
Reza Moradia, Javad Hosseinia

aDepartment of Chemistry, Tuyserkan Branch, Islamic Azad University, Tuyserkan, Iran.

*Correspondence should be addressed to Dr. Reza Moradi, Email: reza.moradi_bi@yahoo.com

Background & Aims of the Study: Dyes are one of the most hazardous materials in various industries which can problems in health human, environment and ecosystem. The purpose of this study is the removal of Acid Orange 25 (AO25) diazo dye in aqueous solutions by adsorption onto clinoptilolite (CP) zeolite: study kinetic and isotherm model: experimental design and optimization.

Materials & Methods: CP zeolite have been characterized by scanning electron microscopy (SEM), Energy dispersive X-ray (EDX) and Fourier transform infrared (FT-IR). The effective factors for the removal of dye were determined and optimized using Taguchi (L9 (34)) orthogonal array experimental design method with four factors having three levels for each factor. The most influenced of each factor on the process determined using Analysis of Variance (ANOVA) method. The isotherms of dye adsorption such as: Langmuir and Freundlich were studied.

Results: The Taguchi results showed that pH=4 (level 1), dye concentration=30 ppm (level 2), agitation speed=160 rpm (level 3) and adsorbent dosage=55 mg/l (level 2) was optimum conditions for this process. The interaction between pH×adsorbent dosage was the most influencing interaction. The percent of each process parameter on the removal of dye was found to be in the following the order: pH (7.217%), dye concentration (2.604%), agitation speed (86.539%) and adsorbent dosage (3.618%). The results showed that the dye adsorption onto CP followed Langmuir isotherm. Adsorption kinetics of dye onto CP followed the pseudo-second-order kinetic model.

Conclusions: The results showed that the adsorption process can be suitable method to removal dyes in aqueous solutions.

Keywords: Zeolite, Adsorption kinetic, Taguchi experimental design, Isotherm, Azo dye, Iran.
differs from adsorption, in which a fluid (the adsorbate) is dissolved by or permeates a liquid or solid (the adsorbent), respectively. Adsorption is a surface-based process while adsorption involves the whole volume of the substance. The term sorption encompasses both processes, while desorption is the reverse of it (6,7). The adsorption process for removal of dyes in aqueous solution was studied by many investigators (8-11). Zeolitic adsorbent (12,13) were researched and used to dye removal.  

Taguchi design is a type of factorial design experiment that can be used to optimizing processes. The Taguchi experimental design reduces cost, improves quality, and provides robust design solutions. The advantages of Taguchi method over the other methods are that numerous factors can be simultaneously optimized and more quantitative information can be extracted from fewer experimental trials. Taguchi design (14-16) has been used for optimization of process parameters for dye removal.  

Aims of the study:  
In this study, CP zeolite was characterized by SEM, EDX and FT-IR analysis. The isotherm model and adsorption kinetic of dye onto CP was studied. The effects of operational parameter such as pH, dye concentration, agitation speed and adsorbent dosage on the process were studied and optimized using Taguchi (L₀ (3⁴)) orthogonal array experiment design and the bigger is better response category.  

Materials & Methods  
Materials  
The AO25 dye was obtained from Merck Company (Germany) and was used without further purification. The structure and characteristics of AO25 is shown in Table 1. The pH values were adjusted at desired level using dilute NaOH and H₂SO₄. The CP was obtained from Afrand Tuska Company (Iran) extracted from deposits in the region of Semnan. Cp chemical compounds by EDX standard quantification analysis are shown in Table 2. Other chemicals used in the paper were purchased from the Merck Company (Germany). Double distilled water was used for preparation of requisite solutions.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Structure</th>
<th>C.I.</th>
<th>MW (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AO25</td>
<td><img src="image" alt="Structure" /></td>
<td>20160</td>
<td>420.38</td>
</tr>
</tbody>
</table>

Table 1) The structure and characteristics of dye.
In this study, the morphologies of the adsorbent were taken by SEM model Philips XL30 with EDX analyzer. The FT-IR spectroscopy was measured on PerkinElmer Spectrometric Analyzer using KBr pellet in wave number range of 450-4000 cm\(^{-1}\) was studied. UV/Vis Spectrophotometer, Jenway (6505) was employed for measuring absorbance using glass cells of path length 1 Cm.

**Taguchi experimental design**

For determination of optimal condition, the Taguchi experiment design was used. This method included the following steps (17):
- The effective parameters on the test results were determined.
- Levels of each parameter was identified separately (interaction between parameters was to be considered).
- The suitable orthogonal array and the assignment of process parameters to the orthogonal array were chosen.
- On the basis of orthogonal array, the required experiments were carried out.
- The statistical analysis was done.
- The ANOVA statistical procedure was used to analysis the results of the experiment.

In this study, Taguchi (L\(_9\)) orthogonal array experimental design consisting of four factors having three levels each was employed and are shown in Table 3. Orthogonal array the experimental design method was chosen to determine the experimental plan, is presented in Table 4. In order to see the effects of noise-sources removing pollutants, each test was repeated three times under the same conditions. Optimizing statistical function was chosen as indicators. Three classes of statistical function were bigger is better, smaller is better and nominal is best (18). In this study, the statistical function, quality characteristic type: bigger is better and data type: average standard deviation values were used to define the optimal conditions.

Qualitek-4 software was used for the design of experiments, analysis and optimization of process.

**Table 2) Clinoptilolite chemical compounds.**

<table>
<thead>
<tr>
<th>Formula</th>
<th>Conc.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(_2)O</td>
<td>2.01</td>
</tr>
<tr>
<td>MgO</td>
<td>0.72</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>11.81</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>66.5</td>
</tr>
<tr>
<td>MnO</td>
<td>0.04</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>0.01</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>3.12</td>
</tr>
<tr>
<td>CaO</td>
<td>3.11</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.21</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>1.3</td>
</tr>
<tr>
<td>Loss of ignition (L.O.I)</td>
<td>12.05</td>
</tr>
</tbody>
</table>

**Apparatus**

The morphologies of the adsorbent were taken by SEM model Philips XL30 with EDX analyzer. The FT-IR spectroscopy was measured on PerkinElmer Spectrometric Analyzer using KBr pellet in wave number range of 450-4000 cm\(^{-1}\) was studied. UV/Vis Spectrophotometer, Jenway (6505) was employed for measuring absorbance using glass cells of path length 1 Cm.
adjusted at the desired level using dilute NaOH 0.1N or H₂SO₄ 0.1N (the pH values were measured with Horiba M12 pH meter). The dye adsorption was done by mixing of adsorbent in flask. Then mixture was agitated on shaker (IKA - KS 130 basic) for 30 min. The solution samples were taken at certain time intervals (0-50 min) and adsorbent was separated by centrifuged. The change on the absorbance of all solution samples was monitored and determined at certain time intervals during the adsorption process. At the end of the equilibrium period, the dye concentration was determined by using a UV/Vis Spectrophotometer. The amount of dye adsorbed at equilibrium \( q_e \) (mg/g) was calculated by (Eq.1):

\[
q_e = \frac{(C_0 - C_e)V}{m},
\]

where \( C_0 \) (mg/l) is the initial dye concentration, \( C_e \) (mg/l) the dye concentration at equilibrium, \( V \) (l) the volume of the solution and \( m \) (g) is the mass of the adsorbent. The amount of dye adsorbed at time \( t \), \( q_t \) (mg/g) was calculated by (Eq.2):

\[
q_t = \frac{(C_0 - C_t)V}{m},
\]

where \( C_t \) (mg/l) is dye concentration at any time \( t \). The dye removal percent (%) was calculated by (Eq.3):

\[
\text{Removal} (%) = \left(1 - \frac{C_e}{C_0}\right) \times 100
\]

### Results

#### The characterization of CP

Fig. 1 shows the SEM image of CP. The scale of CP powder was characterized. Regarding the specified scale, the size of CP is micrometer. In the SEM image, the CP surface morphology is shown. Also, adsorption sites are clearly seen. Chemical composition of the CP analyzed by EDX. The EDX spectrum image of CP is presented in Fig. 2. As it can be seen, elemental of each peak has been identified.

![Figure 1) SEM image of CP](image1.png)

![Figure 2) EDX spectrum of CP](image2.png)

Fig. 3 shows the FT-IR spectrum of CP in the wave number range from 450 of 4000 cm⁻¹. The stretching vibrations of O–H group have emerged about 3400-3500 cm⁻¹. The strongest absorption peak at 1084 cm⁻¹ is assigned to the framework stretching vibration band of Si(Al)-O in tetrahedral Si(Al)O₄ in CP. The structural bands at 450-900 cm⁻¹ are responsible for the stretching vibrations of T-O, T-O-T, and O-T-O bonds in tetrahedral SiO₄ and AlO₄ (19-21).
Adsorption kinetics

The controlling mechanism of the adsorption process, kinetic models are used to analysis the experimental data. The rate of adsorption process can be identified with the kinetic adsorption data. Many kinetic sorption models studied for test the experimental data in adsorption process. Using the correlation coefficients ($R^2$), confirms the experimental data with the model. If the higher value is closed to unity, it means that model used for the kinetics is justified. In this research, we choose two kinetic models, pseudo-first-order kinetic model and pseudo-second-order kinetic model, are tested to find the best fitted model for the experimental data. The pseudo-first-order kinetic model (22) is generally shown in (Eq.4):

$$\frac{dq_t}{dt} = k_1(q_e - q_t),$$  
(4)

where $q_t$ and $k_1$ are the amount of dye adsorbed at time $t$ (mg/g) and the rate constant of pseudo-first-order kinetics (min$^{-1}$), respectively. Integrating (Eq.4) with the boundary conditions ($t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$) show the linear (Eq.5):

$$\ln(q_e - q_t) = \ln q_e - k_1 t,$$  
(5)

a plot of $\ln(q_e - q_t)$ versus $t$ presents a linear relationship from which $k_1$ and $q_e$ are the slope and the intercept, respectively.

The pseudo-second-order kinetic model (23) applied to adsorption kinetic can be written at (Eq.6):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2,$$  
(6)

where $k_2$ is the rate constant of pseudo-second-order kinetics (g/mg.min). Integrating (Eq.6) with the boundary conditions ($q=0$ to $q=q_t$ and $t=0$ to $t=t$) show the linear (Eq.7):

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \left(\frac{1}{q_e}\right)t.$$  
(7)

If the second-order kinetics is applicable, the plot of $t/q_t$ versus $t$ will be a linear relation. The values of $k_2$ and $q_e$ will be determined from the intercept and the slope of the plot. Kinetic constants obtained by linear regression (Fig. 4 and 5) for the two models are listed in Table 5.

![Figure 3) FT-IR spectrum of CP](image)

![Figure 4) Pseudo-first-order kinetic of adsorption dye onto CP](image)

**Table 5** Adsorption kinetic parameters of dye adsorption onto the CP.

<table>
<thead>
<tr>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$ (min$^{-1}$)</td>
<td>$q_e$ (mg/g)</td>
</tr>
<tr>
<td>0.0219</td>
<td>3.0014</td>
</tr>
</tbody>
</table>
Removal of Acid Orange25 Diazoe Dye in Water...

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Adsortion isotherm

Adsortion isotherm demonstrates the relationship between equilibrium concentrations of adsorbate in the solid phase, and in the liquid phase at the constant temperatures. Adsorption isotherms are often obtained using experimental data in which the equilibrium data are attempted by various isotherm models. There are the initial experimental tests that determine feasibility of adsorption treatment. There are many different isotherm models have been suggested for the adsorption of solutes in a liquid solution onto a solid surface. In this paper, the Langmuir and Freundlich isotherms were used to describe the equilibrium adsorption. The Langmuir isotherm model assumes monolayer coverage of adsorbate over a homogenous adsorbent surface with a finite number of identical sites, and there is no interaction between the adsorbate molecules. The Langmuir model (24) can be described as follows at (Eq.8):

\[ q_e = \frac{b q_m C_e}{1 + b C_e} \]  

(8)

where \( C_e \) is the equilibrium concentration of dye solution (mg/l), \( q_e \) the equilibrium capacity of dye on the adsorbent (mg/g), \( q_m \) is the monolayer adsorption capacity of the adsorbent (mg/g), and \( b \) is the Langmuir adsorption constant (l/mg) related to the free energy of adsorption.

The empirical Freundlich adsorption isotherm is obtained on the assumption that the sorption takes place on a heterogeneous adsorbent surface, where the sorption energy distribution decreases exponentially. This equation is also applicable to multi layer adsorption and is expressed by the (Eq.10) (25):

\[ q_e = K_f C_e^{1/n} \]  

(10)

where, \( K_f \) and \( n \) are the Freundlich constants which represent the adsorption capacity and adsorption intensity of the sorbent, respectively. (Eq.10) can be linearized by taking logarithms as:

\[ \log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \]  

(11)

from which the Freundlich constants can be determined.

To study the applicability of the Langmuir and Freundlich isotherms for the dye adsorption onto CP are plotted (Fig. 6 and 7). The values are shown in Table 6.
Effect of dye concentration
The effect of initial concentration of dye (from 20 to 40 ppm) on removal efficiency is shows in Fig. 9. The removal percent at first increase then decreased with an increasing in the dye concentration. So, the optimal dye concentration 30 ppm (level 2, 55.169%) was selected.

Effect of pH
pH is one of the main factors influencing the removal dye compounds in the adsorption process. Fig. 8 shows adsorption of dye onto CP at different pH from 4 to 8. The adsorption of dye onto CP decreases with increasing pH. Fig. 8 clearly shows that the best results were obtained in acidic solution, (pH= 4, level 1).

Effect of agitation speed
Fig. 10 showed the effect of agitation speed from 120 to 160 rpm in this process. The removal percent increases with increasing agitation speed. Fig. 10 clearly shows that the best results were obtained the 160 rpm of agitation speed in level 3.
in this process was agitation speed. In Fig. 13, the effect of each variable such as pH, dye concentration, agitation speed and adsorbent dosage on other variables has been defined. Based on the results of the experiment, the interaction between pH×adsorbent dosage has the highest value. The interaction between factors pair are listed in Table 7.

**Effect of adsorbent dosage**

Fig. 11 showed the effects of adsorbent dosage (g) on dye removal percent. At this stage, the effect of different adsorbent dosage between 35 to 75 mg/l was tested. The results in Fig. 11 shows that increasing the adsorbent dosage to 55 mg/l (level 2) removal percent increased and with the increase more than this dosage, removal percent decreased.

**Figure 10)** Effect of agitation speed in removal process

**Figure 11)** Effect of adsorbent dosage in removal process

**The effect of each variable on other variables in dye removal process**

Fig. 12 shown, based on the Taguchi experiment design, the most effective parameter
In this study, the removal of dye in water solutions in adsorption process onto CP applied using Taguchi experimental design. The removal of dye by adsorption process was studied by many investigators (26-28). The effects of operational parameter such as: pH, dye concentration, agitation speed and adsorbent dosage on the process were studied and optimized.

pH is one of the effective parameter on dye adsorption process. Fig. 8 shows the adsorption of dye onto CP decreases with increasing pH. For anionic dyes, the adsorption of an adsorbent towards them decreases with increasing pH values because of the electrostatic repulsion (29). An electrostatic repulsion exists between the negatively charged surface of the CP and negatively charged anionic dye. So, maximum dye removal was obtained in pH=4.

As was observed in Fig 9, dye removal at first increase then decreased with an increasing in the dye concentration. The decrease of dye removal with increase of dye concentration (shown in Fig. 9) could be attributed to the lack of available active adsorption sites required for the high initial dye concentration (30). Fig. 10 showed the effect of agitation speed from 120 to 160 rpm in this process. The removal percent increases with increasing agitation speed. The increase in agitation speed reduces the boundary layer, which leads to an increase in the transfer coefficient of the boundary layer. Thus, best results were obtained the 160 rpm of agitation speed in level 3.

The results in Fig. 11 shows that increasing the adsorbent dosage to 55 mg/l (level 2) removal percent increased and with the increase more than this dosage, removal percent decreased. The influence of adsorbent dosage could be explained as follows: The increase in dye adsorption with adsorbent dosage can be attributed to an increase in the adsorbent surface, which increased the availability of adsorption sites. However, if the dye removal decreased with the increasing adsorbent dosage.

**ANOVA method**

The influence and relative importance of these factors are quantitatively given by the ANOVA method. The results of ANOVA are listed in Table 8. The percent (p (%)) of each process parameter on the removal of dye was found to be in the following the order: pH (7.217%), dye concentration (2.604%), agitation speed (41.686%) and adsorbent dosage (3.618%). The row which is marked as other/error indicates the errors which are caused by uncontrollable factors (noise) that is factors which are not included in the experiment and experimental error. It is defined as the influence of one factor on the total observed variance in the experiment. A bigger value means that the factor contributes more to the final result. It can be seen that agitation speed has the biggest contribution between the factors. These conditions are determined according to the significances of the factors. This is expressed by the F-ratio which is defined as the ratio of variance due to the effect of a special factor on the variance compared to the error term. It means that the factors with an F-ratio less than one have no significant effect compared to the error. Table 9 shows the optimum conditions in dye removal. The percentage contribution of each process parameter on the removal of dye was found to be in the following the order: pH (11.839), dye concentration (5.051), agitation speed (41.686) and adsorbent dosage (8.401).

**Discussion**

<table>
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<th>No.</th>
<th>Interaction</th>
<th>Columns</th>
<th>SI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH × Adsorbent dosage</td>
<td>1×4</td>
<td>62.94</td>
</tr>
<tr>
<td>2</td>
<td>Dye concentration × Adsorbent dosage</td>
<td>2×4</td>
<td>53.33</td>
</tr>
<tr>
<td>3</td>
<td>Agitation speed × Adsorbent dosage</td>
<td>3×4</td>
<td>34.19</td>
</tr>
<tr>
<td>4</td>
<td>Dye concentration × Agitation speed</td>
<td>2×3</td>
<td>32.75</td>
</tr>
<tr>
<td>5</td>
<td>pH × Dye concentration</td>
<td>1×2</td>
<td>17.15</td>
</tr>
<tr>
<td>6</td>
<td>pH × Adsorbent dosage</td>
<td>1×3</td>
<td>11.00</td>
</tr>
</tbody>
</table>

Columns: Represent the column locations to which the interacting factors are assigned.

SI: Interaction severity index.

**Table 7) Interaction between Factors.**

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Table 8) Analysis of variance (ANOVA).

<table>
<thead>
<tr>
<th>Factors</th>
<th>DOF</th>
<th>Sum of Squares</th>
<th>Variance</th>
<th>F-Ratio</th>
<th>Pure Sum</th>
<th>(P%)</th>
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<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>1391.904</td>
<td>695.952</td>
<td>3187.454</td>
<td>1391.467</td>
<td>7.217</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>502.655</td>
<td>251.327</td>
<td>1151.078</td>
<td>502.218</td>
<td>2.604</td>
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<tr>
<td>C</td>
<td>2</td>
<td>16684.747</td>
<td>8342.373</td>
<td>38207.983</td>
<td>16684.311</td>
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<tr>
<td>D</td>
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<td>698.058</td>
<td>349.029</td>
<td>1598.549</td>
<td>697.621</td>
<td>3.618</td>
</tr>
<tr>
<td>Other/error</td>
<td>9</td>
<td>1.964</td>
<td>0.218</td>
<td></td>
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<tr>
<td>Total</td>
<td>17</td>
<td>19279.331</td>
<td></td>
<td></td>
<td>100.00%</td>
<td></td>
</tr>
</tbody>
</table>

DOF*: Degree of freedom.

The decreased is due to adsorption sites remaining unsaturated during the adsorption process (31). Another reason for this result may be the overlapping of adsorption sites due to overcrowding of adsorbent particles.

The correlation coefficients ($R^2$) in Table 5 for the pseudo-first-order kinetic model are relatively low, and cannot be used a kinetic model. For the pseudo-second-order kinetic model, the $R^2$ value is 0.914, therefore second-order model to describe the adsorption process of dye onto the adsorbent.

The $R^2$ values show that the dye removal isotherm does not follow the Freundlich isotherm (Table 6). The calculated $R^2$ values for Langmuir isotherm model show that the dye removal isotherm can be approximated as Langmuir model. This means that the adsorption of dyes takes place at specific homogeneous sites and a one layer adsorption onto adsorbent surface.

Table 9) Optimal conditions in dye removal.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Level Description</th>
<th>Level</th>
<th>Contribution</th>
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</thead>
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<tr>
<td>A</td>
<td>4</td>
<td>1</td>
<td>11.839</td>
</tr>
<tr>
<td>B</td>
<td>30</td>
<td>2</td>
<td>5.051</td>
</tr>
<tr>
<td>C</td>
<td>160</td>
<td>3</td>
<td>41.686</td>
</tr>
<tr>
<td>D</td>
<td>55</td>
<td>2</td>
<td>8.401</td>
</tr>
</tbody>
</table>

The Taguchi results showed that pH=4, dye concentration=30 ppm, agitation speed= 160 rpm and adsorbent dosage=55 mg/l was optimum conditions for this process. Based the Taguchi experiment design, the most effective parameter in this process was agitation speed. Also, the interaction between pH and adsorbent dosage has the highest value. The percent ($p\%$) of each process parameter on the removal of dye was found to be in the following the order: pH (7.217%), dye concentration (2.604%), agitation speed (86.539%) and adsorbent dosage (3.618%). The results showed that dye adsorption onto CP followed Langmuir isotherm. Adsorption kinetics of dye followed the pseudo-second order kinetic model.

Footnotes

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Conflict of Interest:
The Authors have no conflict of interest.

References