Optimization of Congo red dye adsorption from wastewater by a modified commercial zeolite catalyst using response surface modeling approach

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**ABSTRACT**

In the present work, Zeolite A was modified by using hexadecyltrimethylammonium bromide (HDTMABr) for adsorption of the Congo red (CR) dye from synthetic aqueous solutions. The Modified Zeolite A (MZA) was characterized by XRD, SEM, and FTIR. The influence of solution pH (in the 4–12 range), ionic strength (0.1–1 M), contact time (180 min), initial CR concentration (20–60 mg/L), temperature (24–36 ℃), and an adsorbent dose (1–3 g mL/L) on the % dye removal and adsorbent capacity were studied. A combined effect of the initial CR concentration and temperature on the CR removal % by MZA was also studied by applying response surface methodology (RSM). Experimental values were in a good agreement with those predicated by a second-order quartic model. A maximum of 99.24% dye removal and adsorbent capacity of 21.11 mg/g was achieved under the following conditions: pH = 7, initial CR concentration = 60 mg/L, temperature = 24 ℃, ionic strength = 0.1 M, adsorbent dose = 3 g/L and 90 min contact time. The equilibrium data were subjected to the Langmuir, Freundlich and Temkin isotherms, with the latter providing the best fit while kinetic adsorption studies were conducted by applying three models. The results indicated that the removal process was best described by the pseudo-second-order model. The present study demonstrates that modified MZA can be utilized for the highly efficient CR dye removal.

**Key words** | Congo red dye, dye removal, modified Zeolite A, RSM

**HIGHLIGHTS**

- The commercial Zeolite A was successfully modified by (HDTMABr), the MZA utilized for the highly efficient Congo red dye removal.
- Selection of optimal conditions for dye removal by modified Zeolite A.
- Adsorption mechanism has been proposed.
- The results demonstrate the exothermic nature of the adsorption process for the removal of dye by modified Zeolite.

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Environmental pollution by chemical waste is a major problem in the manufacturing process, necessitating that all harmful discharges be treated to minimize their harmful effects (Netpradit et al. 2003; Albayati et al. 2020). In many industries, such as plastic, textile, cosmetic, rubber, paper, and so on, organic chemicals are typically used for coloring products. Chemical structures of waste products, and dyes released from those industries are resistant to degradation and difficult to treat by most known methods. Hence, release of those effluents into the aquatic surroundings is extremely dangerous (Abbas et al. 2012; Al-Dahri et al. 2018). Most artificial dyes are highly toxic to the aquatic ecosystem (Vimonses et al. 2013; Aravind Raj et al. 2013).

However, pretreating them before discharge into the environment can be a challenge, as they exist in many structural varieties, such as acidic, dispersing, azo, diazo, anthroquinone-based and complex mineral dyes, which can be a cationic, a non-ionic or an anionic type. Congo red (CR) is an anionic dye [1-naphthalene sulfonic acid, 3,3’-(4,4’-biphenylenebis (azo)) bis(4-amino-) disodium salt] and a diazo dye and is obtained by coupling tetrazotised benzidine with two molecules of naphthionic acid (Vimonses et al. 2009; Aravind Raj et al. 2019), forming a structure as shown in Figure 1.

Dye-containing wastewater can be treated by various methods, such as coagulation/flocculation, chemical oxidation, filtration, membrane separation and microbial degradation; however, their success in mitigating dye toxicity is limited (Doğan et al. 2008; Liu et al. 2014). Extant studies have shown that adsorption is the most effective wastewater treatment technique, due to its low cost, simplicity of operation, and high efficiency (Sabri et al. 2015; Alardhi et al. 2020). As CR is not easily eliminated by biodegradation, it should be subjected to the adsorption process to limit its discharge into the environment. This has prompted many researchers to investigate different types of adsorbent materials in order to identify the most optimal one for CR treatment, such as carbon-based materials (Ahmad & Kumar 2010), silica composites (Ghorai et al. 2015), cellulosic materials (Jin et al. 2015) and chitosan-related materials (Vakili et al. 2014). Natural and low-cost adsorbents, such as tea waste (Foroughi-dahr et al. 2018), orange peel (Munagapati et al. 2019) and beech wood sawdust (Dulman & Cucu-man 2009) have also been investigated. Zeolites have emerged as a highly promising natural adsorbent due to their porous structure and negative charge. Thus far, zeolite modification by surfactants has been applied in order to enhance the adsorption capacity of a wide range of adsorbents, including tetramethylammonium (Bouffard & Duff 2000), hexadecyltrimethylammonium (HDTMA) (Kuleyin 2007), octadecyldimethylbenzyl (ODMBA), cetylpyridinium bromide (CPB) (Liu et al. 2014) and cetlytrimethylammonium bromide (Zohra et al. 2008). Most modifying agents applied to surfactants are synthetic long-chain molecules with minimal biodegradability and potential toxicity (Liu et al. 2014). Due to the electrostatic repulsion between the negatively charged unmodified zeolite surface and anionic CR dye, a surface of the commercial Zeolite (A) treated with a cationic surfactant becomes positively chargeable.
charged and can attract CR. Cationic surfactant adsorption onto the negatively charged adsorbent surface is controlled by (1) formation of the surfactant monolayer through ion exchange and electrostatic attraction and (2) formation of the surfactant bilayer via hydrophobic interactions (Foroughi-dahr et al. 2015). In this work, the key adsorption parameters were examined experimentally, because this is the most cost-effective way to determine how each operating variable depends on its principal effect and how other variables interact (Daham et al. 2017; Dil et al. 2018). The work commenced by developing a model for the response surface methodology (RSM), followed by designing a polynomial equation of the actual process, after the optimal conditions were identified and their accuracy was assessed via an analysis of variance (ANOVA). The benefit of this approach stems from its output in the form of a tridimensional graph that can be used to assess the model performance, while allowing the most suitable surface response for optimal conditions to be identified (Zare-Dorabei et al. 2016). In this research, we expand on these studies by developing a commercial zeolite A to increase its efficiency by a cationic surfactant (HDTMABr) for adsorption of Congo red from synthetic aqueous solutions. Several factors influencing the dye adsorption were studied, namely pH, initial CR dye concentration, adsorbent dosage, temperature and ionic strength in batch mode, using a central composite design (CCD) of RSM. The adsorption kinetics and thermodynamic parameters were also investigated, and three isotherm models were applied to the experimental data.

MATERIALS AND METHODS

Materials

A commercial Zeolite A (Linde Type A), Congo red (CR, C_{32}H_{22}N_{6}Na_{2}O_{6}S_{2}, >99%), and hexadecyltrimethylammonium bromide (HDTMABr, CH_{3}(CH_{2})_{15}N(Br)(CH_{3})_{3}, >99%) were obtained from Sigma-Aldrich and used without further purification.

Methods

The commercial Zeolite A was modified via the following method: 10 g of the commercial Zeolite A were mixed with 500 mL of surfactant solution (HDTMABr) at 55 mmol/L concentration, to which the surfactant solution was gradually added. The reaction mixture was mechanically agitated at 50 °C for 4 h. Next, the modified adsorbent was washed with distilled water and then filtrated until no Br- was observed. The product was cooled to room temperature and centrifuged before being washed with distilled water and oven-dried at 60 °C for 12 h. Finally, the adsorbent product was ground in an agate mortar before being passed through a 80-mesh sieve and stored in a sealed glass container.

Characterization of the modified adsorbent

In order to further characterize an interactivity of the surfactant and adsorbent molecules, several analyses were performed to clarify the CR adsorption process. The commercial Zeolite A and modified Zeolite A (MZA) were analyzed using a Fourier Transform Infrared (FTIR) spectrophotometer (Bruker-Tensor 27, Germany). Scanning electron microscope (SEM) images were also taken by an Oxford MV 2500 microscope and were used to study the surface morphology of the samples. The XRD data for the commercial and modified Zeolite A were obtained using a Mini Flex powder diffractometer (Rigaku, Japan) adopting Cu Kα (k for Ka = 1.54059 Å) over the range of 10 < 2θ < 80 with 0.02° step size. XRD was used to investigate crystalline materials (Kedves et al. 2020, 2021).

Adsorption experiments

CR adsorption on the modified adsorbent was examined using batch process methodology. For this purpose, five process variables - initial dye concentration, temperature, contact time, ionic strength and pH were modified to investigate their influence on the adsorption capacity and CR percentage removal at the operating conditions given in Table 1. All tests were carried out using 50 mL of dye solution with a CR initial feed concentration in the 20–60 mg/L range. The solution was placed in 100 mL sustained conical flasks and the desired adsorbent quantity was applied. Next, the samples (dye and adsorbent) were shaken at a constant rate of 200 rpm at 24 °C for 12 h.

| Operating conditions | Value |
|----------------------|-------|
| Initial CR concentration (mg/L) | 20–60 |
| Temperature, T (°C) | 24–36 |
| pH | 4–12 |
| Ionic strength, M | 0.1–1 |
| Contact time, min | 180 |
| Interval time, min | 10 |
with an orbital shaking incubator, periodically withdrawn and separated from the dye solution by centrifugation at 806 G-force for 90 min. The simulated wastewater samples with different initial CR concentrations were prepared by adding distilled water while the concentrations were measured using a UV/visible Agilent Technology (Cary 60 UV-VIS, Germany) spectrometer at $\lambda = 496$ nm. The CR removal efficiency was estimated as follows (Liu et al. 2014):

$$R\% = \frac{C_i - C_e}{C_i} \times 100$$  \hspace{1cm} (1)$$

where $R\%$ is the CR percentage removal efficiency, and $C_i$ and $C_e$ are the initial and equilibrium (residual) CR concentrations (mg/L), respectively. The CR adsorption capacity was calculated using the following expression (Liu et al. 2014):

$$q_e = \frac{C_i - C_e}{m} \times V$$  \hspace{1cm} (2)$$

where $q_e$ is the quantity of CR adsorbed on the adsorbent (mg/g), $V$ is the volume of dye solution in contact with the adsorbent (L), and $m$ is the amount of added adsorbent (dry basis, in g).

### Experimentation and adsorption process optimization

In most experiments, one factor is changed with time; however, this does not allow the combined effect of all the factors and their interactions to be investigated systematically. Design of Experiments (DOE) was thus adopted to apply the response surface method (RSM) to several factors affecting the study outcomes, displaying the combined effect of several variables on a response surface (Majid et al. 2019). In the present work, Design-Expert 7.0.0 software was utilized to design the experiment involving CR removal and the CCD approach was used to choose a number of experiments ($N$) to be carried out to determine the optimal process variables (initial dye concentration and temperature). $N = 13$ was determined as the optimal choice for CCD with two independent variables. This consisted of the standard 2nd factorial points with their origin at the center, 2n axial points fixed at a distance, and $n_0$ replicate points at the center (Daham et al. 2017; Dil et al. 2018; Majid et al. 2019). The two independent variables used in this research were coded as follows:

$$Z_i = \frac{X_i - X_0}{\Delta X_i} \times V$$  \hspace{1cm} (3)$$

where $X_i$ is the dimensionless coded value of the independent variable, $X_0$ is the value of $X_i$ at the center point, and $\Delta X_i$ is the step change value. The selected process variables, with their limits, units and notations, are given in Table 2.

The process response variable of the CR adsorption behavior on MZA can be explained by the following second-order polynomial model:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2$$  \hspace{1cm} (4)$$

$Y$ is the predicated variable; \(\beta_0\) denotes a constant; \(\beta_1\) and \(\beta_2\) are the linear parameter coefficients; \(\beta_{11}\) and \(\beta_{22}\) are the second-order parameter coefficients; and \(\beta_{12}\) is the interaction parameter coefficient.

### RESULTS AND DISCUSSION

#### Characterization of commercial and modified Zeolite A

SEM analysis is a useful tool for determining the surface morphology of the adsorbent. SEM images of commercial Zeolite A and that modified with HDTMABr (MZA) are shown in Figure 2(a)–2(c). Scanning electronic micrographs show a uniform morphology and a cubic shape of particles for both materials. However, the zeolite crystals could be seen clearly at a surface of the zeolite crystals after the HDTMABr surfactant was agglomerated, thus confirming that HDTMABr molecules were adsorbed onto the zeolite surface. This phenomenon emphasizes that the surface charge was changed from the negative to positive. The layers are organized by the attachment of the surfactant alkyl chains to the outer surface of the monolayer by means of hydrophobic–hydrophobic interactions. Therefore, the external surface of the modified adsorbent has become positive and thus more appropriate for the adsorption of an anionic adsorbate such as the CR molecules (Foroughidahr et al. 2015).

| Variables | Limits |  |
|---|---|---|
| Initial dye concentration, $C_0$ (mg/L) | $X_1$ | 20 | 40 | 60 |
| Temperature, $T$ (°C) | $X_2$ | 24 | 30 | 36 |
The FTIR spectra in Figure 3 shows that a structure of the zeolite modified with HDTMABr produces the commercial zeolite characteristic peaks. For the commercial zeolite, symmetric stretching vibrations of bridge bonds at 447–495 cm\(^{-1}\) matched O–Si–O peaks, whereas the 514–582 cm\(^{-1}\) (complex band) symmetric stretching vibrations of bridge bonds were assigned to Si–O–Si and bending vibrations O–Si–O peaks, and 665 cm\(^{-1}\) symmetric stretching vibrations of bridge bonds were attributed to Si–O–Al and Si–O–M, where M is the exchangeable Na\(^+\) ion metal species (Mozgawa et al. 2011; Hashemian et al. 2013).

Moreover, 931–1,055 cm\(^{-1}\) is a broad band range of the antisymmetric stretching vibration of the tetrahedral Si(A1)–O bonds, whereas the external vibration of bonds between the tetrahedral corresponds to bands at wavelengths in the 1,107–1,182 cm\(^{-1}\) range. The Si–OH, Si–OH–Al and -OH hydroxyl groups lie in the region of 1,658 cm\(^{-1}\) and 3,300–3,732 cm\(^{-1}\) (Pechar & Rykl 1983; Hashemian et al. 2013). For the modified zeolite, the intensity at 1,471 cm\(^{-1}\) is assigned to the symmetric bending of CH\(_3\), while those at 2,885–2,962 cm\(^{-1}\) are assigned to aliphatic C–H group (Foroughi-Dahr et al. 2013).

The XRD pattern of the of two zeolitic materials (commercial and modified zeolite) is illustrated in Figure 4. It
can be noticed that the XRD reflection peaks ranges $2\theta = 10$ to 70 shows that diffractive peak locations of the commercial zeolite after loading HDTMBr into the frame voids do not change either before or after an adjustment. This indicates that charging HDTMBr surfactant into the adsorbent’s system voids does not distort the zeolite structure. Higher stress on MZA matrix atoms (Al, Si, O) as well as compensating sodium and potassium ions cause shifts in relative peak intensities (Fungaro et al. 2013; Abbas et al. 2018).

**Effect of process variables on the adsorption process**

**Effect of pH and ionic strength**

Figure 5 shows the effect of the solution pH to the % CR dye removal and adsorption capacity at the initial concentration of 30 mg/L, adsorbent dose of 3 mg/L and 24 °C. The adsorbed amount does not change significantly due to the variation in the pH from 4 to 12. The hydrophobic interfaces between CR and HDTMABr chains appear to be the main mechanism affecting anionic dye adsorption while the pH does not influence the adsorption process. These results are in agreement with the previously reported findings (Fungaro et al. 2013; Cheng et al. 2016).

Figure 6 shows the effect of ionic strength on CR adsorption onto MZA at pH 7.0, 30 mg/L initial concentration, 2 mg/L adsorbent dose and 24 °C. The results show a weak influence of the ionic strength, as the capacity of adsorption declined slightly (from 7.18 to 6.39 mg/g) owing to the competition between CR and chloride anions of sodium chloride for the active sites from the solid surface. These results indicate that the electrostatic interface between the MZA surface and CR are not the predominant interaction in the CR adsorption onto modified Zeolite A and are in line with those reported in (Liu et al. 2014) according to the results obtained from all experiments performed at pH 7 and 0.1 M ionic strength.

**Effect of dosage**

Adsorbent dosage is one of the important parameters in the adsorption process, as it determines the capacity of the
adsorbent at a given initial concentration (Ouazene & Sahmoune 2010). Experimental results showed that, at the initial dye concentration of 20 mg/L and 24 °C, CR removal percentage increased rapidly from 80.5% to 99.24% when the MZA dosage was increased from 1.0 to 3.0 g/L, as shown in Figure 7, which suggests that a number of sites on the adsorbent surface have increased (Napia et al. 2012). From Figure 7, it can be seen that the adsorbent capacity decreases along with the increase in MZA dosage in the adsorption medium from 10.71 to 7.21 mg/g. A plateau region at 2.5 g/L can be observed, which denotes the MZA amount in the saturation step. This decrease in the adsorbent capacity is attributed to the concentration gradient between CR on the adsorbent surface and solution. Hence, as adsorbent loading increases, CR adsorption onto a specific amount of the adsorbent decreases, resulting in a decreasing \( q_e \) value (Kumar et al. 2010). Moreover, this decrease in the adsorbent capacity may be due to a reduced total available surface area of the adsorbent as a result of overlapping or aggregation of adsorption sites, which would increase the MZA diffusion path length (Munagapati et al. 2015). As seen in Figure 7, the curves approach a plateau as the adsorbent weight increases, due to the increase in the number of available adsorption sites when more adsorbents are used, and thus greater availability of the exchangeable sites or the surface area of the adsorbent (Kumar et al. 2010). As the CR concentration is constant, an increase in the adsorbent dose increases the surface area for adsorption. Since the adsorbent particle size is almost constant, the surface area will be directly proportional to the amount of the adsorbent in the system (Mincea et al. 2013). This plateau (2.5 g/L) represents the amount of the adsorbent at a saturation stage. The present trends are in accordance with the findings reported elsewhere (Abbas et al. 2018; Al-Dahri et al. 2020). Consequently, 3 g/L the adsorbent dose was used in all experiments.

**Effect of contact time**

Effects of the contact time on the CR adsorption capacity onto MZA at three different initial dye concentrations and 24 °C are illustrated in Figure 8. At given initial dye concentration, the contact time is one of the factors affecting the likelihood of reaching equilibrium, after which the remaining concentration is unchanged. Other authors have
reported a positive relation between the adsorption capacity and initial dye concentration (Netpradit et al. 2003; Al-Dahri et al. 2020), and it appears that a rapid initial uptake occurs, whereby equilibrium is reached after 80–90 min for all concentrations. The adsorption capacity at equilibrium increased from 9.71 to 21.11 mg/g as the initial CR concentration increased from 20 to 60 mg/L due to solute transfer between the dye (sorbate) and MZA (sorbent) interactions. Higher initial CR concentrations can yield higher adsorption rate, whereby the resistance to the dye uptake diminishes as the mass transfer driving force increases. The present trends are in accordance with the available findings (Almeida et al. 2009; Abbas et al. 2018).

Response surface methodological approach for the percentage dye removal

Four models – a linear, an interactive (2FI), second-order quadratic, and second-order cubic models – were applied to the experimental findings related to the % dye removal using the statistical software Design-Expert 7 to obtain the regression models. The summary statistics for all models are shown in Table 3. The second-order quadratic model was found to provide the best fit to the experimental data.

As shown in Table 4, the ANOVA results confirm that the second-order quadratic model is the most suited for describing the CR removal process using MZA. The selected second-order quadratic model yielded the following numerical correlation to predict the percentage dye removal (R1):

$$R_1 = 131.04466 - 2.65145 \times X_1 + 1.49960 \times X_2 + 0.026888 \times X_1 \times X_2 + 0.016063 \times X_1^2 - 0.063050 \times X_2^2$$  (5)

where $X_1$ is the initial CR dye concentration (mg/L), and $X_2$ denotes the temperature (°C).

Table 5 shows the $R_1$ values predicted by applying the quadratic model, confirming good agreement between the observed and predicted values. The actual vs. the predicted values of percentage dye removal are plotted in Figure 9, confirming a good agreement between the observed and predicted values.

| Source  | Sum of squares | df | Mean square | F Value | p-value | Prob > F |
|---------|---------------|----|-------------|---------|---------|----------|
| Model   | 1,222.96      | 5  | 244.59      | 72.95   | <0.0001 | significant |
| A-A     | 752.06        | 1  | 752.06      | 224.31  | <0.0001 |          |
| B-B     | 315.14        | 1  | 315.14      | 93.99   | <0.0001 |          |
| AB      | 41.64         | 1  | 41.64       | 12.42   | 0.0097  |          |
| $A^2$   | 114.02        | 1  | 114.02      | 34.01   | 0.0006  |          |
| $B^2$   | 14.23         | 1  | 14.23       | 4.24    | 0.0784  |          |
| Residual| 23.47         | 7  | 3.35        |         |         |          |
| Lack of fit | 23.47  | 3  | 7.82        |         |         |          |
| Pure error | 0.0000  | 4  | 0.0000      |         |         |          |
| Cor total| 1,246.43     | 12 |            |         |         |          |

| Source          | Std. Dev. | R-squared | Adjusted R-squared | Predicted R-squared | PRESS |
|-----------------|-----------|-----------|--------------------|---------------------|-------|
| Linear          | 4.23      | 0.8562    | 0.8274             | 0.6881              | 388.70|
| 2FI             | 3.91      | 0.8896    | 0.8528             | 0.6329              | 457.53|
| Quadratic       | 1.83      | 0.9812    | 0.9677             | 0.8132              | 232.82|
| Cubic           | 0.60      | 0.9985    | 0.9965             | 0.8299              | 212.01|
|                |           |           |                    |                     |       |
The percent contribution of each term in the current model was calculated as (Majid et al. 2019):

\[ PC\% = \frac{SS}{\sum SS} \times 100 \]  

(6)

where \( PC\% \) is the percentage contribution and \( SS \) is the sum of squares. These findings are reported in Table 6.

Figure 10 shows the influence of the initial CR dye concentration and the temperature on the percentage dye removal. It is evident that the % CR dye removal by MZA decreased as the initial dye concentration increased across the entire temperature range (up to 36 °C). Furthermore, higher % dye removal was obtained at lower initial CR dye concentration for all temperatures, as ample active sites existed on the adsorbent surface. However, when the initial CR dye concentration is increased, active sites are no longer sufficient to adsorb the CR dye molecules (AbdulRazak & Rohani 2018; AbdulRazak et al. 2018). The dye adsorption process may be endothermic or exothermic in nature depending on the dye type (Salleh et al. 2011). For the anodic dyes, it is mostly exothermic, and from Figure 10, it is obvious that % dye removal increases as the temperature decreases across the experimental range, indicating that the CR dye removal process is exothermic in nature, in line with conclusions reached by Shahri et al. (2018). This behavior may be due to the weakening of forces between the adsorbate and the MZA active sites (Dwivedi et al. 2016).

### A selection of optimal conditions for CR removal by modified Zeolite A

To demonstrate the current model’s adequacy for predicting maximum CR dye removal, Design-Expert 7.0.0 was applied and 97.02% was obtained as the maximum CR dye removal percentage with high desirability = 0.996 at the following optimal conditions: initial CR concentration = 20 mg/L and temperature = 24 °C. Under these conditions, three experiments were conducted and % dye removal of 97.15% was obtained, which is in a good agreement with the predicted value.

### Thermodynamic study

The effect of temperature on adsorption was investigated in the range from 297 °K (ambient temperature) to 309 °K. When the adsorption temperature increased, MZA adsorption capacity decreased, as shown in Figure 10, indicating that CR adsorption was favorable at low temperatures, and the adsorption bond became weak forces. Moreover, these results refer to the exothermic process for CR adsorption on the modified Zeolite A. The exothermic adsorption process is usually a diffusion process control. The mobility of the dye ions increases as the temperature increases; however, the interactions between dye and the MZA active sites decrease. On the other hand, the swelling effect within the internal zeolite structure occurs at higher temperatures, allowing CR dye to exit from the pores (Sohrabnezhad & Pourahmad 2010; Salahshoor & Shahbazi 2016). The thermodynamic factors of the process, such as enthalpy (\( \Delta H \)), entropy (\( \Delta S \)), and Gibbs free energy changes (\( \Delta G \)) of dye adsorption on MZA, were estimated. The standard enthalpy changes were determined as \(-156.03 \) to \(-12.89 \) kJ/mole, where the negative value indicates that the adsorption was exothermic and chemical in nature. Negative values of the Gibbs free energy changes indicate that adsorption was spontaneous. Generally, the Gibbs free energy changes are in the range shown in Table 7, which focuses on chemical adsorption (Sohrabnezhad & Pourahmad 2010; Salahshoor & Shahbazi 2016).

### Kinetic study

To investigate the mechanism underlying the interactions between the adsorbate and adsorbent, different kinetic equations were applied, namely pseudo-first-order, pseudo-second-order and intra-particle diffusion models.
A pseudo-first-order kinetic model is (Foroughi-dahr et al. 2018; Salahshoor & Shahbazi 2019):

\[
\log\left(\frac{q_e}{C_0} - q_t\right) = -\frac{k_1}{2.303} t
\]

where \(k_1\) denotes the pseudo-first-order adsorption rate constant (min\(^{-1}\)),

\(q_e\) is the amount adsorbed at equilibrium (mg/g);

\(q_t\) represents the amount adsorbed at any time; and contact time (min).

Kinetic parameters of the pseudo-first-order model were obtained by fitting the data to a linear regression as in Equation (7), where the slope of a plot \(\log(q_e - q_t)\) vs. \(t\) is equal to \(k_1/2.303\) and the intercept is \(\log(q_e)\), as reported in Table 8. As can be seen from Table 8, the pseudo-first-order kinetic rate constant \(k_1\) values ranged from 0.0135 to 0.0229 min\(^{-1}\) at various operating temperatures and initial CR concentration. The experimental \(q_e\) value did not agree with calculated values, based on the high standard deviation (SD). This shows that CR adsorption onto MZA does not conform to the pseudo-first-order kinetics, as previously concluded by other authors (Foroughi-dahr et al. 2018; Salahshoor & Shahbazi 2019).

A pseudo-second-order kinetic model is (Foroughi-dahr et al. 2015; Salahshoor & Shahbazi 2016):

\[
t\cdot q_t = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t
\]

where \(k_2\): the pseudo-second-order adsorption rate constant (g·mg\(^{-1}\)·min\(^{-1}\)).

Pseudo-second-order kinetic parameters were obtained from the plot \((t/q_t)\) vs. \(t\), and are shown in Table 8. The findings conform to the experimental results. However, R values appear to be greater than those for the pseudo-first-order model, as can be seen from Table 8. Moreover, the calculated \(q_e\) values from the model of the pseudo-second-order are more fairly agreed than the pseudo-first order with the experimental ones, which evidence with the lower value of SD. In addition, these results show that this model is most suited to describing the mechanism of the CR adsorption on MZA under the assumption that the limiting rate may be chemisorption involving valence forces through the exchange or sharing of electrons between the positive adsorbent site and adsorbate (Salahshoor & Shahbazi 2016).
Intra-particle diffusion study:

An intra-particle diffusion model was applied in order to investigate the mechanism of CR adsorption on MZA as shown below (Guyo et al. 2015).

\[ q_t = k_{id} t^{0.5} + C \]  

(9)

where \( k_{id} \) is the intra-particle diffusion rate constant (mg·g\(^{-1}\)·min\(^{-0.5}\)).

Intra-particle diffusion kinetic parameters are shown in Table 8. While the pseudo-second order equation was found to fit well to the experimental data, the results yielded by that equation are insufficient to forecast the mechanism of diffusion. The kinetic behavior of the adsorption process was thus further analyzed by applying the intra-particle diffusion equation. External diffusion and intra-particle diffusion can be examined by plotting \( q_t vs. t^{0.5} \) for the three stages on a porous adsorbent for the adsorption process, where the slope represents the rate constant and the intercept denotes \( C \), which is indicative of the boundary layer thickness. When the straight line passes through the origin, internal (intra-particle) diffusion is the rate-controlling step. However, adsorption could consist of some other mechanisms besides intra-particle diffusion (Guyo et al. 2015). Figure 11 shows the fitting of the experimental results with the intra-particle diffusion model.

From Figure 11, it can be seen that plots are not linear throughout the entire time period and can be divided into three linear regions. The multi-linearity of the plots indicates the presence of multi-stage adsorption. The first linear section (10 to 30 min) of the plot is due to the external mass transfer, which enables the adsorbed molecules to be carried

![Figure 11](http://iwaponline.com/wst/article-pdf/83/6/1369/865177/wst083061369.pdf)
through film diffusion to the outer (external) MZA surface. Intra-particle diffusion through pores is represented by the second linear part (30 to 80 min) of the plot, where the solution molecules enter the interior of the adsorption. The third part (80 to 180 min) of the plot reflects an equilibrium stage, in which the intra-particle diffusion begins to slow down and remains stagnant, as all active sites of the adsorbent are occupied by the adsorbing molecules and maximum adsorption is achieved. However, the linear portion of the slope implies that the diffusion rate declines as contact time increases (from $k_{i1}$ to $k_{i3}$) due to the decreasing free path of the molecules in the adsorbate pores. Hence, the film diffusion stage was a significant step in the CR-MZA adsorption (Guyo et al. 2015; Salahshoor & Shahbazi 2016).

### Adsorption isotherms

The adsorption isotherm’s capacity is important to assess the maximum uptake for adsorption. The Langmuir, Freundlich, and Temkin isotherms are commonly used for the analysis of experimental results where the surface adsorbent phase may be treated as a monolayer or multilayer. Adsorption isotherms at three different temperatures (24, 30, and 36 °C) reveal that lower temperatures are more beneficial for CR adsorption on MZA (Foroughi-dahr et al. 2015).

i. Freundlich isotherm

The Freundlich isotherm is given by an exponential formula indicating that the adsorbed concentration on the adsorbent surface always increases. Furthermore, assuming the non-uniform distribution of heat adsorption over a heterogeneous surface, the Freundlich expression can be denoted as (Freundlich 1907; Oubagaranadin & Murthy 2010):

$$q_e = K_f C_e^{1/n}$$

where $K_f$ (mg$^{1-(1/n)}$ L$^{1/n}$ g$^{-1}$) is the Freundlich constant referring to the bonding energy. $1/n$ is a constant indicating the adsorption intensity, as follows: 0–1 favorable, = 0 irreversible and $\geq 1$ unfavorable.

ii. Langmuir isotherm

The Langmuir isotherm indicates that adsorption occurs within the adsorbent at different homogeneous locations without contact between the adsorbent molecules. Therefore, the adsorbent has a finite capacity where all adsorbent positions are equal and energy equivalent. The Langmuir isotherm can be characterized as (Foroughi-dahr et al. 2015):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

Rearranging Equation (11) yields:

$$\frac{C_e}{q_e} = \frac{1}{k_m K_L} + \frac{C_e}{q_m}$$

where $q_m$ (mg/ g) is the maximum adsorption capacity. $K_L$ (L/mg) is the free energy adsorption constant. $R_L$ is the separation factor $= 1/(1 + K_L C_0)$, where $R_L = 0$ indicates irreversible, $0 < R_L < 1$ denotes favorable, $R_L = 1$ represents linear, and $R_L > 1$ an unfavorable process.

iii. Temkin isotherm

The Temkin isotherm is used to measure the heat released by adsorbent molecules on the adsorbent particle surface with the extent of coverage of it, where the heat of adsorption is not represented by a logarithmic but a linear equation. The Temkin isotherm can be represented as (Hall et al. 1966; Salahshoor & Shahbazi 2016):

$$q_e = B_T \ln(K_L) + B_T \ln(C_e)$$

where $K_T$ is the equilibrium binding constant (L/mg), and $B_T$ is the variation of adsorption energy (kJ/mol).

Figure 12 displays graphical relationships that Langmuir, Freundlich, and Temkin isotherms have with the experimental CR adsorption data at the MZA surface and theoretical data. Table 9 provides the isotherm constants, along with the corresponding correlation coefficients ($R^2$). As $R^2$ values of Langmuir and Freundlich isotherms for all temperatures exceed 0.935, this indicates that multifarious isotherms can adequately characterize the CR adsorption. The Langmuir isotherm, however, seems to be in best agreement with the experimental results, since the linear regression coefficients are lower than those obtained from the other two isotherms. In addition, in terms of a dimensionless equilibrium parameter, $R_L$ which is the separation factor used as the basic characteristic of the Langmuir isotherm, can be expressed as $R_L = 1/(1 + K_L C_0)$. The value of $R_L$, as shown in Table 9, was within the $0 < R_L < 1$ range, indicating favorable CR adsorption. The Freundlich constant $(1/n)$ value was between 0.213 and 0.66, confirming favorable CR adsorption.
In addition, the variance in the Temkin isotherm in adsorption BT energy was positive, suggesting that the adsorption reaction was exothermic. Thus, the Freundlich isotherm suggests that adsorption is multilayer and takes place on heterogeneous surfaces, as reported elsewhere (Khalaf & Rohani 2011). The experimental results are shown in Figure 12(b), indicating that Temkin isotherm yields reasonable accuracy ($R^2 \approx 0.977–0.905$) in the 297–305 °K temperature range but it deviates at 309 °K. The same trends were found by Salahshoor & Shahbazi (2016).

### CONCLUSIONS

In the present study, a commercial zeolite was successfully modified by HDTMABr, characterized by XRD, SEM, and FTIR and was used for the CR removal from an aqueous solution. The following conclusions were reached based on the obtained findings:

1. The removal process was affected by the solution pH, contact time, initial dye concentration, temperature and the adsorbent amount. The adsorbent capacity of 21.11 mg/g was achieved under the following conditions: pH = 7, initial CR concentration = 60 mg/L, temperature = 24 °C, ionic strength = 0.1 M, adsorbent dose = 3 g/L and 90 min contact time.

2. The RSM based on CCD was used to determine the combined effect of the temperature and initial dye concentration on the CR dye removal from the aqueous solution by MZA. A second-order quadratic model was proposed by CCD and was found to be in good agreement with the experimental data ($R^2 = 0.9812$).

3. The Temkin isotherm provided a better fit to the obtained adsorption data compared to the Freundlich and Langmuir ones.

4. The kinetic CR adsorption process on MZA was best described by a pseudo-second-order kinetic equation, which outperformed both the pseudo-first-order kinetic and intra-particle diffusion ones.

5. The results demonstrate the exothermic nature of the adsorption process for the removal of CR by MZA.

The finding of this research may usually be confirmation of the suitability for the elimination of anionic, toxic, artificial dyes from water as economically valuable adsorbent. For future study, biomass adsorbent from waste industrial or agricultural by-products may be used to treat water from other common contaminants.

### DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
DATA AVAILABILITY STATEMENT

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

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