

**A NOVEL ROUTE FOR WASTE WATER TREATMENT:  
PHOTO-ASSISTED FENTON DEGRADATION OF NAPHTHOL GREEN B**

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This study was conducted to assess the removal of the Naphthol Green B dye from aqueous medium using the photo-Fenton process. The Fenton reagent, a mixture of hydrogen peroxide and Fe<sup>3+</sup> ions, was used to generate the hydroxyl radical (\*OH) that degrades the dye. Experiments were conducted at laboratory temperature and atmospheric pressure to examine the effect of reaction conditions such as the concentration of Fe<sup>3+</sup> ions, the dye and hydrogen peroxide, pH, and light intensity on the reaction rate. The progress of the photochemical degradation was monitored spectrophotometrically. The optimum photochemical degradation conditions were determined. Naphthol Green B was completely degraded into CO<sub>2</sub> and H<sub>2</sub>O. A tentative mechanism for photochemical bleaching of the dye by the photo-Fenton reaction has been proposed.

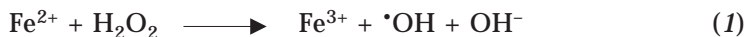
**Keywords:** Photodegradation; Photo-Fenton process; Naphthol Green B; Hydrogen peroxide.

Many dyes are toxic and carcinogenic. Contamination of the environment by toxic chemicals is emerging as a serious global problem. Coloured effluents containing dyes from textile, dyeing and printing industries may cause skin cancer due to photosensitisation and photodynamic damage. On the contrary, bleached dye solutions are non-toxic and harmless. Second, the dye-containing coloured water is hardly of any use, but if the coloured solutions are bleached to give colourless water, it may be used for washing, cooling, irrigation and cleaning purposes. Thus, photochemical bleaching provides a low-cost method to solve the problem of water pollution.

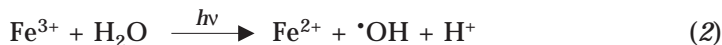
The possibility of using Fenton-based systems in dark reactions<sup>1,2</sup> and under light irradiation<sup>3-6</sup> has been a topic of recent interest in the field of advanced oxidation technologies involving degradation of pollutants

in homogeneous systems. The Fenton reactions in the dark mineralise ca. 40–60% of the total organic carbon (TOC) present<sup>7–10</sup>. Recently, it has been found that illumination of the  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$ – $\text{H}_2\text{O}_2$  system increases the degradation rate of many aromatic organic substances, such as phenols, substituted phenols, nitrobenzene, anisole<sup>11–14</sup>, TNT and RDX<sup>15,16</sup>, Orange II and 4-chloroaniline<sup>17</sup>.

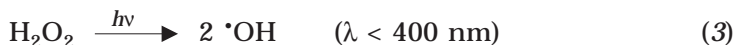
The Fenton reaction<sup>18</sup> produces hydroxyl radicals by the reaction of  $\text{H}_2\text{O}_2$  with  $\text{Fe}^{2+}$  salts.



In the dark, the reaction is retarded after complete conversion of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . The positive effect of illumination on the rate of degradation is due to the photoreduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions producing new  $\cdot\text{OH}$  radicals (and  $\text{H}_2\text{O}_2$ ) according to Eq. (2).



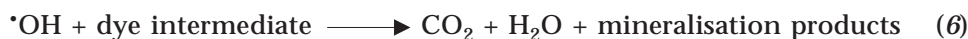
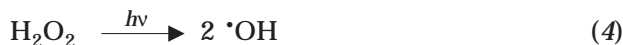
The direct photolysis of  $\text{H}_2\text{O}_2$  also generates  $\cdot\text{OH}$  radicals.



Chen et al.<sup>19</sup> studied the photochemical degradation of azo dyes, Red MX-5B, Reactive Black-5 and Orange G, using low iron concentrations in the Fenton and Fenton-like systems. Daneshvar and Khataee<sup>20</sup> decolourised solution containing a common textile and leather dye, C.I. Acid Red 14 (AR14), at pH 3, using the Fenton, UV/ $\text{H}_2\text{O}_2$ / $\text{O}_2$ , UV/ $\text{H}_2\text{O}_2$ / $\text{Fe}^{2+}$ , UV/ $\text{H}_2\text{O}_2$ / $\text{Fe}^{3+}$  and UV/ $\text{H}_2\text{O}_2$ / $\text{Fe}^{3+}$ /oxalate processes. The influence of Alizarin Violet 3B on the Fenton reaction of organic compounds under irradiation ( $\lambda > 450 \text{ nm}$ ) was examined by Tang et al.<sup>21</sup>. Chaudhuri et al.<sup>22</sup> also chemically oxidised Methylene Blue using a Fenton-like reaction. Prousek et al.<sup>23</sup> reported the utilisation of the Fenton reaction for degradation of dyes present in coloured waste water. Photodegradation of Malachite Green in the presence of  $\text{Fe}^{3+}$ / $\text{H}_2\text{O}_2$  under irradiation with visible light was observed by Wu et al.<sup>24</sup>. Ruppert et al.<sup>25</sup> studied the photo-Fenton reaction as an effective photochemical process to treat polluted water. Mogra et al.<sup>26,27</sup> reported the photochemical degradation of 1,4-dichlorobenzene and chlorobenzene by the photo-Fenton reagent. Walling<sup>28</sup> studied intermediates in the reaction of Fenton-type reagents.

The Fenton reaction is easy and forms no sludge. It has been therefore widely used to degrade pollutants<sup>29,30</sup>. Hydroxyl radical is a powerful ox-

dant which can rapidly and non-selectively oxidise organic contaminants to carbon dioxide and water<sup>31,32</sup>; hence, it is able to degrade pollutants effectively<sup>33,34</sup>. The photo-Fenton reaction is another effective method of preventing pollution. Xiang and Zheng<sup>35</sup> accelerated decolourisation of dyes by combination of UV radiation and Fenton process, which produced the  $\cdot\text{OH}$  radicals directly (Eqs (4)–(6)).



## EXPERIMENTAL

Naphthol Green B (Sisco),  $\text{FeCl}_3$  (CDH) and  $\text{H}_2\text{O}_2$  (30%, Merck), were used. Photochemical degradation of the dye was studied in the presence of  $\text{Fe}^{3+}$  ions,  $\text{H}_2\text{O}_2$  and visible light. Naphthol Green B (0.0879 g) was dissolved in double distilled water (100 ml) to give  $1.0 \times 10^{-4}$  M solution. Anhydrous  $\text{FeCl}_3$  (0.4055 g) was dissolved in double distilled water (500 ml) to give  $5.0 \times 10^{-3}$  M stock solution. Photochemical degradation of Naphthol Green B was investigated in 30 ml of reaction solution that contained the dye,  $\text{FeCl}_3$  and  $\text{H}_2\text{O}_2$  at concentrations  $3.33 \times 10^{-6}$ ,  $1.0 \times 10^{-6}$  and  $1.00 \times 10^{-3}$  mol/l, respectively. The reaction mixture was exposed to the light ( $70.0 \text{ mW/cm}^2$ ), of a 200 W tungsten lamp (Sylvania Laxman). Sunlight was used for higher light intensities. The light intensity was measured with a Suryamapi CEL Model SM 201 powermeter. A water filter was used to cut off thermal radiation. pH of the solution was adjusted by the addition of standardised hydrochloric acid and sodium hydroxide solutions and measured with a Systronics Model 106 digital pH meter. The necessary condition for the correct measurement of absorbance is that the solution must be free of solids. Therefore, a Remi-1258 centrifuge and a Whatman filter paper were attempted to remove the solids but both failed. Hence, a G 3 sintered glass crucible was used for filtration to obtain the desired accuracy in recording the absorbance of the dye with a Shimadzu U.V. 240 spectrophotometer.

## RESULTS AND DISCUSSION

The photochemical degradation of Naphthol Green B (Chart 1) was monitored at  $\lambda_{\text{max}} = 710 \text{ nm}$ . The results of a typical run are given in Table I and Fig. 1.

It was observed that absorbance ( $A$ ) of Naphthol Green B solutions decreased with irradiation time, indicating that the dye was consumed. A plot of  $1 + \log A$  against time is linear, consistent with pseudo-first-order kinet-

ics. The rate constant  $k$  was calculated from the expression  $k = 2.303 \times$  slope. The optimum rate constant for this reaction was determined as  $k = 16.88 \times 10^{-4} \text{ s}^{-1}$ .

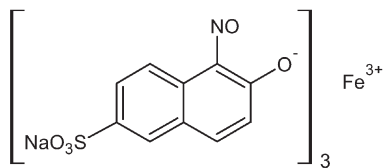


CHART 1

### Effect of pH

The effect of pH on the rate of degradation of Naphthol Green B was investigated in the pH range 2.4–3.8. The results are reported in Table II.

The photochemical degradation depends strongly on pH of the reaction medium as evident from the data in Table II. The reaction rate increases with pH increasing up to 3.2 and then it decreases. The hydroxyl radicals are generated in two steps:

- (i) in the reaction between  $\text{Fe}^{2+}$  and hydrogen peroxide,
- (ii) in the photochemical reaction of  $\text{Fe}^{3+}$  ions with water.

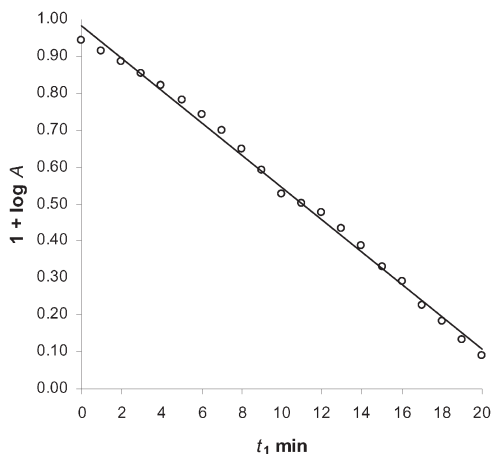


FIG. 1

A typical run of degradation of Naphthol Green B by the photo-Fenton process. Experimental conditions are given in Table I. The slope corresponds to  $k = 16.88 \times 10^{-4} \text{ s}^{-1}$

The increase in pH of the medium favours the step (i) where  $\text{OH}^-$  ions are formed along with hydroxyl radicals, whereas protons are generated in the step (ii). Thus, it may be concluded that the step (i) dominates over the step (ii) at pH below 3.2, and vice versa at pH above 3.2.

TABLE I  
A typical run of degradation of Naphthol Green B by the photo-Fenton process<sup>a</sup>

<i>t</i> , min	<i>A</i>	1 + log <i>A</i>
0	0.876	0.9426
1	0.822	0.9150
2	0.768	0.8855
3	0.714	0.8538
4	0.660	0.8195
5	0.606	0.7825
6	0.552	0.7422
7	0.498	0.6974
8	0.444	0.6474
9	0.390	0.5912
10	0.336	0.5266
11	0.317	0.5021
12	0.299	0.4761
13	0.271	0.4334
14	0.242	0.3854
15	0.214	0.3314
16	0.194	0.2894
17	0.167	0.2248
18	0.152	0.1833
19	0.135	0.1316
20	0.123	0.0913

<sup>a</sup> Experimental conditions: [Naphthol Green B] =  $3.33 \times 10^{-6}$  mol/l,  $[\text{H}_2\text{O}_2]$  =  $1.00 \times 10^{-3}$  mol/l,  $[\text{Fe}^{3+}]$  =  $6.67 \times 10^{-4}$  mol/l, pH 3.2, incident light intensity = 70.0 mW/cm<sup>2</sup>.

TABLE II  
The effect of pH on the rate of photodegradation of Naphthol Green B<sup>a</sup>

pH	$k \times 10^4, \text{s}^{-1}$
2.4	4.30
2.6	7.39
2.8	13.16
3.0	15.76
3.2	16.89
3.4	4.93
3.6	0.50
3.8	0.32

<sup>a</sup> Experimental conditions: [Naphthol Green B] =  $3.33 \times 10^{-6}$  mol/l,  $[\text{H}_2\text{O}_2]$  =  $1.00 \times 10^{-3}$  mol/l,  $[\text{Fe}^{3+}]$  =  $6.67 \times 10^{-4}$  mol/l, incident light intensity =  $70.0 \text{ mW/cm}^2$ .

#### *Effect of Naphthol Green B Concentration*

Effect of varied dye concentration on the reaction rate was studied for reaction conditions given in Table III.

The rate of photochemical degradation was found to increase with increasing concentration of Naphthol Green B up to  $3.33 \times 10^{-5}$  mol/l. On

TABLE III  
The effect of Naphthol Green B concentration on the rate of photodegradation of the dye<sup>a</sup>

[NGB] $\times 10^6, \text{mol/l}$	$k \times 10^4, \text{s}^{-1}$
0.67	10.55
1.33	12.72
2.00	15.19
2.67	16.18
3.33	16.89
4.00	10.55
4.67	9.85
5.33	9.85
6.00	8.97
6.67	6.33

<sup>a</sup> Experimental conditions:  $[\text{H}_2\text{O}_2]$  =  $1.00 \times 10^{-3}$  mol/l,  $[\text{Fe}^{3+}]$  =  $6.67 \times 10^{-4}$  mol/l, pH 3.2, incident light intensity =  $70.0 \text{ mW/cm}^2$ .

further increasing its concentration, a sudden decrease in the rate of degradation was observed. This result may be attributed to the fact that at increased concentration Naphthol Green B may act itself as a filter for the incident light. The high concentration does not permit the light to reach the dye molecules in the bulk solution.

### *Effect of Fe<sup>3+</sup> Concentration*

The effect of concentration of Fe<sup>3+</sup> ions on the rate of photochemical degradation of Naphthol Green B was studied by keeping all the other factors identical. The results are summarised in Table IV.

It is clear from the experimental data that the rate of photodegradation increases with the increasing concentration of Fe<sup>3+</sup> ions up to  $6.67 \times 10^{-5}$  mol/l. This is tentatively explained by increased concentration of Fe<sup>2+</sup> ions in parallel with Fe<sup>3+</sup>, which is accompanied by enhanced generation of <sup>•</sup>OH radicals.

TABLE IV  
The effect of Fe<sup>3+</sup> concentration on the rate of photodegradation of Naphthol Green B<sup>a</sup>

[Fe <sup>3+</sup> ] × 10 <sup>4</sup> , mol/l	k × 10 <sup>4</sup> , s <sup>-1</sup>
0.67	0.88
1.33	1.82
2.00	2.60
2.67	4.16
3.33	5.98
4.00	8.66
4.67	9.96
5.33	11.43
6.00	13.64
6.67	16.89

<sup>a</sup> Experimental conditions: [Naphthol Green B] =  $3.33 \times 10^{-6}$  mol/l, [H<sub>2</sub>O<sub>2</sub>] =  $1.00 \times 10^{-3}$  mol/l, pH 3.2, incident light intensity = 70.0 mW/cm<sup>2</sup>.

### *Effect of Hydrogen Peroxide*

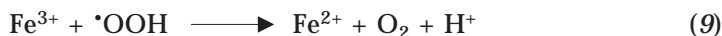
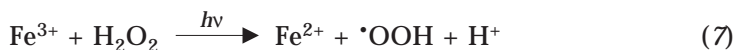
The effect of the amount of hydrogen peroxide on the photodegradation of Naphthol Green B was also investigated. The results are given in Table V.

TABLE V  
The effect of hydrogen peroxide on the rate of photodegradation of Naphthol Green B<sup>a</sup>

$[\text{H}_2\text{O}_2] \times 10^3, \text{ mol/l}$	$k \times 10^4, \text{ s}^{-1}$
0.29	11.26
0.43	11.26
0.57	12.48
0.72	14.33
0.86	15.01
1.00	16.89
1.15	13.77
1.29	12.77
1.43	11.86
2.15	9.79

<sup>a</sup> Experimental conditions: [Naphthol Green B] =  $3.33 \times 10^{-6}$  mol/l,  $[\text{Fe}^{3+}] = 6.67 \times 10^{-4}$  mol/l, pH 3.2, incident light intensity = 70.0 mW/cm<sup>2</sup>.

It was observed that the reaction rate increased with the concentration of  $\text{H}_2\text{O}_2$ , reaching an optimum value  $1.00 \times 10^{-3}$  mol/l. Thereafter, the rate of degradation decreased. This behaviour can be explained by the rates of the reactions (7) and (8). In Eq. (8),  $\cdot\text{OH}$  radicals are consumed rapidly by encountering more  $\text{H}_2\text{O}_2$  molecules. From Eqs (7) and (8),  $\cdot\text{OOH}$  radicals are generated in significant amounts. They react with  $\text{Fe}^{3+}$  (Eq. (9)) and protons are liberated. The production of  $\text{H}^+$  is confirmed by a slight decrease in pH of the reaction mixture at the end of photoreaction. As a consequence, the rate of photodegradation decreases.





### Effect of Light Intensity

The effect of light intensity on the photodegradation of Naphthol Green B was also investigated. The results obtained are reported in Table VI.

A plot of the rate constant versus incident light intensity is linear, which indicates that increasing light intensity accelerates the process. This behaviour may be attributed to higher concentration of active hydroxyl radicals formed according to Eq. (2).

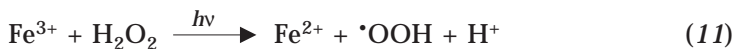
TABLE VI  
The effect of incident light intensity on the rate of photodegradation of Naphthol Green B<sup>a</sup>

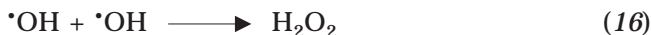
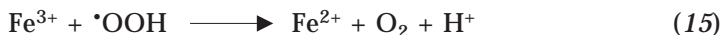
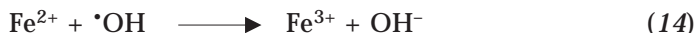
Light Intensity, mW/cm <sup>2</sup>	$k \times 10^4, \text{s}^{-1}$
10.0	10.69
20.0	12.54
30.0	13.93
40.0	14.88
50.0	15.62
60.0	16.20
70.0	16.89

<sup>a</sup> Experimental conditions: [Naphthol Green B] =  $3.33 \times 10^{-6}$  mol/l, [H<sub>2</sub>O<sub>2</sub>] =  $1.00 \times 10^{-3}$  mol/l, [Fe<sup>3+</sup>] =  $6.67 \times 10^{-4}$  mol/l, pH 3.2.

### Mechanism

On the basis of our experimental evidence and the existing literature, a tentative mechanism has been proposed for the photodegradation of Naphthol Green B with the photo-Fenton reagent.





An aqueous solution of ferric ions decomposes water on exposure to light into proton and  $\cdot\text{OH}$  radical, and ferric ions are reduced to ferrous ions. The ferrous ions decompose  $\text{H}_2\text{O}_2$  into hydroxide ion and hydroxyl radical and reoxidise to ferric ions. The reaction of ferric ions with  $\text{H}_2\text{O}_2$  upon irradiation produces  $\cdot\text{OOH}$  radicals. The reaction of  $\cdot\text{OH}$  with  $\text{H}_2\text{O}_2$  also produces  $\cdot\text{OOH}$  radicals. Ferrous ions will undergo oxidation to ferric ions by  $\cdot\text{OH}$  radicals, while ferric ions get reduced to ferrous ions by  $\cdot\text{OOH}$  radicals. The  $\cdot\text{OOH}$  radicals are highly unstable in water and undergo facile disproportionation rather than reacting slowly with the dye molecules. The participation of hydroxyl radicals as active oxidising species was confirmed by using a hydroxyl radical scavenger like propan-2-ol. As a result, the rate of photodegradation was drastically reduced.

The  $\cdot\text{OH}$  radicals are consumed in four different reactions. They can induce dissociation of  $\text{H}_2\text{O}_2$  into  $\cdot\text{OOH}$  and water or they combine to form  $\text{H}_2\text{O}_2$  molecules. Most importantly, they react with Naphthol Green B to give colourless degradation products.

The main advantage of using photo-Fenton reagent is the regeneration of the consumed  $\text{Fe}^{2+}$  ions on illumination. Each  $\text{Fe}^{2+}$  ion can produce many  $\cdot\text{OH}$  radicals in contrast to the dark Fenton reaction. The process is a cyclic one, only a single  $\cdot\text{OH}$  radical being formed per one ferrous ion. This means that the amount of ferrous salt required under photo-Fenton conditions is small compared to that under Fenton conditions, where ferrous ions need to be added in required intervals otherwise the reaction stops after complete conversion of ferrous ions to ferric ones. This is important for industrial application as further separation of ferric ions is not required after the waste water treatment<sup>36-41</sup>.

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