Application of artificial neural networks and response surface methodology for analysis of malachite green removal from aqueous solution using phosphoric acid–modified pumice powder: kinetic and isotherm studies

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Received 16 December 2018; Accepted 24 September 2019

\textbf{ABSTRACT}

The present study aimed at investigating phosphoric acid (1, 6 and 12 N)–modified pumice efficiency in removal of malachite green (MG) dye from aqueous solutions. The effects of different parameters such as pH (3–11), adsorbent dosage (0.2–1.4 g/L), contact time (15–75 min) and the dye initial concentration of 85 mg/L were analyzed. The obtained modified pumice was characterized using the Fourier transform infrared spectroscopy and scanning electron microscopy. Adsorption equilibrium data were analyzed using Langmuir, Freundlich, Temkin and Redlich–Peterson. The results illustrated that the data were following both Langmuir and Freundlich isotherms. Also, the phenol adsorption was modeled using pseudo-first order, pseudo-second order, intraparticle diffusion and Elovich models. The best fit being observed with the pseudo-second-order kinetic model. Finally, the process modeling was carried out using response surface method and artificial neural networks.

\textbf{Keywords:} Adsorption; Pumice; Phosphoric acid; Malachite green; Response surface method; Artificial neural network

\textbf{1. Introduction}

Dye pollution in aquatic ecosystems is considered as one of the most frequent pollutants of the environment in recent years \cite{1,2}. The colored wastewater is produced by various industries such as textiles, automotive, pharmaceutical, tanneries, cosmetics and healthcare. However, a large amount of these dyes are strongly persistent in biodegradation due to their complex structures. Naturally this may result in poisonous, carcinogenic and mutagenic solutions for humans and animals \cite{3}. Such colored effluents are important, regarding esthetics. These reduce sunlight penetration through the water, disturb photosynthetic phenomena and the aquatic flora, as well as affect the aquatic organisms, the biological balance and the decomposition processes in receiving water \cite{4}. Malachite Green (MG) is a cationic dye and one of the high consuming materials. It is utilized in various industries such as cotton, silk, paper, wool, leather, etc. It is also used in the fishing industries as antifungal and microbes to control parasites and fish diseases. The
2. Materials and methods

2.1. Preparation of adsorbate (MG), adsorbent and its modification

All chemical materials used in this study were purchased from the Merck Company (Germany). A specific amount of phosphoric acid was mixed with distilled water, and the phosphoric acid solutions with 1, 6 and 12 N were prepared and used for pumice modification. The hydrochloric acid and sodium hydroxide 1 M were used to adjust the pH of the solution. The Malachite green (MG) dye was purchased from the Merck Company with a catalog number of 105 – 20. And the stock solution (1,000 mg/L) of MG was prepared, and then the operating concentrations of stock solutions were prepared during the process. In the present study, the pumice stone as an adsorbent was collected from Qorveh, Kurdistan, Iran. At first, the pumice was washed thoroughly by de-ionized water to remove its impurities, and this was continued until the effluent's turbidity reached less than 1 NTU. Then 300 g of pumice stone was crushed and sieved with an effective size of 50μ. The prepared powder was washed several times by de-ionized water and then it was dried in an oven at the temperature of 105°C for about 1 h. Then a specific amount of pumice powder was kept in phosphoric acid (1, 6 and 12 N) and placed on a shaker for 24 h. Finally, the modified pumice powder was washed several times by de-ionized water to remove residual phosphoric acid from the adsorbent and then dried at 105°C for 14 h [23].

2.2. Adsorbent characteristics

The chemical and physical properties of bare and modified adsorbent were characterized by Fourier transform infrared spectroscopy (FTIR), XRD and scanning electron microscopy (SEM). The FTIR was carried out using a spectrometer (WQF-510) with a resolution of 4 cm⁻¹ in the range of 400–4,000 cm⁻¹ with the KBr pellets technique. The chemical characteristics were determined by the XRD method (Shimadzu XRD-6000, Kyoto, Japan). The SEM (Philips XL30, Netherlands) technique was used for electron beam image of the adsorbent.

2.3. Experimental design (determining the sample size)

In this study, the DOE software [24] is used to design experiments (the required sample size). The design included 20 runs with 4 central points as shown in Table 1. The pH of 7 for discharging industrial effluent was recommended by the Iranian national standard (No: 2439). In experimental runs, the pH of 7, the absorbent dosage of 0.8 g/L, and the contact time of 45 min were considered. It should be noted that in all experimental runs, the initial concentration of MG dye was 85 mg/L.

2.4. Preparation of samples and adsorption study

MG is an azo dye with molecular formula C₃₄H₃₄N₆CL (molecular weight of 364.5 g/mol; Table 2). The stock solution of 1,000 mg/L was prepared by dissolving 1 g of MG in 1,000 mL de-ionized water. For each analysis, run used the concentrated solution of 85 mg/L. The analysis of samples was carried out in a pH of 3, 5, 7, 9 and 11, the contact time of 15, 30, 45, 60 and 75 min, adsorbent dosages of 0.2, 0.5, 0.8, 1.1 and 1.4 g/L with a mixing rate of 200 rpm.

The residual MG in sample was determined at different times. At first, 15 mL of the solution was centrifuged at 2,000 rpm for 15 min to separate the adsorbent, and then remaining the solute concentration was measured by a spectrophotometer (Cary 50 made by Perkin Elmer) at 665 nm [6]. All experiments were repeated three times to achieve acceptable results. Also, the calibration curve was calculated due to the absorbance rate and dye concentrations to prepare the standard solution.
2.5. Adsorption isotherms study

The adsorption isotherms were used to evaluate the highest absorbance of the pollutants by the adsorbent. They could evaluate how of the adsorbent react regarding absorption materials, also they played an important role in the optimization of applying adsorbent.

In this study, the results were fitted well to Langmuir and Freundlich adsorption isotherms. All experiments were analyzed in five different adsorbent dosages (0.2, 0.5, 0.8, 1.1 and 1.4 g) with other parameters set constant (pH = 7, mixing rate of 200 rpm, 85 mg/L and contact time of 75 min). The amount of solute absorbed on pumice powder was calculated by the following equation [25]:

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

where \( q_e \) is the adsorption capacity at equilibrium (mg/g), \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of solute MG dye, respectively. (mg/L), \( V \) is the volume of solution (L) and \( M \) is the adsorbent weight (g).

2.5.1. Langmuir isotherm

The Langmuir isotherm was used based on monolayer adsorption on the adsorbent surface, which contained a limited and uniform number of adsorption sites. The Langmuir isotherm derivative presented a homogeneous absorption, so that each molecule had enthalpies and constant activation energy [26].

The linear form of the Langmuir isotherm could be calculated as follows:

\[ \frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{bQ_mC_e} \]  

where \( C_e \) and \( b \) are equilibrium concentration (mg/L) and equilibrium constant (mg/L), respectively; and \( Q_m \) is the maximum absorption capacity (mg/g).

One of the most important Langmuir isotherm parameters is dimensionless constant \( R_L \) (separation factor), which is used by Webber and Chakkravorti to calculate the shape of the Langmuir isotherm [27]. \( R_L \) equation is defined as follows:

\[ R_L = \frac{1}{\left(1 + bC_0\right)} \]  

where \( R_L \) is the separation factor, \( C_0 \) is the initial concentration (mg/L) and \( b \) is the Langmuir constant.

Absorption process could be determined using \( R_L \) parameters

<table>
<thead>
<tr>
<th>Factor ( R_L )</th>
<th>Type of absorption process</th>
</tr>
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<tbody>
<tr>
<td>( R_L &gt; 1 )</td>
<td>Undesirable</td>
</tr>
<tr>
<td>( R_L = 1 )</td>
<td>Linear</td>
</tr>
<tr>
<td>( 0 &lt; R_L &lt; 1 )</td>
<td>Desirable</td>
</tr>
<tr>
<td>( R_L = 0 )</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

2.5.2. Freundlich isotherm

In this study, the Freundlich isotherm was used to describe the non-ideal and reversible absorption for multilayer adsorption on heterogeneous adsorbent sites with unequal and non-uniform energy. And it is not limited to single-layer absorption [28].

The linear form of Freundlich isotherm could be represented as follows:

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

where \( q_e \) is the amount of solute adsorbed (mg/g), \( C_e \) is equilibrium concentration (mg/L), \( K_f \) and \( n \) are constants related to the adsorption capacity ((mg/g) (g/L) (l/n)) and intensity of absorption, respectively [29].

2.5.3. Temkin isotherm

The Temkin isotherm could be calculated by the following equation [30]:

\[ q_e = \frac{RT}{b} \ln K_t C_e \]  

where \( q_e \) is the amount of solute adsorbed (mg/g), \( C_e \) is equilibrium concentration (mg/L), \( K_t \) and \( n \) are constants related to the adsorption capacity ((mg/g) (g/L) (l/n)) and intensity of absorption, respectively [29].

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Table 1: Used experimental range of variables

<table>
<thead>
<tr>
<th>Variables</th>
<th>Range and level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact time, min</td>
<td>15 30 45 60 75</td>
</tr>
<tr>
<td>Adsorbent dosage, g/L</td>
<td>0.2 0.5 0.8 1.1 1.4</td>
</tr>
<tr>
<td>pH</td>
<td>3 5 7 9 11</td>
</tr>
</tbody>
</table>

Table 2: Characteristics and chemical structure of phosphoric acid and malachite green

<table>
<thead>
<tr>
<th>Composition</th>
<th>Molecular weight</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acid</td>
<td>97.99</td>
<td><img src="image" alt="Phosphoric Acid" /></td>
</tr>
<tr>
<td>Malachite green</td>
<td>364.9</td>
<td><img src="image" alt="Malachite Green" /></td>
</tr>
</tbody>
</table>
where $R$ is ideal gas constant (8.314 J/mol K), $T$ is absolute temperature (K) and $h_i$ is the Temkin equation constant (J/mol).

### 2.5.4. Redlich–Peterson isotherm

The Redlich–Peterson isotherm could be calculated by the following equation [31]:

$$ q_e = \frac{k_{RP} C}{1 + \alpha C + \beta} $$

(6)

where $k_{RP}$ is the Redlich–Peterson isotherm constant, $\alpha$ and $\beta$ are the Redlich–Peterson isotherm constants.

### 2.6. Reaction kinetic study

To investigate the MG dye absorption processes and the absorption rate control, the reaction kinetic was used. Constancy of the reaction kinetic was calculated by the use of the following Lagergren pseudo-first-order and Hu pseudo-second-order equations [32].

To obtain the reaction kinetics, the mixing time and other parameters were considered constant (the dye absorbance rate at different mixing times of 15, 30, 45, 60 and 75 min, and constant dosage of 0.8 g and 200 rpm).

#### 2.6.1. Pseudo-first order kinetic

The linear form of the first-order kinetic equation was shown as follows [33]:

$$ \log \left(1 - \frac{q_t}{q_{eq}}\right) = -\frac{k_1}{2.302} t $$

(7)

$q_t$ and $q_{eq}$ are the amounts of adsorbed dye at time $t$, and equilibrium (mg/g), $k_1$ is the pseudo-first-order kinetic rate constant (min$^{-1}$).

#### 2.6.2. Pseudo-second order kinetics

The linear pseudo-second-order model can be revealed as follows [33]:

$$ \frac{t}{{q_t}} = \frac{1}{h} + \frac{1}{q_{eq}} t $$

(8)

$$ h = kq_{eq}^2 $$

(9)

where $h$ is the primary absorption rate when $t \to 0$ (mg g$^{-1}$min$^{-1}$), and $k$ is the pseudo-second-order kinetic adsorption constant (g mg$^{-1}$min$^{-1}$).

#### 2.6.3. Intraparticle diffusion kinetics

The intraparticle diffusion model can be revealed as the following equation [34]:

$$ q_t = k_d t^{\frac{1}{2}} $$

(10)

where $k_d$ is the rate constant for intra-particle diffusion models and $t$ is time (min).

#### 2.6.4. Elovich kinetics

The Elovich model can be revealed as the following equation [35]:

$$ q_t = \frac{1}{d} \ln (ct) + \frac{1}{d} \ln t $$

(11)

where $c$ is the initial adsorption rate (mg/g min) and $d$ is the Elovich constant (g/mg).

### 2.7. Artificial neural network

An artificial neural network is a flexible mathematical structure that can identify complex nonlinear relationships between input and output data sets [36,37]. In this study, a multilayer feed forward neural network with a hidden layer was trained by the back-propagation gradient-descendent algorithm. The experimental points were determined using the CCD method (Table 5) to train and test the model. These experimental points were divided into three sets of trainings; validation and testing included 70%, 20% and 20% of the data, respectively. Training data were used to update the weight and biases using the Levenberg Marquardt algorithm, and testing data were used to assess the trained network generalization capability. Also, the error of validation data was monitored during training to eschew over fitting [38]. The network used in this study consists of three input nodes (contact time, adsorbent dosage and pH) in the first layer and an output node (dye removal) in the third layer. For the neurons in the input and output layers, linear function (purelin) and hidden layer, hyperbolic tangent sigmoid function (tansig) was applied [39]. The number of neurons in the hidden layer was employed as a model design parameter due to their significant impact on network performance. Therefore, to determine the optimal number of neurons in this layer, different topologies were investigated and the mean square error (MSE) in each topology was calculated using the following equation [40]:

$$ MSE = \frac{1}{N} \sum_{i=1}^{N} \left(y_{i,pred} - y_{i,exp}\right)^2 $$

(12)

where $y_{i,pred}$ and $y_{i,exp}$ are the predicted and experimental values of the response, respectively, and $N$ illustrates the number of data points.

To avoid random correlation due to random measurements of weights and biases, each topology was repeated 10 times [41].

To compare the ANN and RSM models, the following performance indexes were computed: $R^2$, $R^2_{\text{adj}}$, RMSE, MAE, AAD (Eqs. (13)–(17)) [42].

$$ R^2 = 1 - \frac{\sum_{i=1}^{N} \left(y_{i,pred} - y_{i,exp}\right)^2}{\sum_{i=1}^{N} \left(y_{i,exp} - y_{i,\text{avg}}\right)^2} $$

(13)
\[ R^2_{adj} = 1 - \left( 1 - R^2 \right) \frac{N-1}{N-K-1} \]  

\[ \text{RMSE} = \frac{1}{N} \sqrt{\frac{\sum_{i=1}^{N} (y_{i,pred} - y_{i,exp})^2}{N}} \]  

\[ \text{MAE} = \frac{1}{N} \sum_{i=1}^{N} |y_{i,pred} - y_{i,exp}| \]  

\[ \text{AAD} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{y_{i,pred} - y_{i,exp}}{y_{i,exp}} \right| \times 100 \]

where \( K \) is the number of input variables and \( y_{i,exp} \) is the average of experimental response.

3. Results and discussion

3.1. Characterization of adsorbent

The results of FTIR are shown in Fig. 1, in modifying the adsorbent with phosphoric acid, proton penetrates the adsorbent structure and attacks the O–H bonds of the adsorbent. Thus, it changes the absorption capacity of the O–H bands and octagonal cations. The results also showed that the peak was excited in 1,000 to 3,500 cm\(^{-1} \) bands due to the effect of the acid proton on the O–H. Whereas, the high-pitched peaks could be observed in 788 to 1,066 cm\(^{-1} \) bands, which are related to the Si–O–Si. Also, the bands of 525, 690 and 998 cm\(^{-1} \) are linked to the Si–O–Al [43]. It also indicated that the content of aluminum in the pumice structure is decreased in terms of increased phosphoric acid normality. Therefore, the 3,608 and 3,780 cm\(^{-1} \) peak band, related to AlO–H and Si–OH–Al groups, are decreased with increasing the acid normality [44]. On the other hand, a bandwidth in 3,550 cm\(^{-1} \) will be formed with increasing the acid normality, which is related to SiO–H groups [45]. Table 3 shows the results of the XRF analysis. As it could be observed, the aluminum content of pumice decreased from 19.6% in raw pumice to 14.4% in modified pumice in terms of increased normality of phosphoric acid (12 N). These findings confirmed the results of the FTIR, because the pumice-related peaks have also been reduced due to decreased its aluminum content. Fig. 2 shows the SEM results. The pumice has an irregular structure with porous surfaces, which create a lot of absorption sites on pumice. The pumice modified by the phosphoric acid in three investigated concentrations shows a lot of similarities. Although the surface of the pumice is large due to more porosity, increasing the acid normality is not destroying the pumice structure [46].

3.2. Validity of the RSM model

To determine the correlation between the predicted and actual results, the ANOVA analysis test was used. The ANOVA test was performed to measure the significance and adequacy of the model, and the results are presented in Table 4. The statistical analysis of the results also shows that the actual removal rate of malachite dye is near to predicted value. On the other hand, the \( F \)-value represents the ratio of the squared model to the ratio of the squared errors.
which indicates a high value of the $F$-value, low error rate and high compliance of the model [47]. The $F$-value and $p$-value were used to control the level of the interaction and significance of the independent variables. The high $F$-value shows the high effect of the intended parameter. Although the $p$-value is lower and the $F$-value is higher, the coefficient associated with that factor or the independent variable is more impressive and important. The results indicated that all the parameters mentioned above are suitable for the proposed models ($\text{Prob} > F$ and PLF $< 0.05$, and AP $> 4$). Therefore, this issue implies the reliability of the obtained models to predict the amount of dye removal. The results also showed that the contrast between the actual and predicted values of MG dye removal by the modified pumice decreases with increasing the normality of using acid in adsorbent modification. As, with increasing the normality, the dispersion of points, which represents the percentage of actual removal rate on the line, shows more predicted values.

### Table 4

Malachite dye removal model by phosphoric acid-modified pumice (1, 6 and 12 N) and parameters validity of tests

<table>
<thead>
<tr>
<th>Phosphoric acid</th>
<th>Modified equations with significant terms</th>
<th>Type of model</th>
<th>$F$ value</th>
<th>$\text{Prob} &gt; F$</th>
<th>Mean</th>
<th>SD</th>
<th>$R^2$</th>
<th>Adj. $R^2$</th>
<th>Pred. $R^2$</th>
<th>AP</th>
<th>PRESS</th>
<th>PLF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N</td>
<td>Removal (%) = $+61.32 + 4.48A + 13.81B + 20.71C$</td>
<td>Linear</td>
<td>59.36</td>
<td>$&lt;0.001$</td>
<td>61.32</td>
<td>5.53</td>
<td>0.9176</td>
<td>0.9021</td>
<td>0.8599</td>
<td>31.563</td>
<td>830.26</td>
<td>0.056</td>
</tr>
<tr>
<td>6 N</td>
<td>Removal (%) = $+65.74 + 4.08A + 13.42B + 20.19C$</td>
<td>Linear</td>
<td>44.6</td>
<td>$&lt;0.001$</td>
<td>65.74</td>
<td>5.74</td>
<td>0.9070</td>
<td>0.8896</td>
<td>0.8599</td>
<td>29.38</td>
<td>999.48</td>
<td>0.114</td>
</tr>
<tr>
<td>12 N</td>
<td>Removal (%) = $+70.02 + 4.63A + 12.98B + 20.13C$</td>
<td>Linear</td>
<td>40.17</td>
<td>$&lt;0.001$</td>
<td>70.02</td>
<td>6.48</td>
<td>0.8828</td>
<td>0.8608</td>
<td>0.8235</td>
<td>26.04</td>
<td>1,312.44</td>
<td>0.071</td>
</tr>
</tbody>
</table>


which indicates a high value of the $F$-value, low error rate and high compliance of the model [47]. The $F$-value and $p$-value were used to control the level of the interaction and significance of the independent variables. The high $F$-value shows the high effect of the intended parameter. Although the $p$-value is lower and the $F$-value is higher, the coefficient associated with that factor or the independent variable is more impressive and important. The results indicated that all the parameters mentioned above are suitable for the proposed models ($\text{Prob} > F$ and PLF $< 0.05$, and AP $> 4$). Therefore, this issue implies the reliability of the obtained models to predict the amount of dye removal. The results also showed that the contrast between the actual and predicted values of MG dye removal by the modified pumice decreases with increasing the normality of using acid in adsorbent modification. As, with increasing the normality, the dispersion of points, which represents the percentage of actual removal rate on the line, shows more predicted values.

3.3. Effect of variables on the response

Table 5 shows the average percentage of actual and predicted malachite dye removal rate by the phosphoric acid-modified scoria (1, 6 and 12 N). As the results showed,
the removal of MG dye by the phosphoric acid-modified scoria has significantly increased rather than raw pumice in parallel conditions. The maximum removal efficiency was obtained by the phosphoric acid (12 N), (6 N) and (1 N)-modified pumice. It indicated that the ability of chemical changes in the adsorbent for removal of alumina and silica increases with increasing the acidity due to breaking the molecular bands. Also, the intensity of replacing the hydrogen ions with metals (iron, potassium and titanium) in the adsorbent structure was increased; therefore, the efficiency of adsorbent will be increased consequently, because it causes some changes in pumice structure including a significant increase in the surface area, pores diameter and three-dimensional deformation. So, this change in structure increases the absorbing dye due to increase in the surface area and absorption sites [48]. These results are confirming other researchers’ studies. For example, the study of Ajemba [48] on the nitric acid-modified bentonite showed that the adsorption of silica increased but the content of cations (Al$^{3+}$, Fe$^{2+}$ and Mg$^{2+}$) was decreased significantly in terms of increasing the acid concentration. The reason could be due to the fact that the cations, mentioned above, are eight-sided plates that are entering the solution during modifying the adsorbent with acid. While the silica remains in the adsorbent content in result of its four square structure. Increasing the ratio of Si/[Al$^{3+}$, Fe$^{2+}$, Mg$^{2+}$] increases the free space in adsorbed crystalline tissue, consequently increases the absorption capacity of bentonite. Also, in modifying the adsorbent with nitric acid, the proton cannot fill the vacant cations due to proton acid ion exchange with Na$^+$, K$^+$, Ca$^{2+}$, Al$^{3+}$ and Mg$^{2+}$, so the created free space causes an increase in the absorption capacity of the adsorbent. As well in nitric acid modified-adsorbent, Mg$^{2+}$ cation is separated easily from the adsorbent rather than Al$^{3+}$, Fe$^{3+}$ cations [49]. Guo et al. [50] study indicated that nitric acid increased oxygen groups on activated carbon adsorbent, thus increased the absorption of positively charged pollutants.

Table 5: Mean of actual and predicted removal percentage of Malachite Green dye by the modified pumice with different concentrations of phosphoric acid (1, 6 and 12 N)

<table>
<thead>
<tr>
<th>Variables</th>
<th>Responses (Removal of dye %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run</td>
<td>A: Contact time, min</td>
</tr>
<tr>
<td></td>
<td>1 N</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
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<td>5</td>
<td>45</td>
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<tr>
<td>6</td>
<td>75</td>
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</tbody>
</table>
Figs. 3 and 4 show the comparison among the effects of contact time, adsorbent dose and pH on the efficiency of malachite dye removal by modified pumice. The results indicated that the dye removal rate increases by increasing contact time, adsorbent dose and pH. The highest effect was related to pH, adsorbent dose and contact time, respectively [51]. Findings also indicated that the line slope of the pH (C) was greater than the line slopes of adsorbent dose (B), and contact time (A). Therefore, it confirmed the efficiency of parameter in dye removal process (Figs. 5 and 6). However, with concentration increase, the trend of using acid in modifying pumice, and the slopes are close to each other. It could be due to the removal of dyes increased in terms of increasing the acid normality for modifying the adsorbent. Also, higher affectivity of the pH rather than other factors (absorbent dose and contact time) could be due to the higher affectivity of pH on the physical and chemical properties of adsorbent and adsorbate, because the adsorbent surface is negatively charged with increased pH. Regarding this, the MG is a cationic dye with two nitrogen atoms and methyl agents [52]. Therefore, in alkaline environments, where the charge level of adsorbent is more, dye adsorption rate increases due to electrostatic gravity [53]. Also, the color of malachite changes more chemically for pH more than 9, so its adsorption is increased [54]. Moreover, the dye adsorption decreased with pH decrease, it could be due to creating electrostatic repulsion in an acidic environment in terms of producing the proton ion (H⁺). All in all, the absorption of cationic dye decreased. Furthermore, according to it, the dominant combination of pumice is SiO₂, and this combination is converted to Si³⁺ with decreasing the pH, which also causes electrostatic repulsion and thus reduces the absorption of the cationic dye. The dye slight absorption in an acidic environment was due to the dye penetration in the adsorbent pores. As well, high removal efficiency by acid-modified pumice in the acidic condition is more than bare pumice. Although, pumice modification with acid causes in increasing the positive charge on the adsorbent surface. It is more likely that the cationic absorption should be decreased due to electrostatic repulsion, because pumice modification causes an increase in adsorbent surface and pore volume, which could increase the adsorbent efficiency of acid-modified pumice more than raw pumice despite increasing the electrostatic refraction [52]. Other studies also revealed that the removal of MG dye by wood waste and removal of cationic dye by mango peel are both increased [51]. This study showed that the maximum removal rate of MG dye by activated carbon was observed in pH = 7 within pH 3 to 7. The absorbent surface is negative in pH close to alkaline, so it causes increasing the absorption of the malachite dye. But in acidic pHs, the charge level is positive due to overcoming the hydrogen ion, so the electrostatic repulsion reduces the absorption of the cationic dye. Also, this study showed that for pHs less than 4 the adsorbent surface charge was more positive and for pH of 4 to 6 the adsorbent surface was heterogeneous and a combination of

![Graph](image-url)
a negative and positive charge. But for pHs more than 6, the adsorbent surface was negatively charged due to hydroxyl. The results also showed that the removal rate of more than 50% occurred at the first 30 min and then decreased with increasing absorption time. The high absorption of dye at the initial contact time was reported at pH = 7 due to the negative charge on the adsorbent surface [55]. The results also showed that the optimum area for removal of more than 75% by the phosphoric acid (12 N)-modified pumice was higher than 6 N and this one was more than 1 N (Fig. 7).
3.4. Adsorption kinetics and isotherm

The adsorption isotherms investigation showed that the dye absorption fitted well with both the Langmuir and Freundlich isotherms. The separation coefficient \( R_L \) is the most important parameter in the Langmuir isotherm adsorption, which defines the adsorbent capability in separating and removing absorbents. The results showed that the maximum dye absorption capacity was increased with increased acid normality. So that \( Q_m \) for phosphoric acid (1 and 12 N)-modified pumice increased from 4.54 to 5.55 mg/g, which indicates an increase in the pumice adsorption sites with increasing the acid normality (Table 6). Also, in this study the Langmuir isotherm shows that the \( R_L \) of adsorbent is located in the optimal range (0–10). In other words, the acid-modified pumice is an appropriate adsorbent to remove the dye. These results are inconsistent with the results of Moraci and Calabrò [56]. The Freundlich isotherm study also showed that the maximum absorption coefficient \( K_f \) by the phosphoric acid-modified pumice forms were related to 1 N > 6 N > 12 N, respectively. It indicated that the adsorption sites increased with increased concentration of acid and its effect on the adsorbent structure increases. It can be stated that the acid causes some changes in the pumice structure, including a significant increase in pumice surface area, an increase in the diameter of the pore size and its three-dimensional deformation. Therefore, these structural changes cause an increase in the absorption sites and consequently increase the absorption of dye [57]. Also, the results showed that the absorption rate \( 1/n \) calculated for all acid-modified pumice forms was in an optimal range (0–1). However, with increasing the normalization, the \( 1/n \) rate decreases. This indicated that modifying pumice with different concentrations of acid, different absorbent sites are available for dye adsorption, and hence with increasing the acid normality the absorption rate increases. Because in the Freundlich isotherm, the \( 1/n \) value represented the interaction between adsorbent and absorbent, and as \( 1/n \) tends to zero, that interaction is stronger and more powerful [58]. But Temkin and Redlich–Peterson isotherms cannot describe the data in different acid concentrations (Table 6).

The adsorption kinetic reactions on pumice showed that the adsorption process follows the pseudo-second order kinetic model for all absorbent forms. The results of other researcher’s study on the removal of various cationic dyes with different absorbents, showed that the adsorption data followed the pseudo-second order kinetics [57–62]. Obeying the pseudo-second order models imply that the adsorption process depends on the absorbent concentration, as

![Fig. 6. Confrontation between actual and predicted value of the malachite dye removal by phosphoric acid-modified pumice (a): 1 N, (b): 6 N, and (c): 12 N.](image)

![Fig. 7. Optimum area of removal efficiency more than 75% for phosphoric acid (1, 6 and 12 N)-modified pumice.](image)
3.5. ANN model

In this study, the optimal ANN topology had three inputs, a hidden layer with six neurons and an output layer (1–6–3). The number of neurons in the hidden layer was selected by training different ANN topologies and selecting the optimal based on the maximization of $R^2$ and minimizing MSE. The values of $R^2$ and MSE for modified pumice with phosphoric acid with various concentrations (1, 6 and 12 N) and raw pumice are shown in Table 7. High $R^2$ values for optimal ANN topology confirmed the appropriateness of this method for predicting the repeatability of experimental data. In Figs. 8–11, the predicted data are plotted against the experimental results for the training, validation, testing, and all data sets. These figures illustrate the appropriate fit between the experimental data and the predicted data by the ANN model.

3.6. Comparison of RSM and ANN models

Table 8 shows the comparative performance between ANN and RSM models. According to this table, the RMSE, MAE and AAD values for the ANN model are less than RSM. On the other hand, the $R^2$ values of ANN are higher than RSM, which suggests that experimental data can be predicted more accurately with the ANN model. Additionally, the $R^2_{adj}$ values are closer to $R^2$ in the ANN model, which is related to the better ANN performance. Therefore, these results confirm that the ANN model is more reliable for predicting this nonlinear system.

### Table 6
Calculation of the constants of different isotherms and kinetic equations

<table>
<thead>
<tr>
<th></th>
<th>Acid normality</th>
<th>$Q_m$ (mg/g)</th>
<th>$b$ (L/mg)</th>
<th>$R_L$</th>
<th>$R^2$</th>
</tr>
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<tr>
<td><strong>Langmuir</strong></td>
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<td>4.54</td>
<td>0.076</td>
<td>0.134</td>
<td>0.904</td>
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<td></td>
<td>6</td>
<td>5.05</td>
<td>0.061</td>
<td>0.161</td>
<td>0.992</td>
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<tr>
<td></td>
<td>12</td>
<td>5.55</td>
<td>0.107</td>
<td>0.098</td>
<td>0.99</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
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<td>0.8</td>
<td>0.401</td>
<td>0.902</td>
<td></td>
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<tr>
<td></td>
<td>6</td>
<td>0.74</td>
<td>0.461</td>
<td>0.99</td>
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<tr>
<td></td>
<td>12</td>
<td>1.08</td>
<td>0.374</td>
<td>0.971</td>
<td></td>
</tr>
<tr>
<td><strong>Temkin</strong></td>
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<td>0.17</td>
<td>0.257</td>
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<tr>
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<td>6</td>
<td>0.24</td>
<td>0.21</td>
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<tr>
<td></td>
<td>12</td>
<td>0.42</td>
<td>0.54</td>
<td>0.212</td>
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<tr>
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<td>0.947</td>
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<tr>
<td></td>
<td>6</td>
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<td></td>
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<td></td>
<td>12</td>
<td>0.034</td>
<td>0.936</td>
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<tr>
<td><strong>Pseudo-second order</strong></td>
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<tr>
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<td>6</td>
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<tr>
<td></td>
<td>12</td>
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<tr>
<td><strong>Intraparticle diffusion</strong></td>
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<tr>
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<td>6</td>
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<td>12</td>
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<tr>
<td><strong>Elovich</strong></td>
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<tr>
<td></td>
<td>6</td>
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<td></td>
<td>12</td>
<td>0.0082</td>
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</table>
4. Conclusion

According to the obtained results, the phosphoric acid improved the removal rate of the MG dye through chemical changes (especially the ratio of silica to alumina) in adsorbent structure and also increased the specific surface area. Absorption efficiency increased with increased dose, contact time and pH. To understand the mechanisms of the considered process better, the equilibrium adsorption isotherms and kinetic models were applied. The results indicated that the data have obeyed both Langmuir and Freundlich isotherms. Based on the correlation coefficient,
Fig. 9. Scatter plot of the ANN predicted vs. experimental data of MG dye removal by modified pumice with 6 N phosphoric acid.

Fig. 10. Scatter plot of the ANN predicted vs. experimental data of MG dye removal by modified pumice with 12 N phosphoric acid.
the pseudo-second-order kinetic model described the experimental data. The absorption coefficient ($R_L$) and absorbance intensity ($1/n$) for all adsorbed modified forms were in the optimal range of 0–1, which indicated the appropriate adsorbent effect on dye removal.

After that, RSM and ANN were applied to predict the process. The resulting models were statistically analyzed and compared and the predicted values showed that the ANN model is more reliable for predicting this process.

**Acknowledgment**

The authors gratefully acknowledge the Research Council of Kermanshah University of Medical Sciences (Grant Number: 93049) for financial support.

**References**


