Heterogeneous Fenton-like degradation of Acid Red 17 using Fe-impregnated nanoporous clinoptilolite: artificial neural network modeling and phytotoxicological studies

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Abstract: Heterogeneous Fenton-like removal of Acid Red 17 (AR17) from aqueous solution was investigated. Fe-impregnated nanoporous clinoptilolite (Fe-NP-Clin) was prepared by an impregnation method and used as a catalyst. A complete characterization including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), inductively coupled plasma (ICP), and Brunauer–Emmett–Teller (BET) analyses was done to describe the physical and chemical properties of NP-Clin and Fe-NP-Clin samples. The effects of five operational parameters, i.e. solution pH, H₂O₂ dosage, catalyst loading, AR17 concentration, and reaction time, on the removal efficiency of AR17 were studied. For the first time, an artificial neural network (ANN) model with five neurons at the input layer, 14 layers in the hidden layer, and one neuron at the output layer was designed to predict the removal efficiency of AR17. The correlation coefficient between the predicted results by the ANN model and experimental data was 0.993, demonstrating that the ANN could efficiently predict AR17 removal efficiency under different operating conditions. The phytotoxicity of AR17 and its intermediate compounds formed in the Fenton process was evaluated using the aquatic species *Lemna minor.*

Key words: Heterogeneous Fenton, nanoporous clinoptilolite, decolorization, neural network, phytotoxicity

1. Introduction

Advanced oxidation processes (AOPs) have recently become more practical in various types of industrial processes. The removal of organic pollutants is a major application of these processes for the treatment of wastewater containing colorful effluents.¹ Colorful effluents containing organic pollutants, such as synthetic dyes, are continuously introduced into aquatic water bodies from various textile industries. These compounds cause chronic contamination of the wastewater-receiving water body.² Acid red 17 (AR17) (also called Bordeaux red) is an azo compound widely used in the textile and food industries. It was used as a model pollutant in our study due to its toxic effects on aquatic species and the environment. Table 1 shows some of the properties of AR17. In order to inhibit the hazardous accumulation of dyes in the aquatic environment, it is essential to utilize practical methods to degrade these organic contaminants effectively.³⁴

Among AOPs, the homogeneous Fenton process (Eq. (1)) has been widely utilized as a homogeneous catalytic process for the degradation of diverse organic contaminants.⁵

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Table 1. Characteristics of Acid Red 17.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Chemical structure</th>
<th>Molecular formula</th>
<th>Color Index number</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( M_w ) (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.I. Acid Red 17</td>
<td><img src="image" alt="Chemical Structure Image" /></td>
<td>C_{20}H_{11}N_{2}Na_{2}O_{7}S_{2}</td>
<td>16180</td>
<td>510</td>
<td>502.43</td>
</tr>
</tbody>
</table>

\[
Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + HO^* + H_2O \tag{1}
\]

However, the homogeneous Fenton process has some disadvantages such as possible implementation of the process below a pH of 4, the formation of iron-containing precipitates, and catalyst deactivation by the degraded products.\(^6\)\(^7\) In recent years, the utilization of heterogeneous catalysts in the Fenton process has become more popular, due to their ability to resolve the aforementioned issues related to the homogeneous Fenton process. Iron-containing synthetic and natural zeolites,\(^8\) laponite,\(^9\) and pillared clays\(^10\) are examples of heterogeneous catalysts that have been reported in published articles. Among these catalysts, iron-containing zeolites have been widely applied in heterogeneous Fenton-like processes due to their distinctive physical and chemical characteristics. Moreover, zeolites with high porosity and crystallinity contain a regular cage structure of molecular size (\(\text{Å}\) scale) and have high cation exchange capacity.\(^11\)

Both natural and synthetic iron-containing zeolites have been utilized in heterogeneous Fenton-like processes.\(^12\)\(^-\)\(^14\) Natural clinoptilolite is a famous zeolitic mineral that contains a nonporous structure with pores 100 nm or smaller. It has been widely utilized in various catalytic processes due to its affluence and low cost.\(^15\)\(^16\) Moreover, it is not a toxic substance. These properties attract the authors’ attention to investigate the substitution of a homogeneous catalyst on natural nonporous clinoptilolite (NP-Clin) structure.

The mechanism of the Fenton-like process with Fe-NP-Clin catalyst was not completely clarified. According to the literature, the following reactions are anticipated to occur in a heterogeneous Fenton-like process:\(^17\)

\[
Fe^{3+} - Clin + H_2O_2 \rightarrow Fe - Clin - OOH^{2+} + H^+ \tag{2}
\]

\[
Fe - Clin - OOH^{2+} \rightarrow Fe^{2+} - Clin + HO_2^* \tag{3}
\]

\[
Fe^{2+} - Clin + H_2O_2 \rightarrow Fe^{3+} - Clin + HO^- + HO^* \tag{4}
\]

\[
Fe^{2+} - Clin + HO^* \rightarrow Fe^{3+} - Clin + HO^- \tag{5}
\]

\[
Fe^{3+} - Clin + HO_2^* \rightarrow Fe^{2+} - Clin + O_2 + H^+ \tag{6}
\]

\[
Fe^{2+} - Clin + HO_2^* \rightarrow Fe^{3+} - Clin + HOO^- \tag{7}
\]
Due to the diversity of reactions in heterogeneous Fenton-like processes, the effect and importance of various key parameters included are complex to calculate; this leads to some uncertainties in the design and scale-up of chemical reactors. It is obvious that this issue cannot be resolved by linear multivariate correlation. Mathematical definition of the system via kinetic modeling of the process may be a solution. However, due to the complexity of determining the kinetic parameters in various steps, the kinetic modeling of heterogeneous Fenton-like processes has been very little investigated. In the present work, in order to model the heterogeneous Fenton-like process and investigate the effect and importance of different operational variables on the removal of AR17, an artificial neural network (ANN) was utilized.

ANN is a mathematical algorithm that can generate a relation between independent and dependent parameters of a process without requiring the mathematical description of the reactions involved in the process. This might be very useful in simulating and scaling-up complicated systems under different conditions. Furthermore, it requires less operating time for model development with limited numbers of experiments. Because of the aforementioned reasons, modeling of this process via an ANN is quite appropriate.

In the first step of the present work, Fe-NP-Clin was prepared by an ion exchange method. Then Fe-NP-Clin was used as a heterogeneous catalyst in a Fenton process for the removal of AR17. The physical and chemical characteristics of NP-Clin and Fe-NP-Clin were investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), inductively coupled plasma (ICP), and Brunauer–Emmett–Teller (BET) analyses. According to the results of the characterization step, the mechanism of the impregnation process was proposed. In the second step of this study, the influence of basic parameters including initial pH, \( \text{H}_2\text{O}_2 \) concentration (mmol/L), catalyst concentration (g/L), AR17 concentration (mg/L), and reaction time (min) on the removal efficiency of AR17 was investigated to optimize the effect of variables. Then a relationship between these operational parameters and the response variable, i.e. AR17 removal efficiency, was expressed by an ANN. This relationship using the ANN model was applied for the prediction of AR17 removal efficiency under different operational conditions (modeling section). The phytotoxicity of AR17 and its intermediate compounds released during the heterogeneous Fenton process at different treatment times was evaluated on an aquatic species, *Lemna minor* (*L. minor*).

2. Results and discussion

2.1. Characterization of NP-Clin and Fe-NP-Clin samples

The XRD patterns of the NP-Clin and Fe-NP-Clin samples are depicted in Figure 1. The XRD peaks at \(2\theta = 10.9^\circ, 17.53^\circ, 22.7^\circ, \) and \(27.63^\circ\) correspond to the heulandites framework XRD pattern, JCPDS card (83-1260). Spectrum b in Figure 1 shows the XRD pattern of the Fe-NP-Clin sample. It can be seen that the XRD pattern of the Fe-NP-Clin sample is similar to that of NP-Clin, demonstrating good crystallinity of the obtained Fe-NP-Clin sample. This indicates that the acidic condition during the impregnation process did not cause destruction of the structure of the NP-Clin sample. Moreover, no additional peaks related to iron crystalline phases were detected in the XRD spectrum of the Fe-NP-Clin sample. These results indicate that the iron ions were efficiently exchanged by counterbalanced ions of the NP-Clin framework. The results obtained in the present work are consistent with the results of Gonzalez-Olmos et al.
In order to identify the functional groups of NP-Clin and Fe-NP-Clin, FT-IR analysis was performed (see Figure 2). Spectrum a in Figure 2 shows the absorption bands assigned to the NP-Clin sample. The FT-IR spectrum of Fe-NP-Clin (spectrum b in Figure 2) reveals that the functional groups on the surface of Fe-NP-Clin are similar to those in the NP-Clin sample, indicating that the NP-Clin surface functional groups were not altered significantly during the impregnation process. However, the intensity of the peaks in comparison with spectrum a in Figure 2 decreased due to the acidic condition applied during preparation of the Fe-NP-Clin sample. As an example, the disappearance of the peak at 2835 cm\(^{-1}\) for Fe-NP-Clin implies that the C–H bonds did not vibrate any longer because of the changes caused at NP-Clin active sites during the Fe-impregnation process. According to Doula et al.\(^1\) the formation of different iron species in the pore and/or channels of NP-Clin causes the bonds not to vibrate freely. This leads to a decrease in the intensity of the bands.
The comparative SEM micrographs of the NP-Clin and Fe-NP-Clin samples at different magnifications are given in Figure 3. Figures 3a and 3b show that natural NP-Clin has an agglomerated and rough surface including thin layer structure of NP-Clin. Moreover, according to Figures 3a and 3b, the particle diameter is greater than 0.5 μm. Figures 3c and 3d show that, after the impregnation process, the morphology and the size of the crystallites did not significantly change despite the acidic condition applied during the impregnation process.24–26

![Figure 3. SEM images of (a, b): NP-Clin and (c, d): Fe-NP-Clin samples.](image)

Table 2 presents the microstructural (porosity) characteristics of NP-Clin before and after the Fe-impregnation process. It should be mentioned that the data presented in Table 2 were obtained from BET analysis. The specific surface area of the Fe-NP-Clin sample increased from 23.93 m²/g to 38.15 m²/g in comparison with the NP-Clin sample. It is thought that the formation of noncrystalline Fe-compounds, such as amorphous Fe-oxides, in cationic positions of the NP-Clin channels or at its surface position increased the specific surface area. Moreover, the increase in the total pore volume and pore diameter can be attributed to the formation of various Fe-complexes such as Fe-binuclear complex in internal and external NP-Clin framework.12,27
Table 2. Microstructural characteristics of NP-Clin and Fe-NP-Clin.

<table>
<thead>
<tr>
<th></th>
<th>Fe-NP-Clin</th>
<th>NP-Clin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (m²/g)</td>
<td>38.058</td>
<td>23.925</td>
</tr>
<tr>
<td>Total pore volume (cm³/g)</td>
<td>0.044</td>
<td>0.033</td>
</tr>
<tr>
<td>Pore diameter (Å)</td>
<td>59.042</td>
<td>56.523</td>
</tr>
</tbody>
</table>

ICP can be used to determine the content of various elements such as cadmium, iron, potassium, manganese, phosphorus, sulfur, and zinc in biological and environmental samples. In this work, the amount of iron in NP-Clin was determined by the ICP method before and after the impregnation process. Moreover, the amount of iron in the NP-Clin and Fe-NP-Clin samples was determined to be 5.3 mg/g and 15.7 mg/g, respectively. This implies the high ion exchange ability of the NP-Clin sample.

2.2. Effect of operational parameters

Before investigating the influence of main key parameters, the degradation efficiency of AR17 by different oxidation processes was investigated. The results are presented in Figure 4. The degradation efficiency of AR17 by the Fenton-like process with NP-Clin and Fe-NP-Clin as heterogeneous catalysts was 43.5% and 97.6%, respectively. In addition, the degradation efficiency of AR17 by control experiments was lower than 20%. Therefore, Fe-NP-Clin was selected as a heterogeneous catalyst for further experiments.

![Figure 4](image)

**Figure 4.** Decolorization efficiency of AR17 in different oxidation processes (a): Heterogeneous Fenton with Fe-NP-Clin; (b): Heterogeneous Fenton with NP-Clin; (c) Adsorption onto Fe-NP-Clin sample; (d) Oxidation with H₂O₂. Experimental conditions: [AR17] = 20 mg/L, [H₂O₂] = 3 mmol/L, [Catalyst] = 2.0 g/L, and pH = 5.

2.2.1. Effect of the initial pH of the solution

It is well established that the performance of homogeneous and heterogeneous Fenton processes is dependent on pH. The effect of the initial solution pH on heterogeneous Fenton-like removal of AR17 was examined over a pH range of 3 to 9 (Figure 5a). Figure 5a shows that the degradation efficiency of AR17 is slightly decreased by the increase in pH from 3 to 5 and then it was significantly decreased by the further increase in pH value.
Figure 5. (a) Effect of the initial pH of the solution on the removal efficiency of AR17 by the Fenton-like process. Experimental conditions: [AR17] = 20 mg/L, [Catalyst] = 2.0 g/L, and [H₂O₂] = 3 mmol/L. (b) The concentration of leached iron to the solution under different pH conditions. Experimental conditions: [Catalyst] = 2.0 g/L. (c) Effect of the H₂O₂ concentration on the removal efficiency of AR17 by the Fenton-like process. Experimental conditions: [AR17] = 20 mg/L, [Catalyst] = 2.0 g/L, and pH = 5. (d) Effect of the catalyst concentration on the removal efficiency of AR17 by the Fenton-like process. Experimental conditions: [AR17] = 20 mg/L, [H₂O₂] = 3 mmol/L, and pH = 5. (e) Effect of the initial AR17 concentration on the removal efficiency of AR17 by the Fenton-like process. Experimental conditions: [Catalyst] = 2.0 g/L, [H₂O₂] = 3 mmol/L, and pH = 5. (f) The changes in the absorption spectrum of 20 mg/L AR17 solution during 180 min of the degradation process. Experimental conditions: [Catalyst] = 2.0 g/L, [H₂O₂] = 3 mmol/L, and pH = 5.
Figure 5. (g) Total chlorophyll and carotenoid content in *L. minor* exposed to untreated AR17 solution and 30 min, 60 min, 90 min, 120 min, and 180 min of heterogeneous Fenton-treated solutions after 120 h; values are mean of three replicates. Experimental conditions: [AR17] = 20 mg/L, [Catalyst] = 2.0 g/L, [H$_2$O$_2$] = 3 mmol/L, and pH = 5.

According to the literature, the leaching of iron ions to the solution is higher at low pH values than at neutral and basic pH values. In order to investigate the role of homogeneous iron ions in the degradation of AR17, the amount of iron leaching at different pH levels, i.e. pH 3, 5, 7, and 9, was determined over 180 min. The results are presented in Figure 5b. As can be seen, the leakage of iron ions to the solution at pH 3 was greater than at pH 5. It can be concluded that the enhanced AR17 removal efficiency at pH 3 was due to simultaneous implementation of homogeneous and heterogeneous Fenton processes. This results in the generation of more HO$^\bullet$ radicals and, consequently, the AR17 removal efficiency was increased. Figure 5a illustrates that 69.5% and 54.9% of AR17 was removed at pH 7 and 9 after 180 min of the degradation process.

However, according to the literature, the efficiency of the homogeneous Fenton-like process decreases significantly with pH increase. The acceptable removal of AR17 at pH 7 and 9 was assigned to the particular environment of Fe$^{3+}$ ions inside the structural pores of Fe-NP-Clin, where strong electrostatic forces are present. Such interactions cause the heterogeneous Fenton process to be implemented under mild acidic conditions (such as pH 5 in this work), which is one of the main advantages of this process.

### 2.2.2. Effect of the initial H$_2$O$_2$ concentration

Figure 5c indicates the changes in the removal efficiency of AR17 by changing the initial concentration of H$_2$O$_2$ from 1 mmol/L to 5 mmol/L while the other operational conditions were held constant. It can be seen from this figure that when the H$_2$O$_2$ concentration increased from 1 mmol/L to 3 mmol/L, the AR17 removal efficiency increased rapidly from 83.5% to 97.6%. This can be explained by the increased formation of HO$^\bullet$ radicals, which enhanced the removal efficiency of AR17. However, at high H$_2$O$_2$ concentrations, the AR17 removal efficiency decreased because of quenching of the produced HO$^\bullet$ radicals by H$_2$O$_2$, described in Eqs. (9) and (10).

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O \quad (9)$$

$$HO_2^\bullet + HO^\bullet \rightarrow O_2 + H_2O \quad (10)$$

This led to hydroperoxyl radical (HO$_2^\bullet$) production in the presence of an excess of H$_2$O$_2$, as shown in Eqs. (9) and (10). HO$_2^\bullet$ radicals ($E_0 = 1.7$ V) are less reactive than HO$^\bullet$ radicals ($E_0 = 2.8$ V). Thus, the removal efficiency was decreased.
2.2.3. Effect of catalyst dosage and reusability

The effect of catalyst concentration on the removal of AR17 was investigated by changing the catalyst concentration from 1 g/L to 5 g/L; the results are depicted in Figure 5d. It can be observed that with an increasing concentration of the catalyst from 1 g/L to 2 g/L, the removal efficiency of AR17 was significantly increased from 79.6% to 97.6%. By increasing the catalyst concentration, the number of available active sites is increased too; this led to the adsorption of more AR17 and \( \text{H}_2\text{O}_2 \) molecules and to the production of more hydroxyl radicals, which increased the removal of AR17 under the applied operating conditions.\(^8\)\(^,\)\(^34\) However, as can be seen in Figure 5d, above a dosage of 2 g/L, the removal efficiency was decreased. This behavior may be related to the influence of several factors. One of them is the quenching of the produced HO\(^\bullet\) radicals by an increased amount of Fe-NP-Clin, as shown in Eq. (5). Another factor is the recombination of the produced HO\(^\bullet\) radicals with a rate constant of \(4.7 \times 10^9\) M\(^{-1}\) s\(^{-1}\) at 25 \(^\circ\)C; this leads to the formation of \(\text{H}_2\text{O}_2\) molecules. Subsequently, the produced \(\text{H}_2\text{O}_2\) molecules can also scavenge HO\(^\bullet\) radicals, as shown in Eqs. (9) and (10), which results in a reduction in removal efficiency.\(^33\) The reusability of the catalyst in sequential uses for the removal of organic pollutants is important from an economic viewpoint.\(^35\) Therefore, five repetitive cycles for the degradation of AR17 were performed. After each experiment, the applied catalyst was recovered, washed with distilled water, dried at 70 \(^\circ\)C for 24 h, and then applied in a new test. The Fe-NP-Clin maintained its activity during five cycles of the Fenton process, implying the chemical stability and reusability of the catalyst.

2.2.4. Effect of initial AR17 concentration

Figure 5e shows AR17 removal using the Fenton-like process at different initial dye concentrations. It can be observed in Figure 5e that the removal of AR17 decreased from 100% to 90.5% by increasing of its initial concentration from 5 to 50 mg/L. This is because under constant conditions of the operational parameters certain amounts of HO\(^\bullet\) radicals formed. However, with further increase in AR17, the concentration of HO\(^\bullet\) radicals was not adequate to degrade high concentrations of the dye. As a result, the removal efficiency of the dye declined as the concentration increased.\(^35,36\)

2.2.5. Effect of reaction time

Figure 5f shows the effect of degradation reaction time on the absorption spectrum of AR17. It is evident that an increase in the reaction time period increased the removal efficiency due to the successive degradation of dye molecules by the formed HO\(^\bullet\) radicals. It can also be observed from Figure 5f that most of the degradation occurred within the first 90 min of the reaction and then reached a constant level with a further increase in the reaction time. This illustrates that 90 min is needed for the degradation of 95% of the AR17 molecules and the produced colorful intermediates by a heterogeneous Fenton-like process. Moreover, Figure 5f shows that after 90 min the decrease in the peak at \(\lambda = 309\) nm started little by little by the further increase in the oxidizing time. This is due to the mineralization of AR17, which is related to the degradation of colorless intermediates at \(\lambda = 309\) nm. Therefore, it can be deduced that oxidation time is an important parameter in the mineralization of pollutants by various AOP methods. According to the achieved results, it can be deduced that the optimum conditions for maximum removal of 20 mg/L AR17 at 180 min of reaction time are pH of 5, \(\text{H}_2\text{O}_2\) initial concentration of 3 mmol/L, and catalyst dosage of 2 g/L.

2.2.6. Phytotoxicological studies

Various aquatic species have been used in the related literature to investigate the toxicological effect of initial pollutant and its intermediate compounds produced during the oxidation processes. Aquatic species have many...
advantages as test organisms, such as their simple structure, rapid rate of growth, ease of culturing, and high degree of sensitivity to a vast number of pollutants.\textsuperscript{37} In tests based on aquatic species, various endpoints are targeted, with the most common assessments being chlorophyll, carotenoids contents, and enzyme activities.\textsuperscript{38} In the present work, the ecotoxicity study was performed to determine the phytotoxicity of AR17 and the intermediates generated during the heterogeneous Fenton process. Figure 5g demonstrates the content of photosynthetic pigments of the fronds subjected to control and initial AR17 solutions plus 30, 60, 90, 120, and 180 min of heterogeneous Fenton treated solutions.

Figure 5g shows that the total chlorophyll content in \textit{L. minor} subjected to 30, 60, and 90 min heterogeneous Fenton treated solution was significantly decreased, possibly due to the presence of unreacted H\textsubscript{2}O\textsubscript{2}, which is a toxic compound, and the toxic produced intermediates. However, as can be seen in Figure 5g, the total chlorophyll content in \textit{L. minor} subjected to a 180 min heterogeneous Fenton treated solution was significantly enhanced in comparison to the \textit{L. minor} subjected to untreated AR17 solution. This implies the need for a long oxidation time to achieve toxicity reduction. These results indicate that the heterogeneous Fenton process with Fe-NP-Clin promotes the overall phytotoxicity reduction of the solution under the applied operational conditions.

2.3. Artificial neural network modeling of a heterogeneous Fenton-like process

An ANN can develop a relation between input parameters and an output response of the process under different operating conditions.\textsuperscript{39,40} The mathematical relationship between the output and input parameters is given in Eqs. (11) and (12).\textsuperscript{41}

\begin{equation}
D_t = \sum_{i=1}^{M} W_{ti} X_i \quad (11)
\end{equation}

\begin{equation}
Y_t = \varphi(D_t + B_t), \quad (12)
\end{equation}

where \(X_1, ..., X_M\) are the input data, \(W_{t1}, ..., W_{tM}\) show the weights of neuron \(t\), \(D_t\) shows the linear combiner output due to the input data, \(B_t\) represents the bias, \((\varphi)\) is the transfer function, and \(Y_t\) represents the output data from the neuron.

In this context, first a relation between operational variables and the response variable is developed by an ANN. Then this relationship (ANN model) is applied for predicting the response variable under different operational conditions (modeling section). In this section, modeling of a heterogeneous Fenton-like process using an ANN is demonstrated. The samples were divided into training, validation, and test subsets of 68, 22, and 22 samples, respectively. The validation and test sets were randomly chosen from the experimental data to evaluate the validating and modeling ability of the model. The input data were normalized in the range of \(-1\) to \(1\), because the applied transfer function in the hidden layer was tangent sigmoid. Using this procedure, all the data \((Y_i)\), containing the training, validation, and test sets, were scaled to a new value \(Y_{norm}\) using Eq. (13).\textsuperscript{17,20}

\begin{equation}
Y_{norm} = 2 \left( \frac{Y_i - Y_{i,min}}{Y_{i,max} - Y_{i,min}} \right) - 1 \quad (13)
\end{equation}

where \(Y_{i,min}\) and \(Y_{i,max}\) are the extreme values of variable \(Y_i\).
2.3.1. Selection of the optimal ANN topology

An ANN configuration (topology) is composed of several layers of processing units that are termed neurons, nodes, and transfer functions. The input data are processed through these neurons and transfer functions and are sent to the neurons in the hidden layer. The connections between the input, hidden, and output neurons have a related parameter indicating the strength of these connections, termed weight, defined in Eq. (11). An important step in the development of an ANN model is the optimization of its configuration. In this work, a three-layered feed forward back propagation neural network (5:14:1) was applied for modeling of AR17 removal by the Fenton-like process for the first time.

The train scaled conjugate gradient ‘trainscg’, hyperbolic tangent sigmoid ‘tansig’, and a purely linear transfer function ‘purelin’ were selected as the training, the input to hidden layer, and the hidden layer to the output layer transfer functions, respectively. The relations of the aforementioned transfer functions are given in Eqs. (14) to (16)

\[
\text{Logsig}(x) = \frac{1}{1 + \exp(-x)} \tag{14}
\]

\[
\text{Tansig}(x) = \frac{2}{1 + \exp(-2x)} - 1 \tag{15}
\]

\[
\text{Purelin}(x) = x \tag{16}
\]

Therefore, it can be concluded that the ANN model performs a nonlinear functional assessment from previous observation to the future values \(Y_t\) as described in Eq. (17)

\[
Y_t = f(X_i, W_{ti}) + B_t \tag{17}
\]

Figure 6a shows a typical ANN with five neurons in the input layer, fourteen neurons in the hidden layer, and one neuron in the output layer with their related transfer functions. The input parameters were initial pH, initial \(\text{H}_2\text{O}_2\) concentration (mmol/L), initial catalyst dosage (g/L), initial AR17 amount (mg/L), and oxidizing time (min). AR17 removal efficiency was the output variable.

Table 3 displays the range of the investigated variables. For specifying the optimum number of hidden nodes, different sets of configurations were used, in which the number of nodes was altered from 2 to 20. Different types of functions were employed to determine and compare the performance of the ANN for the various configurations. In the present work, mean squared error (MSE), was used to determine the optimum configuration of the ANN model and its parameters.
Table 3. ANN variables and their ranges.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH</td>
<td>3–9</td>
</tr>
<tr>
<td>Input layer</td>
<td>1–5</td>
</tr>
<tr>
<td>H$_2$O$_2$ dosage (mmol/L)</td>
<td>1–4</td>
</tr>
<tr>
<td>Catalyst concentration (g/L)</td>
<td>5–50</td>
</tr>
<tr>
<td>Initial dye concentration (mg/L)</td>
<td>0–180</td>
</tr>
<tr>
<td>Reaction time (min)</td>
<td></td>
</tr>
<tr>
<td>Output layer</td>
<td></td>
</tr>
<tr>
<td>Decolorization efficiency (CR%)</td>
<td>0–100</td>
</tr>
</tbody>
</table>

Figure 6b depicts the relationship between network error and number of neurons in the hidden layer for both the training and test data. As can be seen, the MSE was minimum at about 14 neurons for the training and test data.

In order to compute the training and test errors, all the output data were denormalized; then they were compared with the experimental values. Figures 7a to 7c show the comparison between the predicted and experimental values of the output variable for the training, validation, and test data sets using the ANN model, respectively. As can be seen from the data in Figures 7, the R$^2$ values of the plots are 0.993, 0.994, and 0.993.
for the training, validation, and test data, respectively. A high \( R^2 \) value demonstrates that there is a small difference between the experimental and predicted values of the output parameter for various subsets. It also confirms that the selected topology (5:14:1) includes suitable generalization ability. This generalization ability is essential to predict the performance of the process under various operational conditions.

The relative importance of input parameters, which presents the effect of each input variable on the output variable, was computed using the neural net weight matrix as given in Eq. (18).

\[
P_s = \frac{\sum_j (W_{sj}U_{jk} / \sum_i W_{ij})}{\sum_i \sum_j (W_{ij}U_{jk} / \sum_i W_{ij})}
\]

(18)

where \( P_s \) represents the importance of the \( s \)th parameter, \( W_{ij} \) stands for the weight that joins the \( i \)th input data to the \( j \)th neuron of the hidden layer, \( U_{jk} \) is the weight that connects the \( j \)th hidden layer neuron to the \( k \)th output neuron, \( m \) shows the number of input variables, \( n \) is the number of neurons in the hidden layer, and \( k \) stands for the number of outputs (which is equal to 1 in this work). The relative importance of input parameters is depicted in Figure 7d. As can be seen in this figure, all the independent variables (\( \text{H}_2\text{O}_2 \) dosage, catalyst loading, initial pH of the solution, initial AR17 concentration, and reaction time) had an effect on the removal efficiency of AR17. However, among the variables, reaction time (26.12%) and catalyst dosage (22.41%) had the strongest influence on the heterogeneous removal of AR17. Therefore, all of the five basic variables investigated in this work should be considered in future analysis.

2.4. The possible degradation mechanism of AR17 by a heterogeneous Fenton-like process in the presence of Fe-NP-Clin

Incorporating our results from the XRD, SEM, and FT-IR analyses and the related literature, it can be proposed that \( \text{Fe}^{3+} \) ions inside the zeolites can be in different forms as follows: iron atoms could substitute in the framework, they can be at ion-exchange positions in the form of oxygen-bridged binuclear iron species, they can be in the pores as small clusters of iron species, and they can exist on the external surface as large agglomerates of iron oxides.

In the present work, it is anticipated that during the impregnation process, \( \text{Fe}^{3+} \) ions occupy the exchangeable sites of counterbalanced ions through an ion-exchange procedure and form isolated mononuclear and binuclear iron species bonded to ion exchange sites on the NP-Clin surface. Moreover, since no Fe deposits were detected in the XRD spectrum of the Fe-NP-Clin sample, the aforementioned species are possibly responsible for the catalytic activity. Conversely, if the deposition of Fe compounds occurred on the surface of the catalyst, the performance of the catalyst should decrease with sequential uses due to the continuous leakage of surface iron compounds to the solution.

3. Experimental section

3.1. Chemicals and reagents

All chemicals used in the present study were of analytical grade and were used without purification. \( \text{FeCl}_3\cdot6\text{H}_2\text{O} \), \( \text{HCl} \), \( \text{NaOH} \), \( \text{H}_2\text{O}_2 \) (30%), and \( \text{H}_2\text{SO}_4 \) were obtained from Merck (Germany). The natural clinoptilolite sample used in this research was obtained from the Mianeh region in the northwest of Iran and was prepared by
Kan Azar Co. (Tabriz, Iran). Its characteristics are given in Table 4. AR17 was obtained from Alvan Saabet Co. (Tehran, Iran).

Table 4. Chemical composition of NP-Clin.

<table>
<thead>
<tr>
<th></th>
<th>P$_2$O$_5$</th>
<th>MnO</th>
<th>TiO$_2$</th>
<th>MgO</th>
<th>Fe$_2$O$_3$</th>
<th>Na$_2$O</th>
<th>CaO</th>
<th>K$_2$O</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>0.01%</td>
<td>0.04%</td>
<td>0.21%</td>
<td>0.72%</td>
<td>1.3%</td>
<td>2.1%</td>
<td>3.11%</td>
<td>3.12%</td>
<td>11.81%</td>
<td>66.5%</td>
</tr>
</tbody>
</table>

3.2. Characterization instruments

In order to characterize the NP-Clin and Fe-NP-Clin, the following analyses were done: (1) the crystal structure and phase identification was performed by XRD analysis (Panalytical-X'Pert PRO diffractometer, Eindhoven, the Netherlands) with CuKα radiation (40 kV, 30 mA) and a PIXcell solid state detector; (2) the FT-IR spectra of the samples were obtained by a FT-IR spectrometer (Tensor 27, Bruker, Germany); (3) SEM analysis (S-4200, Hitachi, Japan) was executed to investigate the surface morphologies of the samples; (4) the porosity characteristics of the samples were assessed by physical adsorption of N$_2$ gas at 77.35 K using Micromeritics, ASAP-2010, USA. (5) ICP (GBC Integra XL, Australia) technique was used to determine the Fe concentration in the bulk of the samples; (6) the concentration of aqueous Fe$^{2+}$ ions was determined according to a spectrophotometric method$^{46}$ on a UV-Vis spectrophotometer (Lightwave S2000, UK).

3.3. Preparation of Fe-NP-Clin

Natural NP-Clin particles with the size of 354 μm were washed with distilled water several times and then dried for 12 h at 60 °C. Fe-NP-Clin was prepared by means of liquid ion exchange technique slightly different from that of Gonzalez-Olmos et al.$^{22}$ For this purpose, 50 g of NP-Clin particles with 150 mL of 0.125 M FeCl$_3$.6H$_2$O and 200 mL of 1 M HCl solution were put in a Pyrex flask with a total volume of 500 mL. HCl was added slowly with stirring in order to adjust the pH to 3. The flask was placed in a water bath at 60 °C for 6 h. Then the sample was washed with water until the pH of the sample in water was close to neutral pH. Then the samples were dried in an oven in air at 60 °C over night. This procedure was performed three times in order to obtain the Fe-NP-Clin sample. Then the obtained sample was calcined at 550 °C in a furnace for 5 h.

3.4. Heterogeneous Fenton-like process

Degradation experiments of AR17 were executed in batch mode by a 500-mL cylindrical reactor supplied with a magnetic stirrer at atmospheric pressure and room temperature. The desired concentration of AR17, catalyst (Fe-NP-Clin), and H$_2$O$_2$ were fed into the glass reactor. The solution pH was adjusted to the desired level using dilute NaOH and H$_2$SO$_4$; the pH was measured with a pH meter (Metrohm 654, Switzerland). At distinct time intervals, samples were withdrawn and the concentration of the dye in the sample was analyzed using a UV–Vis spectrophotometer (Lightwave S2000, UK) at the maximum wavelength ($\lambda_{max} = 510$ nm). The color removal efficiency (CR (%)) was calculated as the percentage ratio of decolorized dye concentration to the initial concentration. It is worth mentioning that the experiments were replicated three times and the mean values of the experiments were reported in this work.
3.5. Phytotoxicological evaluations

3.5.1. Plant species and growth condition

Fronds of duckweed *L. minor* were taken from Tabriz wetland (Iran) and were disinfected with 0.5% v/v sodium-hypochlorite for 2 min in the laboratory. Then they were washed with distilled water and cultivated in modified Steinberg culture medium including 3.46 mM KNO$_3$, 1.25 mM Ca(NO$_3$)$_2$, 0.66 mM KH$_2$PO$_4$, 0.072 mM K$_2$HPO$_4$, 1.94 $\mu$M H$_3$BO$_3$, 0.63 $\mu$M ZnSO$_4$, 0.18 $\mu$M Na$_2$MoO$_4$, 0.91 $\mu$M MnCl$_2$, 2.81 $\mu$M FeCl$_3$, and 4.03 $\mu$M EDTA (all from Merck, except for EDTA and H$_3$BO$_3$ from Carlo Erba).

3.5.2. Phytotoxicity experiments

Twenty fully grown fronds of *L. minor* were carried to a 500-mL beaker containing 10 mL of growth medium to which 300 mL of AR17 (treated and/or untreated) solution was added. The control sample included fronds of *L. minor* grown in distilled water and 10 mL of nutrient medium. A solution containing 20 mg/L AR17 was treated under optimal conditions with the heterogeneous Fenton process. Samples were taken after different time spans of 30, 60, 90, 120, and 180 min to analyze their phytotoxicity. Then the content of photosynthetic pigments was evaluated. The experiments were done under constant conditions at 25 °C under 16/8 (light/dark) photoperiod.

3.5.3. Determination of total chlorophyll and carotenoids content

Chlorophylls and carotenoids are considered highly significant pigments for the photosynthesis activity of green plants. The total content of chlorophyll and carotenoids was spectrophotometrically measured in plants after their extraction from fronds with 100% acetone according to the method proposed by Lichtenthaler.

4. Conclusion

The performance of Fe-NP-Clin as a heterogeneous catalyst was investigated in a Fenton-like process for the removal of AR17 from an aqueous solution. The Fe-NP-Clin catalyst was prepared by an ion exchange method under acidic conditions. The physical and chemical properties of the Fe-NP-Clin catalyst were characterized by XRD, FT-IR, SEM, BET, and ICP analysis. The XRD spectra of the samples demonstrated that no crystalline phases related to Fe-compounds were deposited on the Fe-NP-Clin catalyst surface. SEM images showed that the morphology of the natural NP-Clin microparticles was not significantly altered during the impregnation process. The effects of five basic operational parameters on the removal of AR17 were then investigated to determine the maximum removal efficiency of AR17 from the solution. The results demonstrate that the heterogeneous Fenton process in the presence of Fe-NP-Clin is able to remove 97.6% of 20 mg/L AR17 in 180 min when the pH is 5 and the H$_2$O$_2$ and catalyst dosages are 3 mmol/L and 2 g/L, respectively. Moreover, an ANN was used to model the removal of AR17 during a heterogeneous Fenton-like process in the presence of Fe-NP-Clin. The results show that a three-layered feed forward back propagation neural network with the optimum topology of 5:14:1 is able to successfully predict the removal of AR17. The correlation coefficient between the experimental values and the ANN predicted values was 0.993, indicating that the developed ANN algorithm could efficiently model the degradation of AR17 under various operational conditions. Phytotoxicological results revealed that the heterogeneous Fenton process under the obtained optimum operational conditions reduced the overall phytotoxicity of the solutions during 180 min of reaction successfully.
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References