Degradation of Nitrobenzene in an Aqueous Environment through Fenton-like Process Using Box–Behnken Design Method

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Background & Aims of the Study: Recently, the advanced oxidation processes have received growing attention in industrial wastewater treatment. In this project, the degradation and mineralization of an aqueous environment containing nitrobenzene (NB) as the main carcinogenic contaminant were inspected by a Fenton-like process. In addition, the influence of operational variables, such as initial concentrations of H\textsubscript{2}O\textsubscript{2}, Ferric ion, and pH on the removal of NB was investigated.

Materials and Methods: The Box-Behnken design (BBD) of experiments and the response surface methodology were applied to explore the effects of three independent variables on the response functions to get the optimum conditions. Analysis of variance (ANOVA) was used to determine the significance of the effects of independent variables on the response function. Different amounts of variables were optimized for the removal of NB in the Fenton-like processes.

Results: At optimum conditions (H\textsubscript{2}O\textsubscript{2} and Ferric concentrations of 15.33 and 1.30 mM, respectively, and a pH of 6.23) and after 30 min of reaction, the removal efficiency for NB and chemical oxygen demand (COD) were 99.0% and 56.7%, respectively.

Conclusion: The Fenton-like process influenced the removal of NB; however, it could only remove the COD to some extent. The obtained results at optimized circumstances were outstanding from the environmental point of view.

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Background

Nitrobenzene (NB) is one of the main organic contaminants in water and is extensively used in dyes, explosives, and insecticides. However, it is infamous for its great carcinogenicity, toxicity, and other opposing influences on environments and organisms. Furthermore, NB demonstrates poor activity towards oxidative degradation due to the strong electron-withdrawing features of the nitro-group. According to the U.S. Environmental Protection Agency, the level of NB in water and lake streams should not exceed 17 ppm (1). Therefore, environmental risks have urged the advance of effective methods for NB elimination.

Elimination of NB through reducing it to less poisonous aniline has been investigated and the results have shown that the aquatic environment was still at risk even when the
level of aniline reached the environmental boundary (2). Hence, the progress of operative approaches for NB degradation remains an important challenge. Thanks to the strong oxidative and nonselective features of hydroxyl radical, different advanced oxidation processes (AOPs) are used to degrade organic pollutants in the water phase (3, 4).

Several techniques of AOPs, including Fenton (5), ozonation in alkaline media (6), electro Fenton (7), nano catalytic ozonation (8), and sono-photo-Fenton have been applied for the treatment of organic contaminants in an aqueous environment (9). Chemical treatment techniques, such as chlorination for NB degradation, can form chlorinated products which are non-biodegradable and toxic. The physical approaches just transfer pollutants from one phase to another.

Therefore, the Fenton and photo-Fenton processes (10–13) have been employed for this purpose. They are good choices since they need low-cost chemicals and low energy (14–15). Obviously, the Fenton method creates hydroxyl radicals (OH•) which are based on the reaction between H2O2 and Fe2+ (Equations 1 and 2).

\[
\begin{align*}
H_2O_2 + Fe^{2+} & \rightarrow OH^+ + OH^- + Fe^{3+} \quad \text{(Equation 1)} \\
H_2O_2 + Fe^{3+} & \rightarrow HOO^+ + H^+ + Fe^{3+} \quad \text{(Equation 2)}
\end{align*}
\]

Furthermore, iron (III) can react with the residual amount of hydrogen peroxide and create iron (II) (Equation 2) (16). Nevertheless, it should be noted that the homogeneous Fenton process has some important issues. Homogeneously catalyzed reactions require up to 50–80 mg/l of Fe ions in solution which is well above the Regulation. In addition, at the end of the wastewater treatment, the treatment of the sludge enriched with Fe ions is costly and needs substantial amounts of chemicals and the workforce. Some efforts have been made to solve these problems and investigate the conditions for the recovery of the catalyst. The Fenton-like processes have been employed to form highly reactive hydroxyl radicals with H2O2 in the presence of metal cations under appropriate reaction conditions (17-18).

The comparison of electro-Fenton, Fenton, and photo-Fenton in terms of their efficiency in dye removal was investigated by Huang et al. (19). They tried to transform organic wastewater, such as Remazol Black B dye into inorganic matter using the above-mentioned methods. They found that the removal efficiency was 70% by the Fenton technique, whereas it reached about 93% by the electro-Fenton method. This conclusion was due to the reduction of iron ions in the cathode applied in the process. After the application of ultraviolet light, photo-Fenton had an efficacy of more than 98% that was based on the recovery of iron ions. Based on the results of the above-mentioned research, organic contaminants, like formic acid, which are hard to remove by the Fenton process, could be quickly and completely degraded by the photo-Fenton technique. The oxalic acid, which can be remediated hardly by other approaches can be removed by the electro-Fenton method (19).

In the present study, the synthetic wastewater comprising NB was treated by the Fenton-like process. This research inspected the influence of various variables, including pH, the concentration of hydrogen peroxide, and ferric ion on NB removal using the Box-Behnken design (BBD) method.

### Materials & Methods

#### Materials

The tests were performed employing hydrogen peroxide solution (30% w/w), Ferric chloride (≥99.5%) as a source of iron (III) ions (manufactured in Merck, US), and MnO2 (≥99%) (manufactured in Sigma-Aldrich, Germany). Moreover, double-distilled water was used in all the experiments.
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Figure 1) Experimental setup in laboratory scale: 1) cooling water jacket, 2) magnetic stirrer bar, 3) UV lamp, 4) glass reactor, 5) magnetic stirrers, 6) input wastewater, 7) output wastewater, 8) cooling water input, 9) cooling water output, and 10) electric connection

Photoreactor and experiments

All runs were performed in a one-liter glass photo reactor. The system was prepared with a sampling system (Figure 1). A 15W (UV-C) mercury lamp (manufactured in Philips, Netherlands) was used as the source of light and positioned vertically at the center of the reactor. The reactor was equipped with a water jacket with an external flow controlled by a thermostat to control the temperature at 25° C. The BW 20G water bath (manufactured in JeioTech, Korea) was employed to fix the temperature at 25° C. A stirrer was used to mix the solution and prevent the precipitation of iron ions. The PT-10P pH meter (manufactured in Sartorius, Germany) was employed to adjust the initial pH of the solution. The samples were transferred to a spectrophotometer (DR 5000, Hach, Jenway, USA) at 600 nm to determine the percentage of chemical oxygen demand (COD) removal using standard methods (20).

Approximately 1000 ml of synthetic wastewater was used during each experiment. Ferric and Hydrogen peroxide concentrations and pH were the chosen variables, and the response was the removal of COD in wastewater. It should be noted that the reaction time was 30 min in all tests. The percentage of NB removal was calculated using Equation (3):

\[
\text{Removal of } NB(\%) = \left( \frac{NB_0 - NB_t}{NB_0} \right) \times 100 \quad \text{(Equation 3)}
\]

Where \( NB_0 \) and \( NB_t \) are NB values at the initial and \( t \) times, respectively. The remaining amount of hydrogen peroxide in the samples can interfere with the COD test; hence, it was removed by \( \text{MnO}_2 \) powder. The \( \text{MnO}_2 \) powders were separated by filtration (21).

Statistical analysis and experimental design

The experimental design was employed to optimize the percentage of NB removal in a scientific way. Effects of Ferric concentration \( (C_F) \), hydrogen peroxide concentration \( (C_{HP}) \), and acidity \( (pH) \) on NB removal were explored. The input variables, including \( C_{HP}, C_F, \) and \( pH \), as well as their values and dimensions are presented in Table 1.

The Box-Behnken experimental design needs a fewer number of experiments (15 experiments for three variables) (22). Based on the design of experiments, as a polynomial equation of independent variables, the subsequent model for the response variable \( Y \) was offered (Equation 4):

| Variable                  | Unit | Symbol | Range and levels |
|---------------------------|------|--------|------------------|
| Hydrogen peroxide conc.   | mM   | \( C_{HP} \) | Low (-1) | Middle (0) | High (+1) |
| Ferric Conc.              | mM   | \( C_F \)  | 6     | 12       | 18        |
| pH                        | -    | \( pH \)  | 3     | 7        | 11        |
\[ \text{Res.} = b_0 + \sum b_i x_i + \sum \sum b_{ij} x_i x_j + \sum \sum b_{ii} x_i^2 + \varepsilon \]

(Equation 4)

Where \( \varepsilon \) is the remainder of the equation, \( b_0 \) is a constant number, \( b_{ij} \) is a linear interaction between the input variables of \( x_i \) and \( x_j \) \((i = 1, 2 \text{ and } j = 1, 2, 3)\), \( b_i \) is the slope of the variable, and \( b_{ii} \) is the second order of the input variable \( x_i \) \((i = 1, 2, 3)\). Analysis of variance (ANOVA) was applied to test the significance of the operating variable in the polynomial equation (Equation 4) (23). In the ANOVA, a \( p \)-value of 0.05 was considered statistically significant, and \( p \)-values of less than 0.0500 indicated the significance of model terms. The values greater than 0.1000 indicate that the model terms are not significant.

The statistical significance of the second-order models was defined by F-value. If the calculated F-value is higher than the F-value, the \( p \)-value will be much smaller which indicates the significance of the statistical model. As can be seen in Equation 5, the calculated F-value was gained by dividing the mean squares of regression (including square, linear, and interaction) by the mean squares of residual as the following (24):

\[ F - \text{value} = \frac{MS_{\text{Reg.}}}{MS_{\text{Res.}}} = \frac{SS_{\text{Reg.}}/DF_{\text{Reg.}}}{SS_{\text{Res.}}/DF_{\text{Res.}}} \]

(Equation 5)

Residual degrees of freedom are the total degrees of freedom minus the regression degree of freedom, and the regression degree of freedom is the number of terms minus one (24). Design of the experiments included 15 tests (2 replicates at the central point and 13 tests). All the experiments were performed randomly to reduce experimental errors. Table 2 summarizes the percentages of NB removal.

| Run no. | \( X_F \) | \( X_{CP} \) | \( X_{PH} \) | Responses (%) |
|--------|----------|-------------|-------------|--------------|
| 1      | 1.8      | 12          | 11          | 68.5         |
| 2      | 1.2      | 18          | 11          | 71.0         |
| 3      | 1.2      | 12          | 7           | 97.4         |
| 4      | 1.2      | 12          | 7           | 97.1         |
| 5      | 1.8      | 6           | 7           | 85.9         |
| 6      | 1.8      | 12          | 3           | 78.5         |
| 7      | 1.8      | 18          | 7           | 89.6         |
| 8      | 1.2      | 6           | 3           | 77.3         |
| 9      | 0.6      | 6           | 7           | 81.0         |
| 10     | 1.2      | 12          | 7           | 96.3         |
| 11     | 1.2      | 6           | 11          | 63.5         |
| 12     | 0.6      | 12          | 3           | 71.2         |
| 13     | 1.2      | 18          | 3           | 89.0         |
| 14     | 0.6      | 18          | 7           | 85.1         |
| 15     | 0.6      | 12          | 11          | 60.0         |

**Table 2**) Design of the experiments with three independent parameters and their response

The p-value will be much smaller which indicates the significance of the statistical model. As can be seen in Equation 5, the calculated F-value was gained by dividing the mean squares of regression (including square, linear, and interaction) by the mean squares of residual as the following (24):
removal. The quadratic relationship was gained using the least squares error method to determine the response in terms of the three independent variables as the following:

$$NB\text{ Removal }\% = -13.3 + 3.02X_{H_2O_2} + 63.5X_{Fe^{3+}} + 15.37X_{pH} - 0.0882X_{H_2O_2}^2 - 24.51X_{Fe^{3+}}^2 - 1.1891X_{pH}^2 - 0.028X_{H_2O_2}X_{Fe^{3+}} - 0.0437X_{H_2O_2}X_{pH} + 0.125X_{Fe^{3+}}X_{pH}$$  (Equation 6)

Predicted values of the quadratic model in relationship with the observed values in NB removal are showed in Figure 2 and the estimated values were calculated via Equation 6.

Table 3 shows the results of ANOVA for evaluation of the model. According to Table 3, the degree of freedom for the residual error and model were five and nine, respectively. Comparison of the tabulated F-value in Table 3 with the calculated F-value revealed that the calculated F-value for the model was greater than the tabulated F-value. Therefore, the p-value was very low (<0.0001) and the model was extremely significant.

Terms of $C_{HP}$, $C_F$, $pH$, and their squares had a p-value of less than 0.01; hence, they were highly significant (25). However, the term of the binary interaction between the variables had a p-value of more than 0.05, meaning that the interaction of variables was non-significant. In addition, the p-value of lack of fit was more than 0.05 which indicated the model did not fit the data.

**Effects of operational parameters**

As it was mentioned earlier, the effects of $Fe^{3+}$ concentration (0.6, 1.2, and 1.8 mM),

![Graph showing predicted versus experimental values in the removal of nitrobenzene](image)

**Figure 2** The predicted versus experimental values in the removal of nitrobenzene

| Source       | SS     | DF  | MS      | F-Value | p-value |
|--------------|--------|-----|---------|---------|---------|
| Model        | 2069.41| 9   | 229.93  | 32.47   | 0.001   |
| $XC_{HP}$    | 91.12  | 1   | 91.12   | 12.87   | 0.016   |
| $XC_{Fe^{3+}}$ | 79.38  | 1   | 79.38   | 11.21   | 0.020   |
| $X_{CpH}$    | 351.12 | 1   | 351.12  | 49.58   | 0.001   |
| $X_{CHP}$    | 37.22  | 1   | 37.22   | 5.26    | 0.070   |
| $X^2_{Fe^{3+}}$ | 287.56 | 1   | 287.56  | 40.60   | 0.001   |
| $X^2_{CpH}$  | 1336.43| 1   | 1336.43 | 188.71  | 0.000   |
| $X_{CHP}.X_{Fe^{3+}}$ | 0.04  | 1   | 0.04    | 0.01    | 0.943   |
| $X_{CHP}.X_{CpH}$ | 4.41  | 1   | 4.41    | 0.62    | 0.466   |
| $X_{Fe^{3+}}.X_{CpH}$ | 0.36  | 1   | 0.36    | 0.05    | 0.831   |
| Error        | 35.41  | 5   | 7.08    |         |         |
| Lack of fit  | 35.41  | 3   | 11.80   |         |         |
| Pure error   | 0.00   | 2   | 0.00    |         |         |
| Total        | 2104.82| 14  |         |         |         |

**Model Summary**

|       | S          | $R^2$ | $R^2_{adj}$ | $R^2_{pred}$ |
|-------|------------|-------|-------------|--------------|
|       | 2.66120    | 98.32%| 9529%       | 73.08%       |
hydrogen peroxide concentration (6, 12, and 18 mM), and pH values (3, 7, and 11) on the removal of NB were investigated. The three-dimension (3D) plots versus these variables in the removal of NB are presented in Figures 3 to 5. It should be noted that they are plotted based on Equation 6.

A 3D plot of the NB removal in terms of Ferric and hydrogen peroxide concentration is presented in Figure 3. It was found that the highest percentage of NB removal was gained at the mean values for both variables (Ferric ion and hydrogen peroxide concentrations). In the Fenton-like process, the removal efficiency of NB was decreased with an excessive increase in the Fe (III) concentration. The treatment proficiency was reduced with a decline in H$_2$O$_2$ dosage since the breakdown of H$_2$O$_2$ was decreased in the presence of a catalyst to form hydroxyl radical. However, an extreme H$_2$O$_2$ dosage was not suitable since first, it would raise the treatment cost dramatically. Moreover, an extreme H$_2$O$_2$ dosage results in an excessive scavenger effect of H$_2$O$_2$ on hydroxyl radical (Equation 7) (26-27).

$$H_2O_2 + OH^* \rightarrow H_2O + HO_2^*$$  \hspace{1cm} (Equation 7)

Therefore, the concentration of H$_2$O$_2$ should be in the optimum amounts. For this reason, it was optimized in the present research.

As it was clear in figures 3 to 5, the increase in the catalyst dosage was helpful to some extent. However, the catalyst could not be added without any limitation. The undue loading of the catalyst has a negative effect on the removal of COD since it may lead to the scavenger effect (Equations 8–10).

$$OH^* + Fe^{2+} \rightarrow OH^- + Fe^{3+}$$ \hspace{1cm} (Equation 8)

$$H_2O_2 + Fe^{3+} \rightarrow H^+ + FeOOH^{2+}$$ \hspace{1cm} (Equation 9)

$$FeOOH^{2+} \rightarrow HO_2^* + Fe^{2+}$$ \hspace{1cm} (Equation 10)

If the catalyst is excessive, the extra catalyst would spend the produced hydroxyl radical. Higher amounts of catalyst would clearly increase the treatment cost and result in the production of a large volume of sludge which, in turn, would raise the need for the sludge treatment. Figure 4 shows the percentage of NB removal in terms of hydrogen peroxide concentration and pH.

It was obvious that in mean values of pH, the percentage of NB removal was increased and the changes in the concentration of H$_2$O$_2$ in similar pH values had a low influence on NB removal. In addition, the interaction between the concentration of H$_2$O$_2$ and pH was non-significant. Nevertheless, the removal of NB was slightly higher in the mean values of hydrogen peroxide concentrations, compared to
Discussion

Figure 5 displays the percentage of NB removal in terms of pH and Ferric concentration. It was clear that in the mean value of pH, the percentage of NB removal from wastewater was at the highest level. Effect of Fe$^{3+}$ on NB removal was the same as the effect of hydrogen peroxide concentration. As presented in Figure 5, the best pH in this research was 6.23 based on maximum NB removal. This could be created from the coagulation of ferric species which can play a significant role under neutral pH. These results are in agreement with those of other investigators about the homogeneous Fenton-like catalyst (28).

At pH > 3, the main fraction of Fe (III) precipitates as Fe (OH)$_3$, dwindling the reaction between H$_2$O$_2$ and Fe$^{3+}$ which leads to the manufacture of Fe$^{2+}$. However, at neutral pH, the coagulant properties of Ferric ion overcome this phenomenon. In the alkaline condition (pH at 9), the removal of NB was reduced since the H$_2$O$_2$ degraded faster into H$_2$O and O$_2$.

As shown in figures 3 to 5, it is obvious that the percentage of NB removal can be high in some circumstances. For optimization of the percentage of NB removal, the values of different variables were gained via Design-Expert software (version 7.0.0). These optimum values, along with the percentage of NB removal are summarized in Table 4. As it is obvious, the maximum rate of NB removal was gained under the subsequent conditions: Ferric concentration of 1.30 mM, hydrogen peroxide concentration of 15.33 mM, and a pH of 6.23. Under these conditions, the maximum rate of NB removal by the experiments and model (Equation 6) with three replications were 99.0% and 99.23%, respectively.

In this project, the efficacy of the Fenton-like method versus the initial concentration of the NB can be explored but it was fixed in all runs. the lifetime of hydroxyl radicals is only a few nanoseconds and they can only react where they are produced, therefore the chance of interaction between NB molecules and hydroxyl radicals can be improved by increasing the number of NB molecules per volume unit which results in the enhancement of the degradation efficiency (29).

Table 4) Optimal conditions in the removal of NB

| Parameters                     | Unit | Value |
|--------------------------------|------|-------|
| Hydrogen peroxide concentration | mM   | 15.33 |
| Ferric ion concentration       | mM   | 1.30  |
| pH                             |      | 6.23  |
| Predicted NB removal           | %    | 99.23 |
| Experimental NB removal        | %    | 99.0  |

Conclusion

In this study, the synthetic wastewater containing NB was treated by the Fenton-like process. The BBD method was used and the effect of H$_2$O$_2$, Fe$^{3+}$, and pH on the removal of NB was studied in synthetic wastewater. The ANOVA was used for the analysis of experimental results. The results showed that the operational factors were significant and effective.
A quadratic model was applied to analyze the influence of variables on the percentage of NB removal. At optimum conditions (hydrogen peroxide and Ferric with concentrations of 15.33 and 1.30 mM, respectively, and a pH of 6.23) and after 30 min of reaction, the removal efficiency for NB and COD were 99.0% and 56.7%, respectively. The Fenton-like process was powerful in the removal of NB; however, it could remove the COD to some extent.

Footnotes

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Conflicts of Interest
The authors declare that there was no conflict of interest in this research.

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