as $Pb^{2+}>Cu^{2+}>Cd^{2+} > Zn^{2+}>Cr^{3+}>Co^{2+}>Ni^{2+}$. Since the surface of zeolite is negatively charged, its capacity to adsorb metals like lead, cadmium, mercury, and zinc is high while its capability of Cr(VI) sorption is rather low. The efficiency of Cr removal, incidentally, was investigated using unmodified natural clinoptilolite from aqueous solutions and explained through the corresponding adsorption isotherm model by Jorfi et al. [20]. In studies carried out in recent years, various alternative modifications have been used to donate the natural zeolite an overall positive surface charge resulting in the attraction of negatively charged species such as Cr(VI). It is stated that there is a remarkable increase in the chromium sorption capacity of zeolites modified with cationic surfactants [15]. The surfactant modification significantly changes the chemistry of the surface of the zeolite. By this process, non-polar organic materials and anions can be adsorbed by the natural zeolite which shows a little affinity with them. Long-chain quaternary ammonium salts are cationic surface-active agents that have a permanent positive charge, and are well-known as effective surfactants for zeolite modification. The modifications performed with cationic surface-active materials such as quaternary ammonium salts have rapidly gained importance as they provide zeolites with the potential to act as an anionic ion exchanger. The surfactant modification of zeolite materials changes the surface properties from hydrophilic to hydrophobic [21]. This enables them to remove anionic pollutants from wastewater in the adsorption processes. HDTMA-Br, DTAB (dodecyl trimethyl ammonium bromide), and ODTMA-Br can be given as more often examples of these salts. As the molecules of ammonium salt are too large to enter the canals of zeolite, the modification of zeolite takes place only on the outer surface of crystallites [22]. On the other hand, the analysis of chromium species in the natural samples is still one of the most challenging analytical issues as the toxicity of chromium depends strongly on its species distribution. Among the different analytical techniques applied for the extraction and enrichment of chromium (III, VI), aiming at trace level detection, the dispersive liquid-liquid micro-extraction (DLLME) based method such as deep eutectic solvent with ultrasound-assisted based dispersive liquid-liquid micro-extraction (DES-UA-DLLME) with ionic liquid [23] and ultrasound-assisted supramolecular solvent dispersive liquid-liquid microextraction (UA-SUPRAS-DLLME) [24], which comprises rapid injection of a mixture of extractant and dispersive solvents into a sample solution, has been favoured in recent years because it minimizes the use of solvents, cost and time. This procedure results in the formation of a cloudy solution, in which fine droplets of the extractant solvent are dispersed in the sample, and thus helps to carry out both extraction and pre-concentration within a rapid single step. The speciation of Cr(VI)/Cr(III) adsorbed on humic acid (HA)-microporous zeolite Y and extracted in an ionic liquid (1- butyl-3-methylimidazolium tetrafluoroborate has been studied by Huang and Wei [25]. Although many researchers have examined the effectiveness of modified zeolites for the adsorption of Cr(VI), this is the first study reporting on the hexavalent Cr(VI) removal using the modified Bigadic clinoptilolite, and related parameters on the adsorption process have been described in detail. In addition, the modified adsorbents devised in this study can also be used in the speciation analysis of the solution containing Cr(III,VI), as Cr(VI) is retained selectively.

This study mainly focused on investigating the Cr(VI) removal efficiency of Bigadiç clinoptilolite modified for the first time with ODTMA-Br and HDTMA-Br compounds from the quaternary amine group. There are replaceable cations such as Na, K, Ca, and Mg in the structure of the natural zeolite mineral. Therefore, as the first step of the study, clinoptilolite was conditioned with NaCl and converted into the homoionic form, and then modified with ODTMA-Br and HDTMA-Br. Experiments were conducted with a series of batch tests based on the effect of the adsorption parameters such as contact time, pH, initial Cr(VI) concentration, and adsorbent dosage on the Cr(VI) removal efficiency.

Material and Methods

Reagents and Apparatus

All chemicals except for surfactants were purchased from E. Merck, Darmstadt, Germany, and were of analytical reagent grade. The surfactants, hexadecyltrimethylammonium-bromide (HDTMA-Br) and octadecyltrimethylammonium-bromide (ODTMA-Br) were obtained from Sigma-Aldrich (99%) (St Louis, MO, USA). Cr(VI) stock solution (1000 mg/L) was prepared by dissolving 3.734 g of potassium chromate (K_2CrO_4) and adding 2 mL of 0.5 M HNO_3, and the mixture was diluted with distilled water to a final volume of 1000 mL. The stock solutions were standardized by diphenylcarbazide spectrophotometry and iodometric titrations, and were used in the preparation of working solutions. The required pH adjustments were made by use of 0.1M (or more dilute) HNO_3 and 0.1M NaOH. A 0.05 M solution of the Cr(VI) reagent, diphenylcarbazide, was prepared by dissolving 0.6056 g in 50 mL of acetone. The concentration of Cr(VI) solution was measured using diphenylcarbazide spectrophotometric method with the aid of a Carry 1 E UV-Vis spectrophotometer at 540 nm (Agilent, Tokyo, Japan). The measurements of Cr were confirmed using an atomic absorption spectrometer with an air-acetylene flame (Varian SpectrAAFS-220 model, Melbourne, Australia). All pH measurements were made with a Metrohm E-512 pH meter equipped with a glass electrode (Herisau, Switzerland).

Clinoptilolite Supply, Preparation and Modification

The clinoptilolite-rich mineral used in this study was obtained from Bigadic¸ in Western Turkey. The mineral was ground and sieved for the experiments between 250-425 mm, and then washed with distilled water to eliminate the soluble impurities and dried in an oven at 105ºC, and finally stored in a desiccator for further applications. The chemical composition of natural clinoptilolite is given in Table 1 [26]. The characterization of the clinoptilolite sample used in this study was carried out by Akdeniz and Ülkü [26]. They examined the thermal properties of the sample with TGA-DTA/DSC techniques. In addition, X-ray powder diffraction (XRD) was used to investigate the surface characteristics of the clinoptilolite sample. The parent mineral sample was reported to have contained mainly clinoptilolite (80-85%), additionally 5-10% quartz < 5% analcime and/or mordenite. The general chemical

Table 1. Chemical composition and specific surface area (BET) of Bigadic-raw clinoptilolite mineral.

Major constituents	% Weight
Al_2O_3	12.37
Si_2O	62.17
BaO	0.24
CaO	3.52
Fe_2O_3	0.82
K_2O	1.03
MgO	1.61
Na_2O	0.11
BET (m^2/g)	17.25

formula of the natural clinoptilolite may be given as $(Ca_{1/2}, Na, K)_6Al_6Si_{30}O_{72}$. $24H_2O$, where the Si/Al ratio in the zeolitic structure affects the adsorption properties of clinoptilolite [17].

To obtain a homoionic material, 50 g purified clinoptilolite sample was first treated twice with 500 mL 1 M NaCl in 1:10w/v ratio, and then with 150 rpm constant agitation in a shaker (Gallenkamp Orbital shaker incubator (Apeldoorn, The Netherlands)) for 24 h. Thereafter, the sample was washed with deionized water until neutral pH was maintained and the chloride free solution was achieved by checking with a silver nitrate solution as the indicator.

Modification of the Sodium-Clinoptilolite-Rich Tuff Sample (CpNa)

Alkyl quarternary ammonium cationic surfactants hexadecyltrimethylammoniumbromide (HDTMA-Br) and octadecyltrimethylammoniumbromide (ODTMA-Br) were used as modifier organic agents. The modified clinoptilolites were produced to change the surface properties of the natural mineral material and allow the final products obtained to sorb anionic Cr(VI) from aqueous solutions (Fig. 1). Thus, 10 g sodium-clinoptilolite-rich tuff (CpNa) samples were mixed individually with HDTMA-Br and ODMTA-Br cationic surfactants in the range of $1.5x10^{-3}$- $6x10^{-2}$ mol/L different initial concentrations for 24 h at pH = 8.0 in room temperature. Finally, the samples were separated by centrifugation at 10000 rpm for 10 min and washed with deionized water and air-dried. The amount of ODTMA and HDTMA retained by clinoptilolite was calculated by analyzing total organic carbon values in the filtrate using a total organic carbon Shimadzu TOC-5000A (TS 8195) model (Tokyo, Japan). The difference of C and N contents between Na form clinoptilolite and its surfactant-treated form was used to calculate the external cation exchange capacity, which was 35.0 mmol/100 g for HDTMA-loaded and 38.0 mmol/100g for the ODTMA-loaded clinoptilolites.

Cr(VI) Adsorption Procedures

To determine the batch adsorption capacity of the surfactant loaded sorbent for Cr(VI) as well as the effect of the contact time ((15-280 min), aqueous chromium concentration (50-400 mg/L), and solution pH (1.0-11.0), sorption experiments were performed by batch equilibration at 25±2ºC keeping the concentration of the modified sorbent constant at 0.25 g/50 mL. The suspensions were brought to the desired pH by adding sodium hydroxide and nitric acid. The adsorption capacity (mg/g) was calculated as the difference between Cr(VI) ions concentration of the pre- and post-adsorption solutions divided by the weight of the dry modified clinoptilolit sorbent. The adsorption capacity of the sorbent was calculated using the following mass balance equation (Eq. 1):

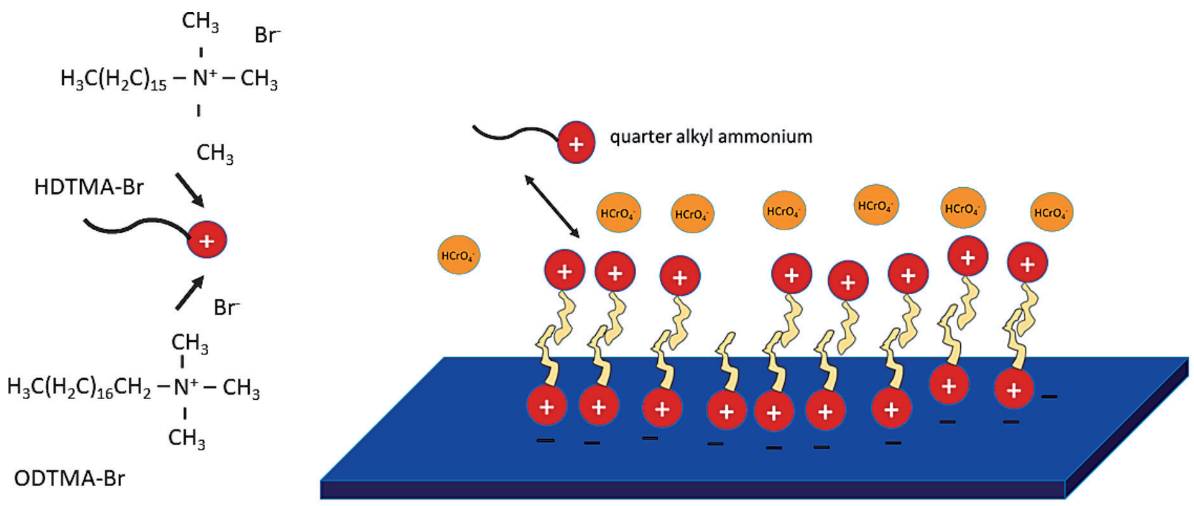

Fig. 1. The schematic representation of the anionic chromium(VI) retention onto the HDTMA/ODTMA-modified clinoptilolite.

$$q_e = \frac{(C_0 - C_f)V}{m} \quad (1)$$

The adsorption percentage was calculated using (Eq. 2):

$$Adsorption\ (\%) = \left((C_0 - C_f)/C_0\right) x100 \quad (2)$$

where q_e is the amount of sorbate taken up by the natural sorbent, V is the solution volume in a liter, m is the amount of natural sorbent in gram, C_o is initial sorbate (Cr(VI)) concentration (mg/L) and C_f is the measured final (equilibrium) soluble sorbate (Cr(VI)) concentration in solution, respectively. The order and nature of the reaction were identified via kinetic studies and fitting the adsorption data to Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models.

Results and Discussion

Optimum Surfactant Concentration

The saturation limit of long-chain quaternary ammonium surfactants adsorbed by minerals was examined as a function of different initial surfactant concentrations. As can be seen from Fig. 2, the adsorption of surfactants reached a saturation capacity of the minerals surface with a 3.0 x10^{-2} mol/L initial surfactant concentration, and the corresponding sorption amounts of ODTMA and HDTMA were found as 3.72x10^{-4} mol/g and 3.5x10^{-4} mol/g, respectively.

The saturation limit of quaternary ammonium surfactants adsorbed by minerals was determined as a function of a different initial surfactant concentration. As shown in Fig. 2, the amount of the modifiers adsorbed by clinoptilolite increased up to the saturation limit with an increasing initial surfactant concentration.

The adsorption of surfactants reached a saturation capacity of the mineral surface with 3.0 x10^{-2} mol/L the same initial surfactant concentration and the corresponding sorption amounts of ODTMA and HDTMA were found as 3.72 x 10^{-4} mol/g sorbent and 3.5 x 10^{-4} mol/g sorbent, respectively. The effectiveness of the modification was also tested by the modified sorbents based on the retention rates of chromium. According to the chromium removal rates, sufficient ODTMA and HDTMA quantities were determined as 2.0 x 10^{-2} M and 3.0 x 10^{-2} M initial concentration values. Thus, the cation(external) exchange capacity (ECEC) of clinoptilolite mineral was 35.0 mmol/100 g for HDTMA and 38.0 mmol/100g for the ODTMA modifiers which was equal to 1.24 ECEC with HDTMA and 1.0 ECEC with ODTMA, respectively. Hence, the amount modifier required for a single layer surfactant formation was calculated as 1.2 ECEC. Later experiments were conducted using 1.2 ECEC [22, 27].

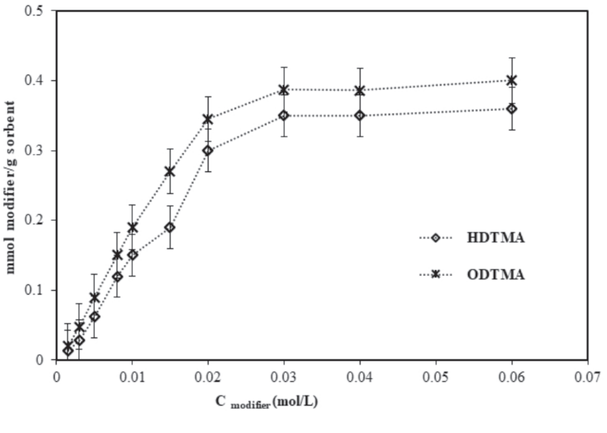

Fig. 2. The adsorption of HDTMA and ODTMA surfactants on the clinoptilolit mineral surface.

The sorption of large surfactant molecules on clinoptilolite minerals is restricted to external sites only. The mechanism of this surface modification is mainly based on ion-exchange, namely the interaction between cationic surfactants (HDTMA-Br and ODTMA-Br) with extrastructural cations on the surface up to external cation exchange capacity (ECEC) of negatively-charged clinoptilolite.

The diameter of the clinoptilolite internal pore is sufficiently large for exchangeable cations such as Na, Mg, Ca present already on the mineral lattice but too small to enter for long-chain surfactant cations. Therefore, the adsorption of these cations occurs in the external exchange sites only and does not correspond to the total cation exchange capacity of minerals. Thus, only the external cation exchange capacity (ECEC) of the mineral can be determined using alkylammonium ions. Typically, the adsorption of ionic surfactants on a solid surface is based on the formation of a monolayer surface micelle (hemimicelle) at the solid-liquid interface via strong ionic bonds. This micelle formation occurs spontaneously at or below a certain surfactant concentration defined as the critical micelle concentration (CMC). If the surfactant concentration exceeds the CMC, the hydrophobic tails of the surfactant molecules assemble into aggregates forming a bilayer(admicelle) on the surface by means of Van der Waals forces and H bonds, as shown in Fig. 1.

Effect of the Solution pH

One of the most important adsorption parameters is pH, as it affects both the sorbent surface properties and the ionic forms of species in the solution equilibria and hence controls the sorption capacity. Fig. 3 shows the effect of pH on the retention of hexavalent chromium onto HDTMA- and ODTMA-modified clinoptilolite from Cr(VI)-Na_2CrO_4 aqueous systems.The uptake of chromium(VI) reached the maximum level at pH 2.0 and pH 3.0 with ODTMA and HDTMA treated clinoptilolite, respectively. Based on the chemical species distribution diagrams of Cr(VI) for a K_2CrO_4

aqueous system at different pH values, we may infer that the chromium(VI) retention in all probability occurred through the interaction between protonated amine groups on the treated clinoptilolite surface and bichromate ($HCrO_4^-$) which was a dominant oxy-anionic species of chromium (VI) between pH 2.0 and 6.0. Additionally, at pH<1.0, the predominant species was chromic acid (H_2CrO_4), while the CrO_4^{2-} form existed in basic pH values [8]. Bichromate anions were accumulated on the clinoptilolite surface with the effect of the modified surface having positively charged exchange sites from the positive amine group ($-NR_3^+ \ldots HCrO_4$) [8, 10] as schematized in Fig. 1. In basic solutions, chromium exists in the form of CrO_4^{2-}. The related chemical equilibria may be written for the Cr(VI) in aqueous solution: $H_2CrO_4 \leftrightarrow HCrO_4^- + H^+$ (p*K*a = 4.1); $HCrO_4^- \leftrightarrow CrO_4^{2-} + 2H^+$ (p*K*a = 5.9).

In addition to the active role of amino groups commonly known in the retention of Cr(VI), it is strongly possible that -OH functionalities in silanol (≡SiOH) and aluminol (≡AlOH) groups found in abundant clinoptilolite tuffs are also very effective. However, this type of retention is most likely caused by surfactant-free (uncovered) aluminosilicate surfaces. In aqueous solutions, these oxides are covered with -OH groups where they are subject to protonation or deprotonation depending on the pH value of the solution. The $HCrO_4^-$ species can be easily bound with OH^- ions at active surfaces under acidic conditions. Consequently, charged species such as chromium(VI) anions are adsorbed onto charged metal oxide surfaces by electrostatic attraction and/or through surface complexation according to the following reactions: $\equiv MOH + H^+ \rightleftarrows \equiv MOH_2^+$ / $\equiv MOH \rightleftarrows \equiv MO^- + H^+$, where ≡M stands for metal (hydr)oxide surfaces [28].

Effect of Time

The effect of time on the hexavalent chromium removal by treated-Cp was conducted at different initial chromium concentrations (50, 100, 200 mg/L) by keeping pH 2.0 for ODTMA and 3.0 for HDTMA-treated-Cp, the sorbent dose (0.25 g/50mL), the stirring speed (150 rpm), the temperature constant (25±1ºC) and varying the contact time (15-280 min). The effect of time on the amount of chromium adsorbed and corresponding removal rates were shown in Fig. 4. The percentage of chromium removal was considerably steeper for the first 90 mins at the 50 and 100 mg/L initial concentration of Cr(VI) for both treated-Cp. A maximum Cr (VI) uptake reached equilibrium in the 135th and 150th min for ODTMA- and HDTMA-treated Cp with 50 and 100 mg/L respectively. Based on the increased concentration of chromium in solution, chromium adsorption was significantly steeper (i.e. showed a higher increase in qe with Ce) than the solution containing lower chromium ion and decreased in the following order: 200>100>50 mg/L. However, the removal efficiency decreased as estimated. On the other hand, in the first about 100 minutes of the adsorption process, the chromate retention rates of modified clinoptilolites were quite high, as there were many adsorption sites on the surface of the sorbents. In the initial modified surface, the binding probability was high, and as a result, adsorption proceeded with at a high rate. As the active sites were gradually filled up by the retained species, the adsorption process became slow and the kinetics could become more dependent on the rate at which the adsorption was transferred from the bulk phase to the exact adsorption sites. Chromium(VI) adsorption with both modified sorbents reached the maximum level in 3 h with the extension of time. Finally, the maximum Cr(VI) adsorption was observed as 3.65 mg/g for ODTMA-treated Cp and 2.85 mg/g for HDTMA-treated Cp.

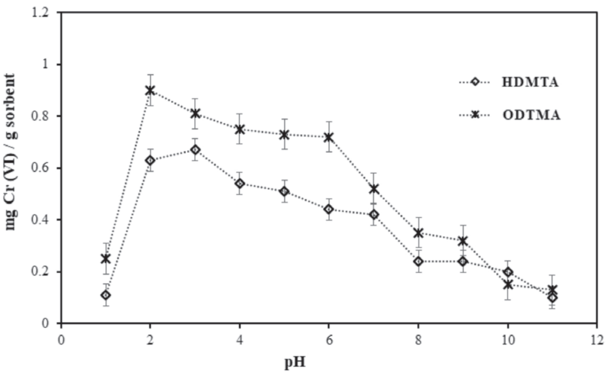

Fig. 3. The effect of solution pH on the adsorption of Cr(VI) from Cr(VI)-Na_2CrO_4 aqueous systems on the HDTMA and ODTMA treated clinoptilolite (V_o = 50 mL, C_i = 25 mg/L, m = 0.25 g, t = 24 h, T = 25ºC).

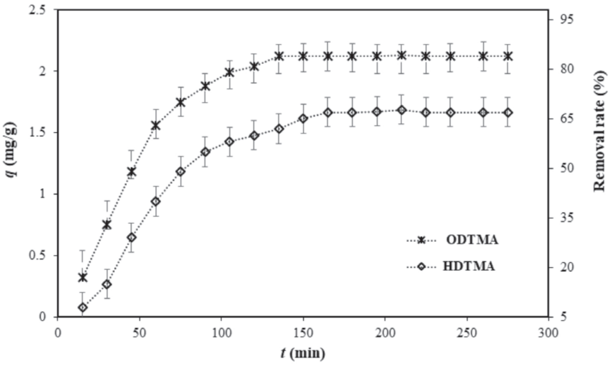

Fig. 4. The adsorption of Cr from Cr(VI)-Na_2CrO_4 aqueous systems by ODTMA-Cp and HDTMA-Cp as a function of time (V_o = 50 mL, C_i = 50 mg/L, pH = 2.0; 3.0, T = 25ºC).

Adsorption Kinetics

The adsorption kinetics indicated the adsorption rate of chromium(VI), which is an important parameter to evaluate the adsorption performance of the modified sorbents. In this work, Lagergren pseudo-first-order kinetic model was used to describe the adsorption of Cr(VI) on to ODTMA and HDTMA-Cp. The pseudo-first order equation is expressed as follows:

$$log \frac{(q_e - q)}{q_e} = -\frac{k_{ad}\,.t}{2.303} \quad (3)$$

where q_e and q are the amounts of chromium(VI) adsorbed at equilibrium and given time *t*(mg/g), respectively, and $k,_{ad}$ is the rate constant of the pseudo-first-order adsorption (1/min) calculated from the slope and intercept of the linear plots of *log* $(q_e - q)$ versus time (*t*) shown in Fig. 5 and listed in Table 2. As it can be seen from Table 2, good linearities were found with linear regression coefficient (R^2) equal to 0.997 and 0.9964 for ODTMA-Cp and HDTMA-Cp, respectively, clearly indicating that pseudo-first-order equation was followed. The theoretical analysis suggested by Azzizian et al. 2018 [29] addresses the cases in which the initial concentration of adsorbate is either relatively low or high. By the Langmuir kinetic model, at lower initial concentration values, the rate of sorption is normally determined by the adsorbate concentration in solution, but with relatively higher values of the initial concentration, the rate of uptake becomes increasingly controlled by the available sorption sites [30]. Azzizian et al. show that relatively high values of the initial concentration of an adsorbate tend to give good fits to a pseudo-first-order rate behavior, while relatively low concentrations are often associated with a PSO model.

Adsorption Equilibrium

The experimental data were evaluated according to the Langmuir, Freundlich, and Dubinin Radushkevich isotherm (D–R) models [31]. The Langmuir isotherm equation can be written in the following form:

Table 2. Parameters constants pseudo-first-order for chromium (VI) adsorption.

Initial Cr(VI) concentration (mg/L)	Experimental	Pseudo-first-order		
	$q_{e,\,exp}$ (mg /g)	$q_{e,cal}$ (mg /g)	k_1 (1/min)	R^2
HDTMA-Cp				
50	1.68	2.384	0.022	0.9964
100	2.35	3.642	0.025	0.9919
200	2.85	4.096	0.026	0.9957
ODTMA-Cp				
50	2.1	3.184	0.031	0.9970
100	2.9	3.518	0.033	0.9902
200	3.65	5.264	0.034	0.9907

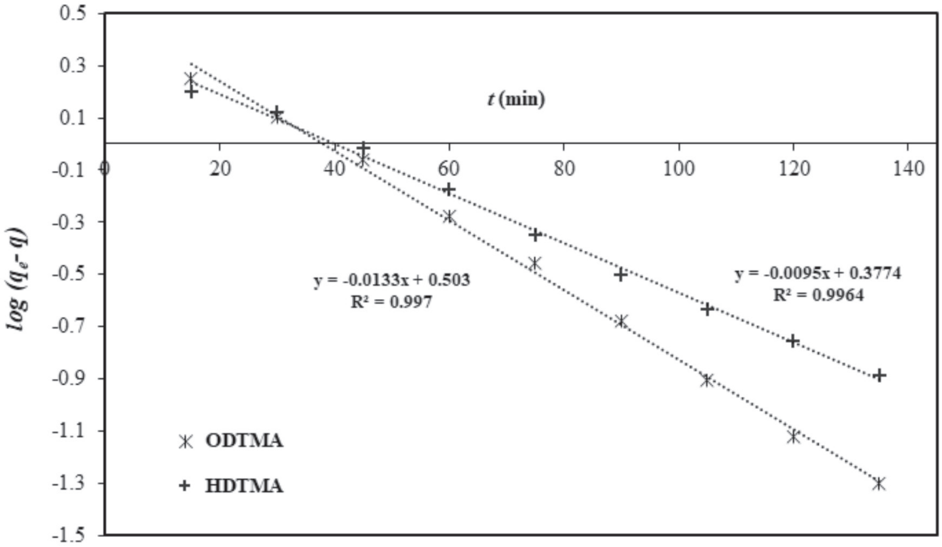

Fig. 5. The pseudo-first-order kinetic model of Cr(VI) on the ODTMA-Cp and HDTMA-Cp (V_o = 50 mL, C_i = 50 mg/L, pH = 2.0; 3.0, T = 25ºC).

$$q_e = q_m \frac{bC_e}{1+bC_e} \quad (4)$$

where q_m (mg/g) is the maximum adsorption capacity (monolayer capacity) of the sorbent, and b (L /mg) is a constant related to the bonding energy of adsorption and affinity to the binding site, respectively. Langmuir isotherm is assumed that adsorption is homogeneous and limited to monolayer coverage, and the maximum adsorption takes place when molecules adsorbed on the sorbent surface constitute a saturated layer. However, Langmuir adsorption isotherm may also be useful in describing heterogeneous surfaces where the adsorption reaches saturation over a critical equilibrium concentration of the adsorbate in the aqueous phase [32]. Thus, it was reported by Krishna et al. [27] that the adsorption of chromium (VI) by a variety of modified clay minerals was best explained by the Langmuir model.

Fig. 6 demonstrates the Langmuir adsorption isotherm of chromium (VI) on modified clinoptilolit tuffs. Zeng and coworkers [33], specified that the maximum adsorptive capacity of HDTMA-modified natural clinoptilolite from Korea for CrO_4^{2-} was 3.55 mg/g at pH 3; this value was almost the same as that found in the current work and could be related by the amount of HDTMA on the surface of the zeolitic network. In addition, the value of $K_L(b)$ obtained in the current study was close to the value found by previous authors, revealing similarities in the associated adsorption energy between CrO_4^{2-} and the HDTMA layer (or bilayer) distributed on the surface of each natural zeolite. As a result, the higher chromate sorption of HDTMA-Cp can be attributable to a higher amount of HDTMA loading on the clinoptilolite, thus, a higher bilayer density. In addition, the value of K_L (b) obtained in the current study was close to the value found by previous authors and revealed similarities in the associated adsorption energy between CrO_4^{2-} and the HDTMA layer (or bilayer) distributed on each natural zeolite surface.

However, the linear regression coefficient (R^2) value of Langmuir isotherm obtained in this study was significantly better than the R^2 value (0.84) found by Zeng et al. [33], Table 3.

Linearized Freundlich's model can be described by the following equation:

$$logq_e = logK_F + \frac{1}{n} logC_e \quad (5)$$

where K_F (mg/g) is related to the relative adsorption capacity and n (g/L) is related to the intensity of adsorption. The constants K_F and n for the tested metal ions are presented in Table 3. Values of n>1.0 indicated the intensive adsorption of chromium(VI) by modified sorbents. However, the Langmuir isotherm model fitted the experimental data better than the Freundlich isotherm model for Cr(VI) considering correlation coefficients (R^2). On the other hand, the Dubinin-Radushkevich isotherm equation is more extensive than the Langmuir equation because it does not accept a homogeneous surface or constant adsorption potential.

The Dubinin-Radushkevich isotherm model is often used to identify the nature of the sorption as being either physical or chemical on a heterogeneous surface [34, 35]. Dubinin suggested that the adsorption proceeds in the volume of adsorbent micropores as opposed to the layer-by-layer adsorption on micropore walls [31].

The linear form of the D-R isotherm is given by the equation:

$$lnq_e = lnq_m - \beta \mathcal{E}^2 \quad (6)$$

where β (mol^2 /kJ^2) is a constant related to mean adsorption energy, q_m (mol/g) is the theoretical saturation capacity, and ε is the Polanyi potential related to equilibrium concentration, which can be calculated from the equation:

$$\mathcal{E} = R.T.ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

The constant β and q_m values are calculated from the slope and intercept of a plot of ln(qe) against $\mathcal{E}^2$, and are given in Table 1. The mean energy of sorption E, which is defined as the free energy transfer from infinity to the surface of the sorbent for one mol of solute, can be calculated using the determined value of β and:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (8)$$

If the value of E is between 8 and 16 kJ/mol, the adsorption process occurs chemically, and if the value of E is less than 8 kJ/mol, physisorption dominates [31]. In this study, the values of E for ODTMA-Cp and HDTMA-Cp sorbents are between 8-16, which indicates that the Cr(VI) adsorption is chemical by nature (Table 1). The correlation coefficients *(R^2)* for the D–R isotherm model were also high being 0.9828 for ODTMA-Cp and 0.9878 for HDTMA-Cp indicating the D–R model was valid.

Effect of Adsorbent Dosage

Adsorbent dosage is one of the most important key parameters affecting the removal efficiency of an adsorbent. Commonly, the removal efficiency increases with increasing the amount of adsorbent dosage. This increase chiefly occurs due to the matching increase in active surface binding sites for a given amount of soluble sorbate as the amount of adsorbent increases. As seen from Table 4, the chromium (VI) removal efficiency varies considerably depending on the solution pH, the initial Cr (VI) concentration and the applied solid/liquid ratios. Because pH affects both sorbent surface properties and ionic forms of species in the

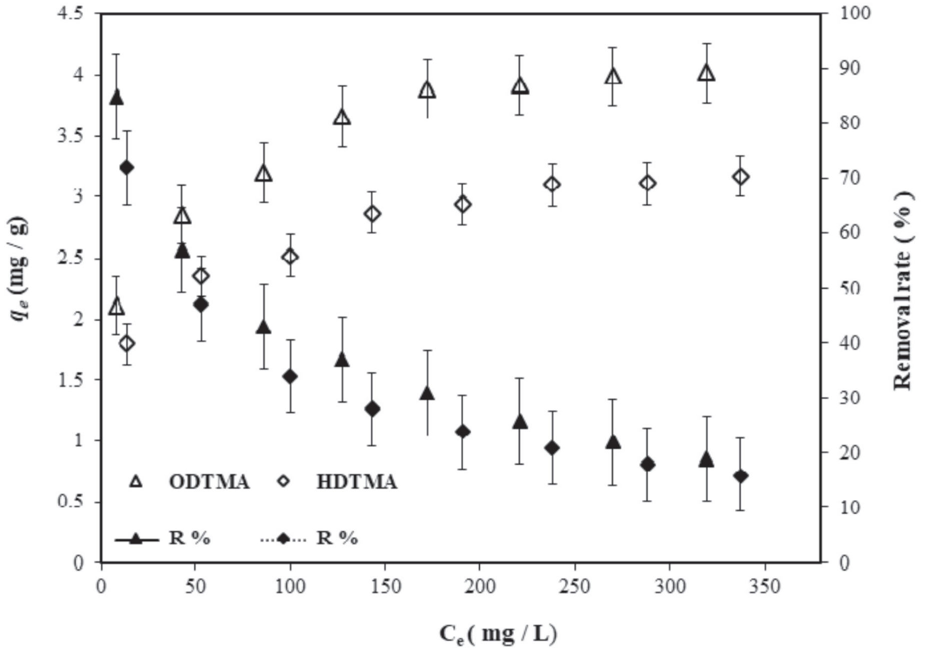

Fig. 6. Langmuir isotherm curves for the adsorption of Cr from the Cr(VI)-Na_2CrO_4 aqueous system by ODTMA-Cp and HDTMA-Cp (V_o = 50 mL, pH = 2.0; 3.0, m = 0.25 g, T = 25ºC).

Table 3. Isotherm parameter constants for Cr(VI) adsorption onto modified clinoptilolite samples.

Sorbent	Langmuir			Freundlich			Dubinin-Radushkevich			
	q_m mg/g	b L/mg	R^2	K_F	n	R^2	q_m mol/g	K_{DR} mol^2/kJ	E Kj/mol	R^2
ODTMA-Cp	4.22	0.24	0.9974	2.908	5.473	0.9839	$1.1x10^{-4}$	0.0022	15.075	0.9828
HDTMA-Cp	3.34	0.15	0.9972	2.245	5.482	0.9869	$8.7x10^{-5}$	0.0023	14.744	0.9878

solution equilibria and hence, controls the sorption capacity. Certainly, it depends chiefly on the type of the adsorbent and modifier. In addition, even if the same sorbent and modifier are used, quite different adsorption amounts can be obtained depending on where the sorbent is supplied and how the modification procedure is applied. Therefore, the comparison of adsorption capacities does not always yield a sufficiently accurate approach. This is most likely to result from the reaction conditions, such as the temperature, the contact time, and the amount of the modifier. In this work, optimum adsorbent dosage was determined as 0.25 g. From the Table, the highest chromate adsorption per unit mass of sorbent is changeable, and mainly increases with the increasing amount of sorbent [10]. This may be related to the excess amount of the adsorbent causing an increase in free adsorption sites. At low metal ion concentration, the ratio of the number of metal ions to the number of available adsorption sites is small, and adsorption is independent of the initial concentration; however, as the concentration of metal ions increases, the situation changes and the competition for adsorption sites becomes challenging. In the study of Szala et al. [22], although the amount of the zeolite sorbent is 4 times higher than the one conducted by Tashauoei et al. [18] using nano zeolite, the reported adsorption capacity value for zeolites is much less than that of nano zeolite. That nanoscale materials have a high specific surface area which offers a higher number of active sites improves the adsorption performance. Thus, the particle size and specific surface area are both significant factors affecting the adsorption functionalities. As for this study, although the adsorption capacity seems to be less than that of Szala et al., the amount of the modified adsorbent in the experiments is also four times less. Likewise, in comparison with this study, Zeng and coworkers [33] consumed 5 times more adsorbents to obtain about the same amount of adsorption capacity using the same type of adsorbent and modifier.

Reusability

In order to determine the reusability of ODTMA modified-clinoptilolite, eight adsorption–elution cycles were applied. The Cr(VI) initial concentration of 25 mg/L was studied. Operational capacity was measured under the experimental conditions without reaching

Table 4. Comparison of some experimental parameters on Cr (VI) adsorption with surface modified/unmodified natural sorbents.

Sorbent type	Modifing agent	(Solid: Liquid) g/L	Optimum pH	Adsorption capacity mg/g	Reference
Avocado shell	-	0.2	1.5	127.63	[5]
Magnetite	$FeSO_4·H_2O$/ $Fe_2(SO_4)_3·xH_2O$	10.0	6.4	9.20	[7]
Bentonite	Chitosan + glutaraldehit (GLA)	2.0	2.0	89.13	[10]
Chitosan	-	13.0	3.0	102.0	[11]
Zeolite	Grape waste Olive waste	5.0	2.0	108.12 100.47	[16]
Nanozeolite	HDTMA	5.0	3.0	14.16	[18]
Zeolite/ Clinoptilolite	HDTMA/ODTMA	20.0	2.0- 3.0	7.80/6.90	[22]
Clay	HDTMA	10.0	≤1.0	41.34	[27]
Al_2O_3	-	2.0	3.0	39.10	[28]
Korea, Pohang- Clinoptilolite	HDTMA	25.0	3.0	3.55	[33]
Bigadic-Clinoptilolite	HDTMA/ODTMA	5.0	2.0	3.65	This study

saturation. Cr(VI) originally present was calculated by the difference between metal loading and eluting concentration. It was observed that 88.7% of the adsorbed Cr(VI) was desorbed in the first cycle, and decreased to 65.3% in the eight cycle. The decrease in the operational batch capacity of the modified-clinoptilolite, even after eight repeated cycles of adsorption and elution, was 23.4, indicating the acceptable reusability performance of used modified clinoptilolite zeolite for full-scale applications considering its high abundance, low cost and ease of access.

Conclusions

Hexavalent chromium adsorption behavior by ODTMA-Br and HDTMA-Br cationic surfactants on Bigadic clinoptilolite mineral was investigated in the laboratory for the first time. Since clinoptilolite, like all other natural zeolitic minerals, has negative charges on its surfaces, the cationic surfactants covered the surface of the clinoptilolite mineral layers as expected. The cationic surfactants produced electrostatic interaction with the negatively charged edges of clinoptilolite and fully expanded the layer structure of clinoptilolite. Although both the modified sorbents used in this research were found to be effective in removing chromate from aqueous solution, ODTMA modified clinoptilolite was more efficient than HDTMA. The maximum chromium retention in the acidic pH range of 2 to 4 was due to the electrostatic interaction between the protonated amine groups on the treated clinoptilolite surface and the dominant oxy-anionic species of hexavalent chromium ($HCrO_4^-$). The equilibrium data have been analyzed using Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models, and the results revealed that the Langmuir model was well-fitted in good linearity in terms of R^2. The results of this research may also highlight the properties of modified clinoptilolite and create an option for their potential use in aquatic environmental remediation. In conclusion, the present work demonstrated that the ODTMA- and also HDTMA- modified clinoptilolite could be possibly utilized as potentially cost-effective adsorbents for the treatment of wastewater containing hexavalent chromium.

Conflict of Interest

The authors declare no conflict of interest.

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