Simultaneous adsorption of Cu\textsuperscript{2+} and Cr (VI) using HDTMA-modified zeolite: isotherm, kinetic, mechanism, and thermodynamic studies

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ABSTRACT

Clinoptilolite modified by hexadecyltrimethylammonium bromide (HDTMA-Br) was used to simultaneously remove copper and hexavalent chromium from aqueous solutions. The surface properties of HDTMA-modified natural zeolite (HMNZ) were characterized using scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET), zeta potential and Fourier transform infrared spectroscopy (FTIR) techniques. SEM images showed that surfactant is adsorbed on the surface of the zeolite, which is confirmed by the FTIR result. The results from BET demonstrated a reduction in the specific surface area and pore volume due to the presence of surfactant molecules on the external surface of zeolite. The effects of important parameters on adsorption efficiency of Cu\textsuperscript{2+} and Cr (VI) were evaluated by Box-Behnken design. The Langmuir isotherm provided the best fit to the equilibrium data of Cu\textsuperscript{2+} and Cr (VI), with the maximum adsorption capacity of 0.068 and 0.0093 (mmol g\textsuperscript{-1}), respectively. The film diffusion mechanism was found to control the mass transfer, and the adsorption reactions were computed as endothermic for Cu\textsuperscript{2+} (\(\Delta H_{\text{ads}}^c = 17.58\) kJmol\textsuperscript{-1}) and exothermic for Cr (VI) (\(\Delta H_{\text{ads}}^c = -26.18\) kJmol\textsuperscript{-1}). The results indicated that surfactant modification changes the surface charge of zeolite from negative to positive, which makes zeolites economic adsorbents with the possibility of simultaneous removal of cations and oxyanions. The results also showed that the removal efficiency of Cr (VI) increases in the presence of copper cations due to there being more positive sites on the adsorbent surface.

Key words | adsorption, copper, HDTMA, hexavalent chromium, RSM, zeolite

HIGHLIGHTS

- Making use of a low-cost adsorbent for effective simultaneous Cu\textsuperscript{2+} and Cr (VI) adsorption through appropriate modification.
- Evaluating the most efficient loading amount of HDTMA on clinoptilolite.

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INTRODUCTION

Today, due to the growth of industries and the advancement of technology, various pollutants have been widely introduced into the environment and have created a lot of problems (Li et al. 2018). Trace metals are an important class of contaminants as a consequence of their unfavourable properties such as toxicity, persistence, and accumulation in the bodies of living organisms, groundwater, and soil, which can cause various disorders and diseases (Deveci & Kar 2013). Arsenic, cadmium, zinc, nickel, lead, mercury, copper, and chromium are metallic and metalloid substances often detected in industrial wastewater (Fu & Wang 2011). Copper and chromium are listed by the United States Environmental Protection Agency (USEPA) as priority control pollutants due to their persistence and irreversible toxic characteristics (Kim et al. 2019). Copper is widely used for a variety of applications. It can enter the environment through mining or by using copper-containing products such as batteries, cell phones, water pipes, semiconductors or natural sources. Copper does essential work in human and animal metabolism. High dosages of copper in the environment are posing an extreme threat to human beings. Excessive ingestion of copper from copper-polluted waters can causes serious toxicological concerns, such as vomiting, cramps and convulsions (Vardhan et al. 2019). Chromium must be removed from wastewater or needs to be modified into its less toxic form before it is discharged into the environment because of the destructive effects such as skin inflammation, liver and kidney failure, vomiting and so on. Chromium exists in the aquatic environment mostly in two stable oxidation forms: Cr (III) and Cr (VI). Cr (III) is essential for the human body and much less dangerous than its hexavalent form. Cr (VI) is being released into the environment mostly by major industries such as leather, wood preservation, tanning, electroplating, paints, and textiles. (Di Natale et al. 2007; Carolin et al. 2017). In the aquatic environment, Cr (VI) mainly exists in $\text{HCrO}_4^-$, $\text{Cr}_2\text{O}_7^{2-}$ ($2 < \text{pH} < 6$) and $\text{CrO}_4^{2-}$ ($\text{pH} > 6$) forms (Szala et al. 2013). Different types of physical, chemical, and biological methods have been used for the treatment of the potentially toxic elements, including precipitation, adsorption, ion-exchange, biosorption, reverse osmosis, filtration, electrodialysis, and solvent extraction (Ngah & Hanafiah 2008; Lee et al. 2017). Physical adsorption is widely used in the removal of hazardous elements because of its benefits such as low operational cost, simplicity, small dimensions of operational equipment, high productivity, and the absence of secondary pollution (Boddu et al. 2008). Zeolites are known adsorbents that can remove metal cations from aqueous solutions due to their negative surface charge. Therefore, zeolites do not tend to uptake anionic pollutants (Zhan et al. 2011). Natural zeolites are safe, environmentally friendly, cheap, have a large surface area and high cation exchange capacity (Merrikhpour & Jalali 2013). Clinoptilolite is the most abundant natural zeolite (Erdem et al. 2004). One of the methods for modifying zeolites is the use of cationic surfactants like Hexadecyltrimethylammonium bromide (HDTMA-Br) (Yusof & Malek 2009). At concentrations less than the critical micelle concentration (CMC), surfactant exists as a monomer, and in concentrations higher than the CMC, surfactant forms micelles in the solution. After modifying zeolites by...
HDTMA with a concentration above CMC, a bilayer structure is formed at the outer surface of the zeolite. This structure contains functional groups with a positive charge, which can be effective in adsorption of hexavalent chromium oxyanions. Besides, HDTMA, due to its large molecular size, is unable to penetrate the internal surface of zeolite, so the internal surface charge of zeolite remains negative. Eventually, HDTMA-modified natural zeolites (HMNZ) can adsorb cationic and anionic trace elements from wastewater simultaneously (Chao & Chen 2012; Huang et al. 2016). In this study, clinoptilolite was modified by different concentrations of HDTMA to enhance its ability for removing Cr (VI) oxyanions. Moreover, simultaneous adsorption of Cu\(^{2+}\) and Cr (VI) by using HMNZ was investigated. Box-Behnken design (BBD) of response surface methodology (RSM) was used to optimize parameters such as initial concentration of Cu\(^{2+}\), initial concentration of Cr (VI) and adsorbent dose using Design Expert software version 11. The BBD method was also used to investigate the effects of Cu\(^{2+}\) and Cr (VI) ions on the adsorption efficiency of each other. Adsorption isotherms, kinetics, mechanisms and thermodynamic data were collected. Different techniques such as Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) and zeta potential were carried out to confirm the adsorption of HDTMA molecules on the surface of HMNZ. Our results showed that HMNZ is an economical adsorbent with the ability to remove cations and anions from aqueous solutions simultaneously.

**METHODS**

**Natural zeolite**

The clinoptilolite used in this work was collected from a mineral deposit located in the province of Semnan, Iran. The natural zeolite was washed several times with deionized water and dried at 60 °C for 24 h. The diameter and the mesh of the zeolite were 0.6 mm and 30–40, respectively.

**Preparation of the surfactant-modified natural zeolite**

Cationic surfactant HDTMA bromide [(CH\(_3\))\(_3\) N (CH\(_2\))\(_{15}\) CH\(_3\)Br], supplied by Merck, was used to modify clinoptilolite. Seven grams of natural zeolite was added to 100 mL of solutions with different concentrations of HDTMA (2.5 CMC, 5 CMC, 10 CMC, 15 CMC, 25 CMC, 50 CMC, and 75 CMC). The solutions were shaken for 24 h at 25 °C, and 200 rpm, then were filtered. Zeolites were washed with distilled water until no bromide ions were detected by AgNO\(_3\) test. The modified adsorbents were then dried in an oven at 50 °C for 24 h. After modification, an adsorption amount of 50 mgL\(^{-1}\) Cr (VI) solution in each specific concentration was evaluated, and the adsorbent with the maximum Cr (VI) adsorption efficiency was selected for later experiments.

**Characterization of the natural zeolite and HMNZ**

The surface morphologies of the natural zeolite and HMNZ were examined by scanning electron microscope (Philips XL30). The N\(_2\)-BET method was used to measure the surface area, pore volume, and average pore diameter of the natural zeolite and HMNZ using a Belsorp mini II analyzer. Zeta potential analysis (Microtrac, Germany) indicated the surface charge of the zeolite before and after modification. FTIR (Nicolet 560) determined the functional groups of the adsorbents.

**Determination of Cu\(^{2+}\) and Cr (VI) concentrations in an aqueous solution**

Batch adsorption experiments were performed by mixing CuSO\(_4\).5H\(_2\)O and K\(_2\)Cr\(_2\)O\(_7\) (Merck) to prepare the solution. Studies were carried out in a 250 mL Erlenmeyer flask with a working volume of 100 mL and the temperature was kept at 25 °C by a thermostatically controlled shaker (Biotek-NB-205VL) with shaking speed of 200 rpm. The pH of all adsorption experiments was maintained at 5 by adding 0.1 N HCl or 0.1 N NaOH. The residual concentration of Cr (VI) in an aqueous solution is conducted by direct UV visible spectrophotometry (WPA, biowaveII, Japan) based on the yellow colouring of the chromate ion in the range of 1–20 mgL\(^{-1}\) at 350 nm wavelength. For concentrations in the range of 0.1–1 mgL\(^{-1}\), the standard method was used, which is by colorimetry with 1, 5-diphenylcarbazide (Merck) at 540 nm. The concentration of Cr (VI) in the range below 1 mgL\(^{-1}\) was measured by mixing 10 mL of sample with 0.2 mL diphenylcarbazide solution and 0.5 mL H\(_2\)SO\(_4\) and it was given 10 minutes for colour development (ASTMD1687-17 2017). For the analysis of Cu\(^{2+}\) ions, 9 mL of sample was mixed with 1 mL of ammonia solution, which produces a blue colour. Then its absorbance was noted in the 650 nm wavelength (Mehlig 1941).

The amount of both pollutants adsorbed by HMNZ was calculated by using Equation (1):

\[
q_e = (C_0 - C_e) \times \frac{V}{M} \left( \frac{\text{mg}}{\text{g}} \right) \tag{1}
\]
where $q_e$ is the Cu$^{2+}$ and Cr (VI) uptake (mg g$^{-1}$), $C_i$ and $C_e$ are the initial and equilibrium concentrations in the solution (mg L$^{-1}$), $V$ is the solution volume (L), and $M$ is the mass of adsorbent (g).

The percentage removal of Cu$^{2+}$ and Cr (VI) was calculated by the following equation:

$$ \text{Removal rate} \,(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (2) $$

where $C_i$ and $C_f$ (mg L$^{-1}$) are the initial and final concentrations of the pollutant, respectively.

**Design of experiment**

The selected parameters in these experiments were investigated by using Box-Behnken design, which is a response surface methodology (RSM). RSM are mathematical and statistical procedures functional for the modelling and analysis of problems when a response of interest (e.g. removal efficiency) is influenced by several variables (Van Tran et al. 2017). A Box-Behnken method is suitable for optimizing the useful parameters with the least number of experiments, and also to analyze the interaction between the parameters (Sephehran et al. 2008; Dubey et al. 2016). Table 1 shows the ranges and levels of the independent variables in terms of actual and coded values. The variables studied were HMNZ dosage ($X_1$): 0.5–2 g, initial Cu$^{2+}$ concentration ($X_2$): 50–100 mg L$^{-1}$ and initial Cr (VI) concentration ($X_3$): 5–20 mg L$^{-1}$. The number of experiments suggested by BBD design for this study was 15 and are calculated by the equation below.

$$ N = k^2 + k + cp \quad (3) $$

where $k$ is the number of factors and $cp$ is the replicate number of the central points (Cobas et al. 2014).

The resulting data were regressed to derive two equations for Cu$^{2+}$ and Cr (VI) responses. All variable parameters and their interactions were considered in both models.

**RESULTS AND DISCUSSION**

**Surface properties and morphology of natural zeolite and HMNZ**

The SEM pictures of clinoptilolite and HMNZ are shown in Figure 1. Because of the HDTMA molecule’s size, it can only adsorb on the external surface of the zeolite. As a result, the modification does not make a significant change in the potential of the external surface of the zeolite. However, it covers some smaller pores in the surface of the zeolite.

Values of the surface area, pore volume, average pore diameter, and zeta potential of both adsorbents are listed in Table 2. After modification, the presence of surfactant molecules on the external surface of the zeolite leads to the coating or blockage of some zeolite pores and ultimately reduces the specific surface area and pore volume. Covering of smaller pores by surfactant also increased the average pore diameter. These results are in good agreement with other studies (Huang et al. 2016; Tran et al. 2018). Surface modification of zeolite by cationic surfactants containing quaternary ammonium functional groups leads to a change in the potential of the external surface of the zeolite from the negative to positive, which causes zeolite to adsorb anions on their outer surface. The zeta potential analysis (at pH = 5, Microtrac, Germany) demonstrated that the surface charges of natural zeolite and HMNZ were negative and positive, respectively.

The FTIR spectra of natural zeolite and HMNZ are shown in Figure 2. The bands at 1,633 and 3,440 cm$^{-1}$ are due to constitutional water molecules present in natural zeolite and HMNZ and OH–bending and stretching modes (Karadag et al. 2007). The existence of a peak in the range between 2,900 and 3,000 cm$^{-1}$, which is observed only in the spectrum of HMNZ, might be due to the presence of C-H aliphatic stretch vibrations and implies that HDTMA is adsorbed on the surface of the zeolite. These peaks are determined to be symmetric and asymmetric vibrations of the CH$_2$ groups of the HDTMA (Anari-Anaraki & Nezamzadeh-Ejhieh 2015; Huang et al. 2016). The strong absorbance located at 1,071 and 1,064 cm$^{-1}$ indicates asymmetric stretching vibrations of Si-O and Al-O bonds on the surface of the adsorbents. Another peak near 605 cm$^{-1}$ is considered to be the bending vibration of Si-O-Si and Si-O-Al groups, while the absorbance of the signal located at

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**Table 1 | Coded parameters and their levels**

<table>
<thead>
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<th>Variables</th>
<th>Levels and ranges</th>
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</tr>
<tr>
<td>$X_2$</td>
<td>50</td>
</tr>
<tr>
<td>$X_3$</td>
<td>5</td>
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</table>
796 cm$^{-1}$ belongs to Si-O stretching vibration mode (Anaraki & Nezamzadeh-Ejhieh 2015; Salim & Malek 2016).

### Effect of surfactant dose on adsorption of Cr (VI)

As shown in Figure 3, with an increase in HDTMA concentration from 0 to 25 CMC, the adsorption capacity of Cr (VI) reached from 0 to 0.88 mg L$^{-1}$. This was because of the increase in the positive charges of the external surface of zeolite due to an increase in the surfactant concentration, which itself increased the adsorption capacity of Cr (VI) (Chao & Chen 2012). Increasing the concentration of surfactant from 25 CMC to 75 CMC reduced the removal efficiency of Cr (VI), which is due to the saturation of adsorbent sites by HDTMA molecules (Tao et al. 2015). Therefore, 25 CMC of HDTMA concentration was used in the experiments.

### Effect of contact time on simultaneous removal of Cu$^{2+}$ and Cr (VI)

The experimental results for Cu$^{2+}$ and Cr (VI) simultaneous adsorption on HMNZ as a function of contact times varying from 15 to 180 minutes were investigated. Increasing shaking time had a significant effect on the adsorption of both metallic ions on the HMNZ; however, it was observed...
that uptake of Cu$^{2+}$ and Cr (VI) on modified zeolite took 150 minutes to attain equilibrium. The adsorption capacity and removal efficiency of Cu$^{2+}$ and Cr (VI) at equilibrium time were 2.5 and 0.78 (mg g$^{-1}$) and 61 and 39%, respectively.

Model and statistical analysis

The effects of parameters such as the adsorbent dose (X1), the initial concentration of Cu$^{2+}$ (X2) and the initial concentration of Cr (VI) (X3) on the removal percentage of Cu$^{2+}$ ($Y_1$) and the removal percentage of Cr (VI) ($Y_2$) were determined. Coded actual data, experimental and predicted responses for simultaneous uptake of copper and hexavalent chromium, are given in Table 3. Figure 4 represents the predicted values versus the experimental values for the adsorption capacity of Cu$^{2+}$ ($R^2 = 0.991$) and Cr (VI) ($R^2 = 0.9974$). As can be observed, the predicted values are close to the experimental values. Tables 4 and 5 show the analysis of variance (ANOVA) for the regression model for Cu$^{2+}$ and Cr (VI) removal efficiencies.

The sum of squares (SS), degree of freedom (DF), mean of squares (MS), $F$-values and $p$-values according to the investigated factors (HMNZ dosage, initial Cu$^{2+}$ concentration, and initial Cr (VI) concentration) are given in Table 6. The predicted $R^2$'s for response $Y_1$ (0.9784) and $Y_2$ (0.9742) are in good agreement with the adjusted $R^2$ of 0.9842 for $Y_1$ and 0.9928 for $Y_2$. The lack of fit $F$-values of 0.1551 for $Y_1$ and 0.52 for $Y_2$ implies that lack of fit is not significant, and the models are fitted well with the experimental data (Kumar et al. 2009). Also, model terms for both responses are significant since their $p$-values are less than 0.05.
Table 3 | Box-Behnken design model for Cu\(^{2+}\) and Cr (VI) adsorption by HMNZ

<table>
<thead>
<tr>
<th>Run</th>
<th>X_1</th>
<th>X_2</th>
<th>X_3</th>
<th>Experimental</th>
<th>Predicted</th>
<th>The removal efficiency of Cu(^{2+}) (Y_1)</th>
<th>The removal efficiency of Cr (VI) (Y_2)</th>
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<td>65.20</td>
<td>65.91</td>
<td>68.80</td>
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</table>

Figure 4 | Predicted vs experimental yield for (a) Cu\(^{2+}\) (b) Cr (VI) removal.
The following model equations express the relationship between independent variables and responses of interest (adsorption efficiency):

\[
Y_1 = +55.48 + 21.71 X_1 - 3.83 X_2 - 2.38 X_3 - 7.46 X_1 X_2 + 3.98 X_1 X_3 + 3.50 X_2 X_3 \quad (4)
\]

\[
Y_2 = +44.09 + 23.88 X_1 + 3.77 X_2 - 5.30 X_3 + 1.87 X_1 X_2 - 1.78 X_2 X_3 - 2.94 X_1^2 - 2.28 X_2^2 \quad (5)
\]

A positive sign of a parameter meant that an increase in the value of that variable had a positive effect on the response of interest and vice versa (Kaçan & Kütahyalı 2012). The HMNZ dose \((X_1)\) coefficient in Equations (4) and (5) is 21.71% and 23.88%, which means that the adsorbent dose had a greater impact on the uptake of \(\text{Cu}^{2+}\) and \(\text{Cr} \text{ (VI)}\) in comparison to the other parameters. A negative value of coefficients belongs to the initial concentration of \(\text{Cu}^{2+}\), and initial concentration of \(\text{Cr} \text{ (VI)}\) in Equation (4) indicates that the presence of both pollutants individually have a negative effect on the adsorption of \(\text{Cu}^{2+}\) ions from aqueous solution; however, the positive sign belonging to \(X_2\) in Equation (5) shows that \(\text{Cu}^{2+}\) ions can increase the removal efficiency of \(\text{Cr} \text{ (VI)}\) from the solution.

Increasing the adsorbent dose raises the adsorption efficiencies of \(\text{Cu}^{2+}\) and \(\text{Cr} \text{ (VI)}\). Higher doses of HMNZ provide more exchangeable sites/functional groups for metal ions, which lead to improving their removal efficiencies (Araga et al. 2013). The percentage removal of \(\text{Cu}^{2+}\) decreased with an increase in the initial concentration of metal ions. The reason for this phenomenon is that at lower initial \(\text{Cu}^{2+}\) concentration, sufficient sites responsible for uptake of copper ions are available. When the concentration of \(\text{Cu}^{2+}\) ions increases, active sites of HMNZ become saturated, which reduces the amount of adsorption (Meitei & Prasad 2014). On the other hand, the percentage removal of \(\text{Cr} \text{ (VI)}\) rose with an increase in \(\text{Cu}^{2+}\) concentration due to the copper cations being adsorbed on the surface of HMNZ, which introduced more positive sites on the adsorbent for chromium oxyanions such as \(\text{HCrO}_4^-\) and \(\text{Cr}_2\text{O}_7^{2-}\) causing the increment in the hexavalent chromium adsorption process.
Interaction effects of two independent variables on responses Y1 and Y2

Interaction terms $X_1X_2$, $X_1X_3$, and $X_2X_3$ for response $Y_1$ and $X_1X_2$, $X_2X_3$, $X_1^2$ and $X_2^2$ for response $Y_2$ were considered statistically significant since they all have $P$-values < 0.05. $X_1X_3$ and $X_2X_3$ due to their coefficients being greater than zero (+) and $X_1X_2$ with coefficient less than zero (−) have positive and negative influences on the adsorption process of Cu$^{2+}$ ions, respectively. On the other hand, only $X_1X_2$ has a positive effect on the removal efficiency of Cr (VI), and the rest have a reductive influence on the adsorption process.

Interactions between independent variables are shown in a 3D surface plot in Figures 5 and 6 for responses $Y_1$ and $Y_2$, respectively. These figures can be used to indicate the most critical interactions between the variables.

The combined effect of adsorbent dosage and initial concentration of Cu$^{2+}$ ($X_1X_2$) on the adsorption of copper ions at constant initial Cr (VI) concentration (15 mgL$^{-1}$) is that the adsorption efficiency increases with increase in the HMNZ dose and decrease in the Cu$^{2+}$ initial concentration (Figure 5(a)). The highest Cu$^{2+}$ removal percentage (88%) was obtained at the adsorbent dose and Cu$^{2+}$ concentration of 2 g and 50 mgL$^{-1}$, respectively. At the constant initial concentration of Cu$^{2+}$ (75 mgL$^{-1}$), an increment in the adsorption efficiency was observed with increasing both the HMNZ dose and initial hexavalent chromium concentration. The highest efficiency ($\approx$78.5%) was obtained when the HMNZ dose and initial Cr (VI) concentration variables were at the maximum point within the range studied (Figure 5(b)). Finally, Figure 5(c) illustrates the effect of concentrations of both pollutants at constant

Figure 5 | 3D surface plot of Cu$^{2+}$ adsorption.
adsorbent dosage (1.25 g). The removal efficiency of Cu$^{2+}$ fell with an increase in concentrations of Cu$^{2+}$ and Cr (VI). The highest removal percentage ($\approx 64\%$) was obtained when the initial concentrations of both metallic ions were at the minimum point within the range studied.

Figure 6 depicts the effects of independent variables on the percentage removal of Cr (VI). At a constant concentration of Cr (VI) (15 mgL$^{-1}$), adsorption efficiency went up when the adsorbent dose and initial Cu$^{2+}$ concentration increased. For example, at an adsorbent dose of 2 g, with an increment of Cu$^{2+}$ concentration from 50 mgL$^{-1}$ to 100 mgL$^{-1}$, the percentage removal of Cr (VI) rose from 57% to 68% (Figure 6(a)). Figure 6(b) signifies that at a fixed adsorbent dose (1.25 g), with a decrease in Cr (VI) initial concentration and an increase in the number of Cu$^{2+}$ cations in the solution, more Cr (VI) oxyanions are adsorbed on the surface of the modified zeolite (52%). From the results, it can be deduced that the presence of Cu$^{2+}$ cations in the solution can enhance the Cr (VI) removal efficiency due to the electrostatic forces.

**Optimization of the adsorption efficiency of Cu$^{2+}$ and Cr (VI)**

The optimum conditions for Cu$^{2+}$ and Cr (VI) adsorption using HMNZ were an adsorbent dose of 2 g, initial Cu$^{2+}$ concentration of 56.5 mgL$^{-1}$ and initial Cr (VI) concentration of 10 mgL$^{-1}$. The predicted removal efficiency for Cu$^{2+}$ and Cr (VI) was 86.5% and 63.60%, respectively. Experiments were conducted under these conditions to confirm the prediction suggested by the models. Experimental removal percentages of Cu$^{2+}$ and Cr (VI) were found to be 80.2% and 63.55%, which were in good agreement with predicted data.

**Adsorption kinetics**

Non-linearized pseudo-first-order and pseudo-second-order models were applied to predict the adsorption data of Cu$^{2+}$ and Cr (VI) as a function of time. The first-order model can be expressed as follows:

$$q_t = q_e \times \left[1 - \exp(-k_1 \times t) \right]$$  \hspace{1cm} (6)

where $q_e$ and $q_t$ (mg g$^{-1}$) are the amounts of adsorbed Cu$^{2+}$ and Cr (VI) on the HMNZ at equilibrium and at time $t$, respectively, and $k_1$ is the first-order absorption rate constant (min$^{-1}$). The values of $R^2$, $k_1$, and $q_e$ are determined from the slope and the intercept of the plot of $q_t$ versus $t$ and are given in Table 7 for Cu$^{2+}$ and Cr (VI), respectively.

The kinetics of sorption represented by a pseudo-second-order model follow Equation (7):

$$q_t = \frac{k_2 \times q_e^2 \times t}{1 + k_2 \times q_e \times t}$$  \hspace{1cm} (7)

where $k_2$ (gmg$^{-1}$ min$^{-1}$) is the second-order adsorption rate constant. The constant $k_2$ is used to calculate the initial sorption rate $h$ (mgg$^{-1}$ min$^{-1}$) (Table 7). The equation is given as (Gupta & Bhattacharyya 2011):

$$h = k_2 q_e^2$$  \hspace{1cm} (8)
One of the aspects raising doubt among researchers is an expectation that any ‘surface reaction’ involved in the adsorption would likely take place quickly relative to the time needed for diffusion-dependent processes to be achieved. It is the expected inability of pairs of unoccupied individual sites on a solid substrate to act as independent entities in any rate-limiting interaction. Pseudo-second-order is the exponential function with hyperbolic function, we can state that for the same values of \( k \) and \( q_e \), the exponential function is faster convergent to \( q_e \).

The pseudo-second-order model resulted in better values of the correlation coefficients. Also, the calculated \( q_e \) values fitted well with the experimental data. As a result, \( \text{Cu}^{2+} \) and \( \text{Cr} (\text{VI}) \) adsorption onto HMNZ followed the pseudo-second-order kinetic model.

### Adsorption isotherms

The equilibrium adsorption of \( \text{Cu}^{2+} \) and \( \text{Cr} (\text{VI}) \) ions on the HMNZ was evaluated using three equilibrium isotherms: Langmuir, Freundlich, and Dubinin–Radushkevich (D-R).

The Langmuir adsorption isotherm assumes that the molecules of the adsorbate form a monolayer on the surface of the solid and there are no interactions between the adsorbed molecules. The nonlinear equation for the Langmuir model is:

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (9)
\]

where \( q_e \) (mg g\(^{-1}\)) is the number of metallic ions per unit mass of adsorbent at equilibrium, \( q_m \) is the maximum adsorption capacity (mg g\(^{-1}\)), \( C_e \) is the equilibrium concentration of remaining \( \text{Cu}^{2+} \) or \( \text{Cr} (\text{VI}) \) ions, and \( K_L \) is the Langmuir constant related to the energy of adsorption (L mg\(^{-1}\)).

The Freundlich isotherm is an empirical equation and assumes that the adsorbent has a heterogeneous surface. One of the significant drawbacks of the Freundlich isotherm is its inability to predict the maximum adsorption capacity.

This isotherm model is represented by the equation below:

\[
q_e = K_f C_e^n \quad (10)
\]

where \( \frac{1}{n} \) is the Freundlich adsorption intensity parameter and reflects the magnitude of the adsorption driving force or surface heterogeneity. The adsorption isotherm becomes favorable for \( n < 1 \), unfavorable for \( n > 1 \), and linear for \( n = 1 \). \( K_f \) is the Freundlich adsorption capacity parameter (mg g\(^{-1}\))/(mg L\(^{-1}\))\(^n\).

The D-R isotherm is used to determine the mechanism of the adsorption process. The equation can be expressed as:

\[
q_e = q_D \times \exp (-\beta \times \epsilon^2) \quad (11)
\]

where \( q_D \) is the maximum adsorption capacity of the sorbent for both ions (mg g\(^{-1}\)), \( \epsilon \) is the Polanyi potential (kJ mol\(^{-1}\)), and \( \beta \) is the constant related to the energy of sorption (mol\(^2\) kJ\(^{-2}\)).

The low free energy of sorption is the free-energy change when one mole of ion is transferred to the surface of the sorbent from infinity in the solution, and it can be calculated by Equation (12):

\[
E = (-2\beta)^\frac{1}{2} \quad (12)
\]

In chemical reactions and ion exchange mechanisms, \( E \) is in the range of 8–16 kJ mol\(^{-1}\) and in physical adsorption \( E \) is below 8 kJ mol\(^{-1}\) (Tran et al. 2017).

With nonlinear data analysis, there are no significant differences between Freundlich and Langmuir models. Although the Langmuir model presented acceptable regression coefficients, a Freundlich-like exponential
progression trend was observed. Accordingly, the Freundlich isotherm gives more accurate results than the Langmuir isotherm for a wide variety of heterogeneous adsorption systems. Nonlinear Langmuir and Freundlich isotherms were used for our experimental data at 288 K and the Freundlich isotherm has shown better regression coefficients and lower standard errors. This isotherm is related to multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface; meanwhile, the Langmuir isotherm assumes monolayer adsorption of one molecule in thickness, with adsorption occurring at a finite number of specific localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. Isotherm models are illustrated in Figure 7. Values of $q_m$ and $K_L$ for Cu$^{2+}$ and Cr (VI) are given in Table 8. The values of $E$ calculated in the D-R model were less than 8 kJmol$^{-1}$ for both adsorbates so it can be concluded that the adsorption process occurs physically.

**Adsorption mechanism**

The adsorption process of copper and chromium ions can be controlled either by film diffusion, intra-particle diffusion, or both. Kinetic models such as the pseudo-first-order and pseudo-second-order are unable to identify the diffusion mechanism, so the intra-particle diffusion kinetic model
was used to investigate the adsorption mechanism.

\[ q_t = k_{id} t^{1/2} + C \]  \hspace{1cm} (13)

where \( q_t \) (mg g\(^{-1}\)) is the amount of pollutant adsorbed at time \( t \) (min), \( k_{id} \) (mg g\(^{-1}\) h\(^{0.5}\)) is the intra-particle diffusion rate constant, and \( C \) (mg g\(^{-1}\)) is representative of the thickness of the boundary layer. A more considerable \( C \) value confirms a significant effect of the boundary layer (Nekouei et al. 2015). The values of \( C \) for Cu\(^{2+}\) and Cr (VI) were 0.594 and 0.477 (mg g\(^{-1}\)), respectively, showing that the intercept is not zero. Consequently, their adsorption process is not controlled by the intra-particle diffusion model. The model represented by Boyd (Equation (14)) was used to determine the rate-controlling step involved in the sorption process.

\[ F = 1 - \frac{6}{n} \sum_{m=1}^{\infty} \left( \frac{1}{m^2} \right) \exp(-m^2 B_t) \]  \hspace{1cm} (14)

\( F \) is the fractional attainment of equilibrium at time \( t \) and formulated as:

\[ F = \frac{q_t}{q_e} \]  \hspace{1cm} (15)

where \( q_t \) (mg g\(^{-1}\)) is the amount of the adsorbate adsorbed at time \( t \) and \( q_e \) (mg g\(^{-1}\)) is the maximum equilibrium uptake, respectively. Rearranging Equation (14) gives:

\[ B_t = -0.4977 - \ln \left( 1 - \frac{q_t}{q_e} \right) \]  \hspace{1cm} (16)

Equation (16) was used to compute \( B_t \) values at different times then plotted against time (Boyd plots) as demonstrated in Figure 8. The linearity of the Boyd plots can be useful to differentiate between film diffusion and intra-particle diffusion mechanisms. The adsorption process will be controlled by the intra-particle diffusion mechanism if the plot is a straight line passing through the origin. Otherwise, film diffusion is the governed mechanism (Wang et al. 2006; Djeribi & Hamdaoui 2008). It can be seen from Figure 8 that the plots are neither linear nor pass through the origin, implying that film diffusion is controlling the adsorption process of Cu\(^{2+}\) and Cr (VI). In general, the external mass transfer controls the sorption process for systems that have poor mixing, dilute concentration of the adsorbate, small particle sizes of adsorbent, and higher affinity of the adsorbate for adsorbent (Vadivelan & Kumar 2005; Hu et al. 2011). In our study, the external resistance slows down the external mass transfer because of mixing speed (200 rpm), low concentration of adsorbates (Cu\(^{2+}\): below 100 (mg L\(^{-1}\)) and Cr (VI): below 20 (mg L\(^{-1}\)) ) and small particle sizes of HMNZ (0.6 mm).

### Thermodynamic studies

Thermodynamic parameters like the Gibbs free energy (\( \Delta G^\circ \)), enthalpy (\( \Delta H^\circ \)) and entropy changes (\( \Delta S^\circ \)) were estimated by Equations (17) and (18) to determine the nature of the sorption process. The values of thermodynamic parameters are given in Table 9. Negative values calculated for \( \Delta G^\circ \) at all temperatures for HMNZ mean that the adsorption process of both pollutants was spontaneous and

**Table 8** Isotherm parameters for Cu\(^{2+}\) and Cr (VI) adsorption on HMNZ (temperature: 298 K)

<table>
<thead>
<tr>
<th>Adsorption models</th>
<th>Cu(^{2+})</th>
<th></th>
<th>Cr (VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( R^2 ) 0.981</td>
<td>( q_m ) (mmolg(^{-1})) 0.068 SE = 0.081</td>
<td>( K_l ) (Lmg(^{-1})) 0.0673 SE = 0.087</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( R^2 ) 0.989</td>
<td>( \frac{1}{n} )</td>
<td>( K_f ) (mgg(^{-1}))/(mgL(^{-1}))(^n) 0.74 SE = 0.044</td>
</tr>
<tr>
<td>Dubinin-Radushkevich</td>
<td>( R^2 ) 0.925</td>
<td>( Q_D ) (mmolg(^{-1})) 0.049 SE = 0.081</td>
<td>( E ) (kJmol(^{-1})) 0.00001 SE = 1.374</td>
</tr>
<tr>
<td>Langmuir</td>
<td>( R^2 ) 0.997</td>
<td>( q_m ) (mmolg(^{-1})) 0.0093 SE = 0.052</td>
<td>( K_l ) (Lmg(^{-1})) 0.106 SE = 0.457</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( R^2 ) 0.998</td>
<td>( \frac{1}{n} )</td>
<td>( K_f ) (mgg(^{-1}))/(mgL(^{-1}))(^n) 0.123 SE = 0.679</td>
</tr>
<tr>
<td>Dubinin-Radushkevich</td>
<td>( R^2 ) 0.912</td>
<td>( Q_D ) (mmolg(^{-1})) 0.0038 SE = 0.02</td>
<td>( E ) (kJmol(^{-1})) 0.0000006 SE = 1.247</td>
</tr>
</tbody>
</table>
thermodynamically favourable. Due to the nature of the process, sorption of Cu$^{2+}$ and Cr (VI) were more favourable at high and low temperatures, respectively. The positive value of $\Delta H^\circ$ (17.588 kJmol$^{-1}$) calculated for Cu$^{2+}$ indicates that the adsorption is endothermic. However, the negative $\Delta H^\circ$ (−26.18 kJmol$^{-1}$) value of Cr (VI) sorption indicated that the interaction between Cr (VI) ions and HMNZ surface is exothermic. The change in adsorption enthalpy of Cu$^{2+}$ and Cr (VI) is less than 84 kJmol$^{-1}$, which represents a physisorption process. Moreover, $\Delta G^\circ$ for physisorption is between −20 and 0 kJmol$^{-1}$. Therefore, it can be concluded that the adsorption of Cu$^{2+}$ and Cr (VI) was driven by a physisorption process (Kuo et al. 2008; Dehghani et al. 2016). Positive value of entropy changes (0.071 kJmol$^{-1}$) in adsorption of Cu$^{2+}$ indicate irregularity and random contact of adsorbed particles to the adsorbent surface. An endothermic reaction occurs due to the positive entropy changes. On the other hand, the negative value of

| $\Delta G^\circ_{\text{ads}}$ (kJmol$^{-1}$) | $\Delta H^\circ_{\text{ads}}$ (kJmol$^{-1}$) | $\Delta S^\circ_{\text{ads}}$ (kJmol$^{-1}$) |
| Cu$^{2+}$ | 288 K | 298 K | 308 K | 17.5882 | 0.071 |
| Cr (VI) | −3,081.29 | −2,312.32 | −1,476.51 | −26.18 | −0.0801 |

Figure 8 | B(t) versus t plot for (a) Cu$^{2+}$ (b) Cr (VI) adsorption onto the HMNZ.

Table 9 | Thermodynamic parameters for the adsorption of Cu$^{2+}$ and Cr (VI) on HMNZ
ΔS° (−0.0801 kJmol⁻¹) in adsorption of Cr (VI) shows the mobility of the adsorbate was more restricted on the adsorbent surface than in solution (Khan et al., 2010).

\[
\ln (K_d) = \frac{\Delta S_{ads}^o}{R} - \frac{\Delta H_{ads}^o}{RT}
\]

where \(K_d\) is the equilibrium constant, \(R\) the gas constant (8.314 Jmol⁻¹K⁻¹) and \(T\) the absolute temperature in Kelvin.

\[
\Delta G_{ads}^o = \Delta H_{ads}^o - T\Delta S_{ads}^o
\]  

CONCLUSION

Natural zeolite was modified by HDTMA, and simultaneous adsorption of \(\text{Cu}^{2+}\) and \(\text{Cr} (\text{VI})\) ions was investigated. The specific surface area of treated zeolite reduced from 14.85 m²g⁻¹ to 9.55 m²g⁻¹ in comparison with raw zeolite, which was due to coverage of the surface pores. The modification also changed the surface charge of zeolite from −37 to +17.9 mV, which provides a dual-electronic property for adsorbing cations and anions at the same time. FTIR spectrum confirms the absorbance of HDTMA molecules on the outer surface of the zeolite. As a result of regression analysis, it was found that adsorbent dose, initial concentration of \(\text{Cu}^{2+}\) and initial concentration of \(\text{Cr} (\text{VI})\) were significant parameters for \(\text{Cu}^{2+}\) and \(\text{Cr} (\text{VI})\) models because of the \(p\)-values being less than 0.05. It was also found that the presence of \(\text{Cu}^{2+}\) cations in solution increased the positive surface charge of the HMNZ, which increased chromium adsorption yield. Two grams of HMNZ, 56.5 mgL⁻¹ of \(\text{Cu}^{2+}\) concentration and 10 mgL⁻¹ of \(\text{Cr} (\text{VI})\) concentration were obtained as optimum points that gave maximum removal efficiency of both pollutants. The results exhibited that the uptake of copper and chromium on HMNZ was described by the Langmuir isotherm and the mass transfer was controlled by film diffusion mechanism. The adsorption reactions were computed as endothermic for \(\text{Cu}^{2+}\) and exothermic for \(\text{Cr} (\text{VI})\) sorption. The authors suggest further experiments should be conducted by the relevant techniques to confirm surface precipitation such as \(\text{CuCr}_2\text{O}_7\) on the surface of HMNZ.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


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