The Photochemical Degradation (PCD) of Nitrobenzene (NB) using UV Light and Fenton Reagent Under Various Conditions

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Abstract: Photochemical degradation contributes to the environmental fate of many pesticides, chemicals, and industrial waste in surface waters. Photochemical degradation (PCD) of nitrobenzene (NB) has been studied using a UV light source and Fenton’s reagent under different experimental conditions. The effect of concentration on PCD of NB was monitored and recorded in the range 0.5 x 10⁻⁴ M to 3.0 x 10⁻⁴ M. The concentration of H₂O₂ was performed from 5.0 x 10⁻⁴ M to 2.5 x 10⁻⁴ M and Fe(II) from 1.0 x 10⁻⁴ M to 5.0 x 10⁻⁴ M, respectively. In terms of concentration, the absorbance increases with increasing the concentration of the solution of NB, H₂O₂ and Fe(II). The initial rate of PCD was recorded at fixed pH 2.42 of solution. Two optima for pH were found for PCD of nitrobenzene ranging from pH 2.42 to 4.20. The intermediates formed during PCD of NB were identified, by which a mechanism was then suggested that PCD is actually found to follow pseudo-first-order kinetics.

Keywords: Nitrobenzene, Fenton’s reagent, Mohr’s salt, photo-degradation, UV-Vis spectra, Pseudo-first-order kinetics.

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INTRODUCTION

In the last decade since 2004, Bangladesh averaged a gross domestic product (GDP) growth of 6.5% that has been largely achieved by its exports ready-made garments, remittances, and the agricultural sector (1,2). Textiles and garments industries are key major export oriented sectors of the country along with other exporting goods like fish, sea-food, jute, and leather. The country also developed self-sufficient industries in pharmaceuticals, steel, and food processing (1–3). Being on the path of a medium developing country, all the structures in any sector are not set-up well. Most of these industries are situated in Dhaka, Chittagong, Khulna, Gazipur, and Narayangong cities which have the Buriganga, the Karnaphuli, the Shitalokkha, and the Poshur rivers, respectively (4,5). These rivers are related, directly or indirectly, to the survival of about fifty million people. More than 60,000 cubic meters of toxic waste, including a majority of textile dying, printing, washing, and pharmaceuticals, are being released into the main water bodies of Dhaka, Chittagong, and Narayangong cities every day (6,7). The waste water and industrial waste turned into the river water cause river pollution so human health remains under risk from contaminated water (8,9).

Wastewater from manufacturing or chemical processes in industries add to the water pollution (9). Because of being comparatively steady chemical structures of aromatic dyes (10). Most of the commercially available dyestuffs are not favorable to decompose and therefore cause severe contamination to the drinking water and irrigation systems (10–14). Many of the dyestuffs have even been identified as harmful for human body and environment, and thus severe attention have been raised about it. Industrial waste water usually contains specific and readily identifiable chemical compounds (15). During the last five decades, a large the number of industries in Bangladesh has grown rapidly in both chemical and agricultural fields. The growth of textile (16), pharmaceutical, and garment industries are the highest among all the industries (1,17). Nitrobenzene (NB) is one of the frequently used chemical for aniline manufacturing, solvent in the manufacturing paints, shoe polishes, floor polishes, metal polishes, explosive, rubber making, textile, pesticide, cosmetic, and pharmaceutical purposes (such as acetaminophen) (8,18–23). NB is a highly toxic organic pollutant (24). NBs and their derivatives cause several harmful health effects, for example, nitrobenzene can reduce the ability of blood to carry oxygen because it causes methemoglobinemia (8,19). Repeated exposure to high level of it may cause anemia, development of bluish colour in the skin, headache, nausea, weakness, sleepiness, vomiting, grouchiness, and dizziness (25). Experimental studies in animals showed that 1,3-dinitrobenzene and 1,3,5-trinitrobenzene cause male reproductive damage and may
reduce sperm production (25). 4-Chloronitrobenzene has been identified as a potent hemoglobin toxicant, whereas 2-chloronitrobenzene is a potent hepatotoxicant (23). For this reason, it was selected to be the model pollutant in this study. General treatments of such polluted wastewater include adsorption (26), ozonization (27), or biodegradation (20), but water pollution is concentrated within a few sub sectors, mainly in the form of toxic wastes and organic pollutants (24). Out of this, a large portion can be traced to the processing of industrial chemicals and to the food products industry. In fact, a number of large and medium sized industries in the region are connected to the Buriganga, the Karnaphuli, and the Shitolokha rivers. Action Plan does not have adequate effluent treatment facilities (16). Most of the heavy industries have effluent treatment facilities by effluent treatment plant (ETP). But small and medium scale industries usually are not concern about pollution control and unable to afford huge cost of waste water treatment equipment as their profit margin is very small. They require further treatments and are very prone to cause secondary pollution (16).

In order to remove colour from waste water, it is necessary to find an efficient technique of industrial effluents’ treatment (10,28). A number of physical and chemical methods has been reported for the removal of dye compounds, mainly nitrobenzene and its derivatives (27,29) such as adsorption on carbon (26), biodegradation (20), ozonization (27) and advanced oxidation processes (AOPs) (30,31) such as Fenton and photo-Fenton catalytic reactions (32), H$_2$O$_2$/UV processes, and semiconductor photo catalysis (13,27,33). Highly reactive species such as hydroxyl radicals (·OH) are produced by advanced oxidation methods. For rapid and non-selective oxidation of organic molecules, hydroxyl radical is a very powerful oxidant that can oxidize organic compounds into carbon dioxide and water, so it is capable to decompose pollutants efficiently. Among the AOPs homogeneous photocatalytic oxidation using Fenton has been widely studied. H$_2$O$_2$ is a very efficient, relatively cheap, commercially available, and chemically stable photo-catalyst (34).

**MATERIALS AND METHODS**

**Used chemicals**
Mohr’s salt, FeSO$_4$·(NH$_4$)$_2$SO$_4$·6H$_2$O (AR.BDH), hydrogen peroxide (BDH), potassium permanganate (AR, BDH), oxalic acid (AR, BDH), buffer solution (ammonium acetate), (MERCK India), nitrobenzene (Analytical grade), sulfuric acid (AR, BDH), sodium hydroxide (AR, BDH) and hydrochloric acid (AR, BDH) were used without further purification. All the aqueous solutions were prepared with deionized water. The stock solution of 1.0×10$^{-2}$M of nitrobenzene was prepared and kept in the dark (31). Mohr’s salt solution (0.01M) was
prepared in 0.05M sulfuric acid solution (35). H₂O₂ solutions were freshly prepared before each experiment and titrated against standard KMnO₄ solution.

**Experiment of photo-degradation**

All the experiments were carried out in a beaker used as the reactor. The source of radiation comprised fluorescent lamps in a wooden box. The top and sides of the box had five (50-watt) fluorescent lamps. The intensity of light at the reactor was measured with a spectro-radiometer (International light, U.S.A., model no IL-588). The intensity was 1.802 x 10⁻⁴ Wcm⁻². The reactor was placed on a magnetically stirred plate and the distance of the solution surface from the lower part of the lamp was fixed. The total system was enclosed in a wooden box, called lamp house. The inner walls of the box were covered with aluminum foil to prevent the absorption of light (31,36,37).

After taking 100 mL of (0.5 × 10⁻⁴ M) NB solution in 100 mL volumetric beaker with (5.0 × 10⁻³ M) H₂O₂ and (5.0 × 10⁻⁴ M) Fe(II) solution, the pH of the solution was measured and recorded at 2.42. The constant pH was controlled by the addition of dilute sulfuric acid and sodium hydroxide before up to the mark. Then absorbance of the solution was measured by UV-visible spectrophotometer at different time intervals in concentration of NB 0.5 × 10⁻⁴ M, 1.0 × 10⁻⁴ M, 2.0 × 10⁻⁴ M, 2.5 × 10⁻⁴ M, and 3.0 × 10⁻⁴ M respectively. This experiment again was carried on at fixed pH 1.5 and 7.0 and recorded. The effect of H₂O₂ activity in 5.0 × 10⁻³ M to 0.025 M H₂O₂ solution in fixed pH 2.42 and 4.20 was measured and recorded. Again, the effect of Fe(II) concentration from 1.0 × 10⁻⁴ M to 5.0 × 10⁻⁴ M were measured and recorded. A peak was recorded at 318 nm at fixed pH at 4.20 in UV-visible spectrophotometer which was confirmed as para-nitrophenol (PNP).

**Determination of the percentage (%) degradation by UV-Vis spectra of NB**

In each experiment, the % degradation was calculated after 30 minutes using the (Eq. 1)

\[
\text{\% of degradation} = \left(1 - \frac{A_t}{A_0}\right) \times 100 \quad \text{Eq.1}
\]

Here, \(A_0\) = absorbance at time = 0 min, and \(A_t\) = Absorbance at \(t = 30\) min.
RESULTS AND DISCUSSION

Determination of the effect of pH in absorbance of photochemical degradation of NB

Absorbances at different pH’s were recorded for the $0.5 \times 10^{-4}$ M solution of NB with reference water at temperature at 31°C was shown in Figure 1.

![Figure 1. Effect of absorbance of NB solution at different pH.](image)

Effect of different concentration on absorption for nitrobenzene

The solution of nitrobenzene 100 mL of $0.75 \times 10^{-4}$ M to $2.25 \times 10^{-4}$ M with $5.00 \times 10^{-4}$ M [Fe(II)] and $5.0 \times 10^{-3}$ M [H₂O₂] was taken for experiment at constant pH at 2.42. The effect on initial concentration of NBs photodegradation was recorded in Table 1, which shows that with increasing the concentration of NB, the absorbance increases.

Table 1. Absorbance of Nitrobenzene at different concentrations at wavelength 267nm

<table>
<thead>
<tr>
<th>Concentration×10^{-4}/M</th>
<th>Absorbance at $\lambda_{\text{max}}$nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X = 0.75$</td>
<td>0.562</td>
</tr>
<tr>
<td>1.00</td>
<td>0.729</td>
</tr>
<tr>
<td>1.25</td>
<td>0.960</td>
</tr>
<tr>
<td>1.50</td>
<td>1.147</td>
</tr>
<tr>
<td>1.75</td>
<td>1.328</td>
</tr>
<tr>
<td>2.00</td>
<td>1.498</td>
</tr>
<tr>
<td>2.25</td>
<td>1.699</td>
</tr>
<tr>
<td>2.50</td>
<td>1.880</td>
</tr>
</tbody>
</table>
Effect of time on absorbance and concentration
The effect of time on absorbance and different concentration with $5.00 \times 10^{-4}$ M [Fe(II)] and $5.0 \times 10^{-3}$ M [H$_2$O$_2$]$_0$ was recorded at constant pH 2.42 and plotted time versus absorbance and concentration (Figure 2). The graph shows that with increasing time, the absorbance slowly decreases i.e., concentration NB also decrease as with decreasing the concentration of NB, the absorbance decrease (Table 1).

![Figure 2. Effect of time on absorbance.](image)

Effect of different concentrations of NB on photodegradation
Solution of nitrobenzene of different concentration with $5.00 \times 10^{-4}$ M [Fe(II)] and $5.0 \times 10^{-3}$ M [H$_2$O$_2$] was taken for experiment at constant pH 2.42 and at temperature 31.0 °C. The absorption of different concentrations with respect to time were recorded in Table 2, which gives evidence that at high concentrations the absorption increases. Furthermore, with increasing time both the concentration and absorption decrease. As the concentration of NB increases both the rate constant and the initial rate increase. This might be due to the following reactions taking place. The reactions shown in (Eq. 2) and (Eq. 3) are important to produce OH· Radicals.

\[
H_2O_2 + h\nu = OH^- + OH^+ \]  \hspace{0.5cm} (Eq. 2)

\[
Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + OH^- \]  \hspace{0.5cm} (Eq. 3)

These suggest that there were enough OH· radicals during the increasing concentration of NB over the range $0.5\times10^{-4}$ M to $3.0\times10^{-4}$ M. However, the increase of initial rate was influenced by the ratio of H$_2$O$_2$ /Fe(II) solution.
Table 2. Effect of different concentration (×10⁻⁴) M of NB on photodegradation in terms of absorbance

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.593</td>
<td>0.833</td>
<td>1.162</td>
<td>1.476</td>
<td>1.791</td>
</tr>
<tr>
<td>1.50</td>
<td>0.587</td>
<td>0.801</td>
<td>1.125</td>
<td>1.418</td>
<td>1.715</td>
</tr>
<tr>
<td>2.50</td>
<td>0.581</td>
<td>0.785</td>
<td>1.098</td>
<td>1.369</td>
<td>1.661</td>
</tr>
<tr>
<td>3.50</td>
<td>0.576</td>
<td>0.763</td>
<td>1.056</td>
<td>1.321</td>
<td>1.591</td>
</tr>
<tr>
<td>4.50</td>
<td>0.571</td>
<td>0.746</td>
<td>1.025</td>
<td>1.287</td>
<td>1.541</td>
</tr>
<tr>
<td>5.50</td>
<td>0.564</td>
<td>0.735</td>
<td>1.006</td>
<td>1.234</td>
<td>1.487</td>
</tr>
<tr>
<td>6.50</td>
<td>0.557</td>
<td>0.724</td>
<td>0.991</td>
<td>1.189</td>
<td>1.401</td>
</tr>
<tr>
<td>7.80</td>
<td>0.553</td>
<td>0.715</td>
<td>0.981</td>
<td>1.141</td>
<td>1.378</td>
</tr>
<tr>
<td>8.50</td>
<td>0.551</td>
<td>0.709</td>
<td>0.971</td>
<td>1.118</td>
<td>1.351</td>
</tr>
<tr>
<td>10.00</td>
<td>0.550</td>
<td>0.701</td>
<td>0.951</td>
<td>1.069</td>
<td>1.305</td>
</tr>
<tr>
<td>12.00</td>
<td>0.543</td>
<td>0.697</td>
<td>0.936</td>
<td>1.045</td>
<td>1.271</td>
</tr>
<tr>
<td>14.00</td>
<td>0.547</td>
<td>0.691</td>
<td>0.923</td>
<td>1.031</td>
<td>1.257</td>
</tr>
<tr>
<td>16.00</td>
<td>0.539</td>
<td>0.688</td>
<td>0.905</td>
<td>1.023</td>
<td>1.241</td>
</tr>
<tr>
<td>18.00</td>
<td>0.531</td>
<td>0.684</td>
<td>0.890</td>
<td>1.011</td>
<td>1.229</td>
</tr>
<tr>
<td>20.00</td>
<td>0.523</td>
<td>0.677</td>
<td>0.880</td>
<td>1.005</td>
<td>1.209</td>
</tr>
<tr>
<td>25.00</td>
<td>0.516</td>
<td>0.666</td>
<td>0.860</td>
<td>0.987</td>
<td>1.181</td>
</tr>
<tr>
<td>30.00</td>
<td>0.508</td>
<td>0.662</td>
<td>0.849</td>
<td>0.971</td>
<td>1.173</td>
</tr>
</tbody>
</table>

When the ratio of H₂O₂/Fe(II) is 10/1, the initial rates observed, during the increasing concentration of NB, when compared with the values obtain using the ratio to be 50/1, it was found that the initial rates were increased at higher rate of H₂O₂/Fe(II) but the percentage of degradation was found to 35% during 30 minutes in both cases. Although it was expected that at a higher ratio of H₂O₂/Fe(II) the higher the rate of degradation percentage would be, but practically it did not happen. This might be due to the scavenging effect of OH⁻ radicals at higher concentrations of H₂O₂. Reactions shown in (Eq. 4), (Eq. 5) and (Eq. 6) might occur under that condition:

\[ \text{OH}^- + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{HO}_2^- \]  \hspace{1cm} (Eq. 4)

\[ \text{HO}_2^- + \text{OH}^- = \text{H}_2\text{O} + \text{O}_2 \]  \hspace{1cm} (Eq. 5)

\[ \text{OH}^- + \text{OH}^- = \text{H}_2\text{O}_2 \]  \hspace{1cm} (Eq. 6)

However, it can be concluded that the rate always increased because there was a high concentration of OH⁻ radicals available to degrade NB.

**Effect of pH on photodegradation of NB**

The effect of pH was studied by varying the pH of the solution from 1.5 to 7.0 keeping the initial concentration of NB, Fe(II) and H₂O₂ constant, the values were 3.0 x 10⁻⁴ M, 5.0 x 10⁻⁴ M, and 2.50 x 10⁻³ M respectively. It was observed that with the increase of pH the
initial rate was increased at pH 2.50 but further increases of pH caused the decrease of initial rate of % degradation. Table 4 suggests 2.50 to be the optimal pH. At this pH 75% degradation was observed in less than 2 hours. The low removal rate at pH values 2.50 might be due to the following reaction (Eq. 7) taking place:

\[ \text{OH}^\cdot + \text{H}^+ + e^- = \text{H}_2\text{O} \] (Eq. 7)

100 mL (3.0 × 10^{-4} M) NB solution was taken in 100 mL volumetric flasks and desired pH was controlled by the addition of hydrochloric acid or sodium hydroxide solution. Absorbance of each of the solutions at different pH was recorded in Table 3, where the concentration of nitrobenzene is 3.0 × 10^{-4} M and reference was water at temperature 31 °C.

**Table 3.** Absorbance in different pH at \(\lambda_{\text{max}}\) 267 (nm)

<table>
<thead>
<tr>
<th>pH of the solution</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.53</td>
<td>0.30</td>
</tr>
<tr>
<td>3.00</td>
<td>0.42</td>
</tr>
<tr>
<td>3.50</td>
<td>0.27</td>
</tr>
<tr>
<td>4.20</td>
<td>0.20</td>
</tr>
<tr>
<td>4.46</td>
<td>0.53</td>
</tr>
<tr>
<td>6.10</td>
<td>0.70</td>
</tr>
<tr>
<td>7.00</td>
<td>0.77</td>
</tr>
</tbody>
</table>

**Effect of concentration of NB by different pH for the photo degradation of NB**

The percentage (%) degradation in different pH after 110 min time [NB]=3.0 × 10^{-4} M, \([\text{H}_2\text{O}_2]\) = 0.025 M, [Fe(II)] =5.0×10^{-4} M was recorded in Table 4. In acidic solution, this reaction predominates causing the decrease of concentration of \text{OH}^\cdot which in turn decreases the degradation of NB.

**Table 4.** Degradation of NB in different pH

<table>
<thead>
<tr>
<th>pH</th>
<th>1.5</th>
<th>1.75</th>
<th>2</th>
<th>2.25</th>
<th>2.5</th>
<th>2.75</th>
<th>3</th>
<th>3.5</th>
<th>4</th>
<th>4.2</th>
<th>4.5</th>
<th>5</th>
<th>5.5</th>
<th>6</th>
<th>6.5</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of NB Deg.</td>
<td>60</td>
<td>61</td>
<td>63</td>
<td>67</td>
<td>72</td>
<td>65</td>
<td>62</td>
<td>78</td>
<td>88</td>
<td>92</td>
<td>85</td>
<td>80</td>
<td>70</td>
<td>60</td>
<td>49</td>
<td>38</td>
</tr>
</tbody>
</table>

The decrease of the degradation rate beyond pH 2.5 might be due to the coagulation of \text{Fe}^{3+} complex formed in the reaction which reduces the amount of \text{Fe}^{2+} for catalysis. When the concentration was changed to one third of the earlier value, the optimum pH was shifted to 4.2, Table 4 shows that, % degradation was above 90. S. H. Lin et al. (38) has
also studied the effect of pH for treatment of wastewater by Fenton process and reported 3.0 as optimum pH.

At higher pH values, there might be the possibility of direct reaction between NB and Fe(III) complexes.

\[ NB + Fe(OH)_2^+ \rightarrow NB \ldots \ldots Fe(III) \rightarrow NB^+ \ldots \ldots Fe(II) \rightarrow \text{Degradation Product} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (Eq.8) \]

This might be the reason for a higher degradation rate at pH 4.2

**Effect of H\textsubscript{2}O\textsubscript{2} concentration on photo degradation of NB**

The kinetics of photo degradation were studied using the effect of H\textsubscript{2}O\textsubscript{2} concentration under constant values of [NB], and [Fe(II)], which were 3.0 x 10\textsuperscript{-4} M and 5.0 x 10\textsuperscript{-4} M respectively, and using optimum pH of 2.42.

From the Figure 3, it is observed that the initial rate increases with the increase of H\textsubscript{2}O\textsubscript{2} concentration. In the concentration 0.025 M of Fe(II) solution it shows the high absorbance with low absorbance being shown with concentration of [H\textsubscript{2}O\textsubscript{2}]: 5.0x10\textsuperscript{-4} M.

![Figure 3. Percentage (%) degradation of NB in presence of Fe(II) at different H\textsubscript{2}O\textsubscript{2} concentration](image)

**Effect of Fe(II) ion concentrations on the kinetics of photodegradation of nitrobenzene by Fenton process at pH 2.42**

811
The effect of Fe(II) concentration on the degradation of NB was studied using two optimum pH values of 2.42 and 4.20 and the concentrations of NB and H$_2$O$_2$ to be $2.5 \times 10^{-4}$ M, 0.025 M respectively.

Figure 4 shows at pH 2.42 initial rates increase with the increasing concentration of Fe(II) ions, which is expected because the production of ·OH radicals by reaction 4(b).

The increases of initial rate with the increase of concentration of Fe(II) were observed in case of pH 4.20. This is the major reaction taking place, as supported by the experimental results, that show as the Fe(II) concentration increases, rate of degradation also increases.

Figure 4. Variation of absorbance of NB with time under different Fe(II) concentrations (a) conc. $1.0 \times 10^{-4}$ M (b) conc. $2.0 \times 10^{-4}$ M (c) conc. $3.0 \times 10^{-4}$ M (d) conc. $4.0 \times 10^{-4}$ M (e) conc. $4.50 \times 10^{-4}$ M and, (f) conc. $5.0 \times 10^{-4}$ M at pH = 2.42, 4.20 [NB]=$2.5 \times 10^{-4}$ M, [H$_2$O$_2$]=0.025 M, Temp = 31.0 °C.

**Estimation of rate constant and reaction kinetics with degradation of NB**

Percentage (%) of degradation of NB has been studied at pH 1.5, 2.0, 2.5 and 3.0. over 60 minutes. In all pH studied, degradation of NB follows a nearly similar order. Among them, percentage (%) of degradation of NB at pH 2.5 is tabulated in Table 5. The results clearly demonstrate that NB significantly decomposed and more than 70% of the initial nitrobenzene disappeared within 60 minutes.

**Table 5.** Change of $c_t/c_0$ with degradation time of NB at pH 2.5

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>% of Degradation</th>
<th>$C_0/C_t$</th>
<th>ln($c_0/c_t$)</th>
<th>Rate constant, $k \text{ (min}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5 also drawn to present the reaction kinetics that was plotted as ln(C_t/C_0) versus time where C_t and C_0 are the concentrations of nitrobenzene at a given time t and time zero i.e., initiated concentration of NB, respectively. The linear regression model fits the data very well reflecting that the reduction of nitrobenzene follows pseudo-first-order kinetics (39). Slope of the straight line calculated from equation of the line y = 0.023x – 0.001 as 0.0230 that shown in Figure 5. The slope indicates the rate constant of photodegradation of NB. So the rate constant of disappearance of NB is 0.0230 min⁻¹. Again at higher concentration of H₂O₂, the reaction only depends on the concentration of radical OH, which also represents pseudo-first-order reaction. Jun Dong et al. (40) have studied degradation of nitrobenzene in groundwater using emulsified nano-zero-valent iron that followed pseudo-first-order reaction and rate constant of nitrobenzene was 0.0942 min⁻¹.

**Figure 5.** Plot of ln(C₀/Cₜ) vs time.

**Product analysis**

Product analysis (Figure 1) shows that the degradation of NB follows a conjugative state. The intermediate compound during the experiment was authenticated and found to be PNP. The degradation of NB might follow the following mechanism:

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

\[ \text{OH}^- + \text{NB} \rightarrow \text{Intermediate (PNP)} \]
At higher concentrations of H\textsubscript{2}O\textsubscript{2} the following reactions might occur:

\begin{align*}
&\text{OH}^{-} + \text{H}_{2}\text{O}_{2} \rightarrow \text{H}_{2}\text{O} + \text{HO}_{2}^{-}.
&\text{HO}_{2}^{-} + \text{OH}^{-} \rightarrow \text{H}_{2}\text{O} + \text{O}_{2}
&\text{OH}^{-} + \text{OH}^{-} \rightarrow \text{H}_{2}\text{O}_{2}
\end{align*}

CONCLUSION

The dependence of percent photodegradation of NB, on initial concentration of NB solution, was studied. The investigation showed that the percentage of photodegradation of NB increases with the increase of initial concentration of NB solution. This is due to the fact that the concentrations of H\textsubscript{2}O\textsubscript{2} and Fe (II) were comparable to NB concentration so that enough ∙OH radicals were produced to oxidize NB throughout the concentrations used.

The effect of concentration of H\textsubscript{2}O\textsubscript{2} on photodegradation of NB was studied and it has been observed that the initial rate of photodegradation of NB increases with the increased concentration of H\textsubscript{2}O\textsubscript{2}. But the increasing rate was not significant due to some scavenger reactions. Similarly, it was found that the photodegradation of NB increases with the increasing concentration of Fe\textsuperscript{2+} suggesting the product of ∙OH via reaction of Fe(II) + H\textsubscript{2}O\textsubscript{2} was important.

The effect of pH on photodegradation of NB solution was studied by varying the pH from 1.0 to 7.0 and it has been deduced that the percent photodegradation was maximum at the pH 2.42 and pH 4.20. The product analysis suggests that the degradation follows stepwise reactions.

\begin{align*}
\text{NB} &\rightarrow \text{X} \rightarrow \text{Degraded product.}
\end{align*}

The disappearance of NB follows pseudo-first-order kinetics.

Conclusively, the present method may be used for the destruction of organic compounds discharged from various industries.

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