The Removal of Methylene Blue from Aqueous Solutions Using Zinc Oxide Nanoparticles With Hydrogen Peroxide

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Abstract
Industrial effluents produce vast amounts of pollutants and account for 20% of industrial wastewater annually. Methylene blue (MB) is one of the most widely used dyes in the medical, pharmaceutical, and textile industries. However, it is toxic to living organisms, and even a short-time exposure to it can be potentially harmful. Therefore, the purpose of this study was to investigate the efficiency of zinc oxide nanoparticles in removing MB from aqueous solutions in the presence of hydrogen peroxide. The effects of various parameters such as pH (3-10), ZnO nanoparticle dose (0.01-0.08 g/L), reaction time (5-50 minutes), initial concentration of MB (20-200 mg/L), and the hydrogen peroxide concentration (0.5-5 mg/L) were studied. The wavelength of maximum absorption (λmax) was 665 nm. The optimal pH value was 5, zinc oxide nanoparticle dose was 0.05 g/L, the initial concentration of MB was 40 mg/L, the concentration of hydrogen peroxide was 2 mg/L, and the contact time was 20 minutes. The efficiency of MB removal was 97.99%. The results showed that zinc oxide nanoparticles in the presence of hydrogen peroxide could remove the MB from aqueous solutions with high efficiency.

Keywords: Methylene blue, Zinc oxide nanoparticles, Hydrogen peroxide, Aqueous solutions

1. Introduction
Environmental pollution is a serious global issue (1). Today, dye-containing effluents are among the biggest challenges of significant industries such as textiles, pulp and paper, leather and plastics, and dyeing. Since these industries consume considerable amounts of water, they introduce significant amounts of dye-containing effluents into the environment (2-4). Methylene blue (MB) is the most common dye used in dyeing cotton, wool, and silk (5,6). Its inhalation can cause respiratory distress, and direct exposure to it leads to local burns, nausea, vomiting, increased sweating, mental disorders, and methemoglobinemia (7,8). The removal of dye from industrial wastewaters is carried out by various methods such as coagulation and flocculation, biological treatment, chemical oxidation, electrochemical treatment, ion exchange, and adsorption processes (5,9,10). According to a previous study, the efficiency of MB adsorption using activated carbon was up to 91%; however, activation and reduction of carbon are not cost-effective (11). Various biological methods have been applied to remove the dye; however, they were inefficient due to their low biodegradability (12).

Magnetic nanoparticles as adsorbents have been investigated recently (13-15). These nanoparticles are particles with dimensions up to 100 nm with magnetic properties (16). They have unique physical and chemical properties (17). Therefore, this study aimed to apply cost-effective zinc oxide nanoparticles with hydrogen peroxide due to their high absorption and environmentally friendly properties. They also have no secondary pollution and are very safe for this application. To establish the thermodynamic parameters, we also measured the pH, the concentration of MB, and the adsorbent solution. We also studied reaction time, oxidized nanoparticles dose, initial concentration of MB, concentration of H2O2, and contact...
time to find the optimal parameters for dye removal.

2. Materials and Methods
The adsorbent used in this research was zinc oxide nanoparticle (ZnO) which was obtained from Pasteur Institute in Tehran. The materials needed in this study include hydrochloric acid (HCl), sodium hydroxide (NaOH) for adjusting pH, zinc oxide nanoparticles, hydrogen peroxide, and MB dye. All test solutions were prepared with distilled water.

2.1. Methods
Distilled water was used to prepare all test solutions. The residual concentration (C₀) of MB dye was also measured using a spectrophotometer (Cecil 1021) at a wavelength of 665 nm. To optimize the factors affecting the process, different values were tested as follows: pH (3, 5, 7, 9-10-12), dose of zinc oxide nanoparticles (0.01, 0.02, 0.03, 0.04, 0.05, 0.06, and 0.08 g/L), initial concentration of MB (20, 30, 40, 50, 100, 150, and 200 mg/L), concentration of hydrogen peroxide (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 mg/L), and contact time (5, 10, 15, 20, 30, 40, and 50 minutes). To optimize every parameter, we kept the others unchanged. The experiments had two replicates (18). First, the stock solution of MB was prepared. Then, different concentrations were prepared from the stock solution. A standard curve was prepared by reading the absorption using a spectrophotometer. In the first step, we studied the optimum dye concentration through different color concentrations at a fixed pH of 5, contact time of 20 minutes, nanoparticle concentration of 0.05 g/L, MB concentration of 40 mg/L, contact time of 20 minutes, and hydrogen peroxide concentration of 0.05 g/L. Therefore, we established the optimal concentration of the dye. The optimal pH was calculated in the second step by adjusting the pH with 0.1 M hydrochloric acid and 0.1 M sodium hydroxide. Next, the effluent concentration of MB for each sample was measured. In this step, a nanoparticle concentration of 0.05 g/L, MB concentration of 40 mg/L, contact time of 20 minutes, and hydrogen peroxide concentration of 2 mg/L were considered. In the third step, we studied different concentrations of ZnO nanoparticles. According to the previous steps, an MB concentration of 40 mg/L, a pH value of 5, a contact time of 20 minutes, and an H₂O₂ concentration of 2 mg/L were considered and the results were measured with a spectrophotometer. In the fourth step, the amount of H₂O₂ was calculated. In this step, a certain amount of parameters was considered as optimal. The amount of H₂O₂ was determined at an MB concentration of 40 mg/L, a pH value of 5, a contact time of 20 minutes, and a nanoparticle concentration of 0.05 g/L. In the fifth step, the contact time was studied at 6 different time points (5-50 minutes), at the optimum dye concentration of 40 mg/L, and optimum pH value of 5, as well as the optimum H₂O₂ concentration of 2 mg/L. The corresponding equations are as follows:

\[ R = \frac{C_0 - C_1}{C_0} \times 100 \]  

(1)

\[ R = \text{Percentage of MB dye removal efficiency} \]

\[ C_0 = \text{Inlet concentration of MB dye} \]

\[ C_1 = \text{MB dye output concentration} \]

3. Results and Discussion
3.1. Effect of Initial MB Concentration on the Removal Efficiency
The first step in the optimization of the MB removal was to determine the optimal initial concentration of MB. The results presented in Fig. 1 showed that the highest removal efficiency of MB was observed at the initial concentration of 40 mg/L. According to this figure, by increasing concentration from 20 to 40 mg/L, the removal efficiency of MB was increased, but at concentrations above 40 mg/L, the removal efficiency decreased. Therefore, the initial optimum concentration of MB in this process was determined to be 40 mg/L. The effect of the initial concentration of MB on the adsorbent efficiency was shown in Fig. 1. The relationship between the equilibrium concentration of MB after adsorption and the adsorption rate on the adsorbent surface was also evaluated. The figure shows that increasing the initial concentration of MB from 20 to 50 mg/L increased the removal rate, and then the value remained constant. The highest removal rate obtained at an MB concentration of 50 mg/L was 94.83%. The reason is that the adsorbent has specific and limited adsorption sites. More adsorption sites are accessible at lower concentrations on the adsorbent surface, leading to rapid adsorption and higher removal efficiency. However, at higher concentrations, as the adsorbate on the adsorbent surface increases, the adsorption sites are occupied rapidly, and the removal efficiency decreases. Faraji et al and Akbari et al also reported similar results (19,20). It is suggested that the increasing adsorption capacity of adsorbents with increasing the initial concentration of MB is due to the increased probability of collision and contact between the adsorbent and the adsorbate (20).

3.2. Effect of pH on MB Removal Efficiency
The second step in the optimization of the MB removal process was to determine the optimal pH. Examination of the results of the following diagram in determining
the optimal pH of MB removal showed that the highest removal efficiency of MB occurred at pH = 5, which is equal to 94.83%. With increasing pH from 3 to 5, the removal efficiency increased, but with increasing the pH from 6 to 10, the removal efficiency decreased. Fig. 2 shows that the removal efficiency was raised by increasing pH from 3 to 5 and decreased at pH values above 5. It seems that this increase occurred due to dye degradation at acidic pH and also formation of a smaller amount of species with low reactivity, such as per hydroxyl radical radicals (OH$^\cdot$) compared to hydroxyl radicals (21). However, by increasing pH, additional OH$^-$ ions may form ferric hydroxide complexes, thereby reducing the hydroxyl radicals and the rate of degradability (22). In addition, the higher pH of the solution may result in large amounts of hydroxyl radical scavenging agents (e.g., carbonates and bicarbonates). They are formed by the mineralization of organic matter and finally decrease of the OH$^-$ concentration (23). The results are consistent with those of the study by Rahdar et al on the removal of ciprofloxacin from contaminated water by nickel nanoparticles (24).

3.3. The Effect of Zinc Oxide Nanoparticle Concentration on the Removal Efficiency
The third step in optimizing the parameters in the MB removal process was to optimize the dose of zinc oxide nanoparticles. Fig. 3 shows the effect of zinc oxide nanoparticle concentration on MB removal efficiency. The results of this diagram show that in the process of removing MB at an optimal pH of 5, a constant contact time of 20 minutes, and a concentration of 40 mg/L MB, by increasing nanoparticle dose from 0.01 to 0.05 g/L, an increase in MB removal efficiency was observed from 85.59 to 95.43%. However, as it is clear from the figure, by increasing the absorbent dose from 0.05 g/L, the removal efficiency of garlic was decreased. The optimum dose of nanoparticles was determined to be 0.05 g/L. The optimum dose of nanoparticles was determined to be 0.05 g/L. Fig. 3 shows the effect of nanoparticle dose on MB removal rate. It can be observed that increasing the amount of adsorbent dose elevated the removal efficiency. Therefore, increasing the nanoparticle dose from 0.01 to 0.05 enhances the removal efficiency. The highest removal rate of 95.43% was seen at a nanoparticle dose of 0.05. The figure also showed that the removal rate decreased at concentrations higher than 0.05 g/L. The growing rate of MB adsorption by increasing the adsorbent may be due to extended active and effective surface area in adsorption. These trends were also reported by Ong et al (25) and have also been confirmed by Sulak et al (26).

3.4. Effect of Hydrogen Peroxide Concentration on the Removal Efficiency
This step was related to the optimization of the dose of hydrogen peroxide in the MB removal process. Fig. 4 shows the effect of hydrogen peroxide on the MB removal efficiency. The figure illustrated how different values (0.5 to 2 mg) increased the removal rate and then decreased it. The results presented in the figure shows that in the process of removing MB, by increasing the dose of hydrogen peroxide from 0.5 to 2 mg/L, the removal efficiency of MB was increased from 83.64 to 95.41%. However, as can be seen from the graph, by increasing the dose of hydrogen peroxide from 2 mg/L, the removal efficiency was decreased, indicating that at the dose of 5 mg/L, the removal efficiency reached its lowest level, which was 70.43%. Besides, higher concentrations reduced the removal of Reactive Blue 19 dye because H$_2$O$_2$ alone could not oxidize organic compounds which are resistant to biodegradation, and the presence of ferrous ions led to the formation of a small amount of hydroxyl radicals (27). These findings are consistent with the study of Barbusinski et al on the removal of Acid Red 18 by Fenton reagent in the presence of iron powder (28). On the other hand, in the presence of hydrogen peroxide, the amount of H$_2$O$_2$ was decreased by increasing pH. This phenomenon is due to the instability of peroxide in alkaline conditions, which leads to the decomposition of peroxide into water and oxygen and reduces the efficiency of the process (29,30). It was observed that the color removal percentage decreased with the increase of peroxide concentration. This phenomenon can be explained by the fact that with the higher concentration of H$_2$O$_2$, the hydroxyl radicals produced in the following reaction react with hydrogen peroxide, and the peroxide itself acts as an OH$^-$ radical absorbent. Finally, it leads to the production of hydroxyl radicals
 radicals (OH˚), which have a lower oxidizing power compared to OH˚ radicals (30-32).

\[
\text{H}_2\text{O}_2 + \text{OH}^* \rightarrow \text{OH}^- + \text{H}_2\text{O}
\]  

(2)

### 3.5. Effect of Contact Time on the Removal Efficiency

The last step in the process was to evaluate the effect of different contact times. As seen in Fig. 5, increasing the contact time from a certain limit led to a decrease in removal efficiency. In other words, the maximum removal efficiency usually occurred in the first 20 minutes of the reaction. Given that time is a factor that has a significant impact on the process in terms of cost and energy, a contact time of 20 minutes was chosen as the optimal contact time. Fig. 5 represents the effects of contact time on the rate of removal by oxidized nanoparticles. It shows that the efficiency was improved by increasing contact time. Therefore, in the first 20 minutes with a 95% removal rate, the removal speed was reduced with a smaller slope. In this way, at 40 minutes, the removal efficiency was only 60%. In the early stages of adsorption, many vacant surface sites were accessible; however, they were occupied over time and could not absorb pollutants any more. This can be due to the restraining forces between the adsorbed molecules on the surface of the solid adsorbent and the liquid mass. Similar results have been reported by Cengiz and Cavas (33). These results are also consistent with the findings of a study by Moghadam et al (34). Moreover, the results of various studies on the removal of MB by nanoparticles are given in Table 1.

### 4. Conclusion

Our results suggested that 0.05 g/L of zinc oxide nanoparticles and 2 mg/L of hydrogen peroxide in 20 minutes could remove the MB from the water with a rate of approximately 97.99%. Zinc oxide nanoparticles are a very potent adsorbent and, at the same time, cost-effective for the removal of various pollutants from water. The application of hydrogen peroxide in this process has also improved the removal efficiency and decreased the required contact time. The removal efficiency of 98% was obtained for the MB in the optimum conditions.

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### Authors’ Contribution

Conceptualization: Fahimeh Moghaddam.
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Supervision: Fahimeh Moghaddam, Somayeh Bagheri.
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Writing—original draft: Fahimeh Moghaddam.
Writing—review & editing: Fahimeh Moghaddam.

### Competing Interests

The authors declare that they have no conflict of interest.

### References


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**Table 1. The Results of Different Studies on the Removal of Methylene Blue by Nanoparticles**

<table>
<thead>
<tr>
<th>Study</th>
<th>Nanoparticle</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zaman et al (35)</td>
<td>Zinc oxide nanoparticles contaminate with lead</td>
<td>90%</td>
</tr>
<tr>
<td>Ansari et al (36)</td>
<td>Zinc oxide nanoparticles</td>
<td>95%</td>
</tr>
<tr>
<td>Darvishi</td>
<td>Magnesium oxide nanoparticles</td>
<td>80%</td>
</tr>
<tr>
<td>Cheshmeh Soltani et al (37)</td>
<td>Milk vetch wood</td>
<td>70%</td>
</tr>
<tr>
<td>Razavi (37)</td>
<td>Titanium oxide nanoparticles</td>
<td>70%</td>
</tr>
<tr>
<td>Tavakoli et al (38)</td>
<td>Nanocomposite</td>
<td>70-10%</td>
</tr>
<tr>
<td>Alomar et al (40)</td>
<td>Bi2O3-SrO-FeO@SiO2 nanocomposite</td>
<td>&gt;80%</td>
</tr>
</tbody>
</table>


