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Comparative decoloration study of Neutral Red by different oxidative processes

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Abstract

Neutral Red was subjected to two different oxidative processes, namely the photo-oxidative process and the Fenton process. The dye was found to undergo substantial and rapid decoloration by both the methods. Conditions were optimized in both the sets of experiments to achieve the most efficient dye decoloration. Additionally the effects of added anions on dye decoloration were examined and it was found that in both cases, the chloride ions caused a significant decrease in the decoloration rate. The kinetics data in both the cases fitted well to the first-order equation. A comparison of the effects of various anions on the decoloration rate revealed dramatic differences in apparent rate constant of decoloration of the dye especially in the presence of phosphate ions. Additionally the Fenton process was found to be more efficient in decolorizing the dye as compared to the photo-oxidative process.

Keywords: Neutral Red; Comparative decoloration; Fenton's reagent; Hydrogen peroxide

1. Introduction

Dye degradation/decoloration has drawn considerable attention by many workers in the last few years due to the numerous environmentally related problems caused by dye-contaminated industrial waste streams [1–3]. Moreover these solutions can be potentially toxic and carcinogenic due to the properties of many dyes [4,5]. On mixing with water bodies, they pose threat to all forms of life, including humans. Various studies in relation to dye removal and its degradation in aqueous systems have been proposed. Some of the common ones are the adsorption, biodegradation, radiation induced degradation and advanced oxidation process (AOP) methods [6–9]. On the contrary, very little literature is available in terms of comparative studies of dye degradation for a specific dye. In this paper, we are reporting results on one such dye, namely Neutral Red (belonging to the quinone–imine class of dyes), which was degraded using two different methods. The first method is the photo-oxidation of this dye with UV in the presence of H_2O_2, whereas, the second method focuses on its decoloration by a Fenton process [10]. The decoloration of this dye was also monitored in the presence of various ions which are commonly present in effluents, so as to examine their effect on the overall rate of decoloration of the dye solution by the two different approaches. The results were analyzed and interpreted on the merits of both the processes.

2. Materials and methods

2.1. Reagents

Neutral Red (F.W. = 288.8) was obtained from Sigma and used without any purification. Deionized water was used to make the dye solutions of desired concentration. Hydrogen peroxide (35% w/w) was obtained from Merck. $FeSO_4$ was prepared as a 0.1 M solution in 1 mM H_2SO_4 solution. UV/vis studies were carried out using a CARY 50 UV/vis spectrophotometer, using a 1 cm quartz cell. For photolytic experiments,

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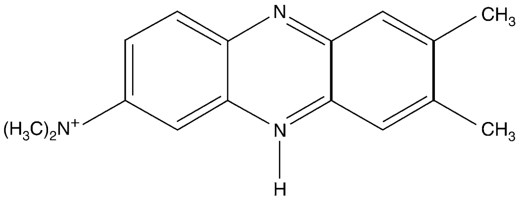

Fig. 1. Chemical structure of Neutral Red.

the samples were irradiated with a UV lamp with an output at 254 nm. HPLC analysis was carried out on an Agilent 1100 Series HPLC work station.

2.2. Preparation of samples and discoloration/degradation studies

All the experiments reported were carried out in a 4 ml quartz cuvette. Briefly, 3 ml of Neutral Red solution was mixed with either H_2O_2 and then exposed to UV radiation or with $FeSO_4/H_2SO_4$ and H_2O_2 (Fenton's reagent). Immediately after the addition of H_2O_2, scans were collected at regular intervals. For experiments examining the effects of different ions on the degradation of Neutral Red, a final concentration of 0.5 mg/ml of various salts was added to the cuvette before the addition of H_2O_2. None of the salts used had any effect on the Neutral Red spectra in the absence of H_2O_2.

2.3. HPLC analysis of the discoloration/degradation samples

For HPLC analysis of the dye decoloration/degradation, 50 ml of dye solutions were taken at either time zero (right after addition of H_2O_2 and no UV irradiation), 15 min or 30 min of UV irradiation after addition of H_2O_2, and the organic component of the mixture was extracted using chloroform. The organic layer was extracted again for a second time with chloroform, and then dried in a rotary evaporator. The dried substance (dye and/or degraded by-products) was then dissolved in 100% methanol and then used for HPLC analysis. The samples were run on C_8-Eclipse column (Agilent) using a 0–100% methanol (water as the base mobile phase) gradient over 30 min, at 1 ml/min.

3. Results and discussion

We were interested in comparing the efficiencies of the two AOPs, namely photolytic oxidation and Fenton chemistry, to degrade a specific dye. We chose a simple and well-known dye for this comparative study. Fig. 1 shows the structure of Neutral Red, a quinine–imine dye. Both photolytic and Fenton processes resulted in efficient time-dependent decoloration of the dye. However, we further examined the effect of varying the different parameters to find the optimum set of conditions for the most efficient degradation.

The scheme for photolytic oxidation of dyes has been reported by us and others [11]. In brief, UV radiation causes photolysis of H_2O_2 to produce hydroxyl radicals ($OH^{\bullet}$), which then reacts with the dye to eventually degrade it:

$$H_2O_2 \rightarrow {}^{\bullet}OH + {}^{\bullet}OH$$

Fig. 2 shows the time-dependent decoloration of Neutral Red upon exposure to H_2O_2/UV reagent. The figure also shows dye decoloration data fitted to first-order kinetic equation as shown below:

$$\ln A_t - \ln A_0 = -kt$$

where A_0 and A_t are the initial and the final absorption values, k is the apparent rate constant and t is the irradiation time.

To confirm that the decoloration observed was in fact due to dye degradation, samples were taken from the photolytic oxidation of the dye and examined by reverse-phase HPLC. As can be seen in Fig. 3, after 15 min of H_2O_2/UV treatment, significant amount of the parent dye peak had been used up, and new product peaks would be seen. This is much more evident in the 30 min sample, in which most of the parent dye peak is gone and numerous additional product peaks are evident. Hence, the decoloration we see in our experiments is in fact due to dye degradation.

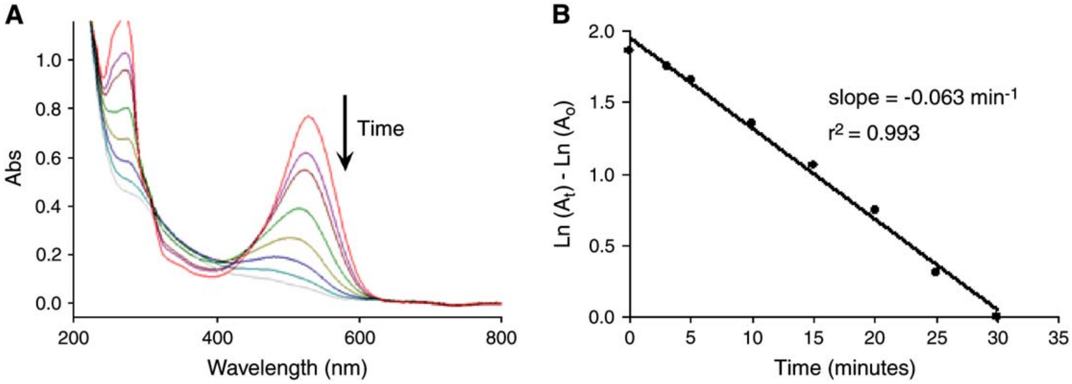

Fig. 2. Time-dependent decoloration of Neutral Red by the photolytic process. (A) UV/vis scan of dye solution after exposure to H_2O_2/UV. Scans were taken at 0, 3, 5, 10, 15, 20, 25, and 30 min. (B) First-order curve fitting of the Neutral Red decoloration data.

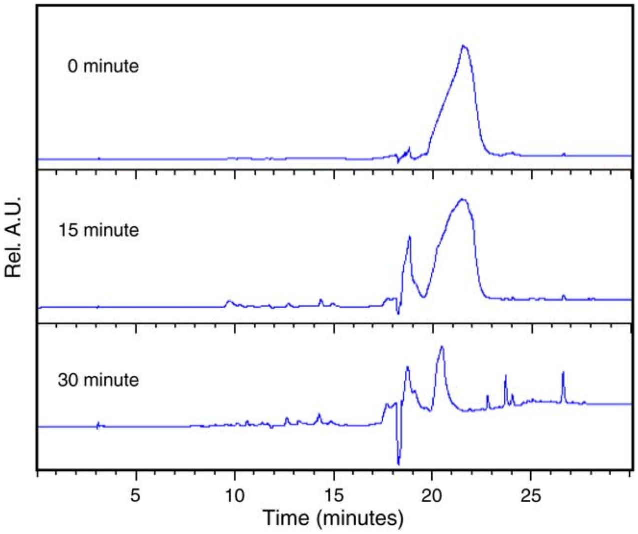

Fig. 3. HPLC analysis of the decoloration/degradation of Neutral Red by the photolytic process. Samples were taken at either 15 or 30 min after exposure to H_2O_2/UV. Time zero sample is Neutral Red with H_2O_2 only (no UV). Samples were prepared as described in Section 2.

In order to find the optimum concentration of H_2O_2 for the photolytic decoloration studies, a fixed concentration of dye solution was subjected to UV radiation with increasing amounts of hydrogen peroxide. Table 1 shows the results from this study, in which increase in the amount of H_2O_2 resulted in faster decoloration of the dye. It is worth pointing that at very high H_2O_2 concentration, the apparent rate of decoloration did not change much. This is probably due to the self-quenching of hydroxyl radicals for H_2O_2. Thus too much H_2O_2 can in fact inhibit photolytic oxidation process.

Similarly, the effect of dye concentration on the decoloration was examined by varying concentration of Neutral Red at fixed concentration of H_2O_2. Table 2 shows that dye decoloration appeared to abruptly fall drastically at 133 μM. Thus, the optimum decoloration of Neutral Red was achieved at 65 μM dye solution with 6.7 mM H_2O_2.

Additional experiments using this optimized decoloration conditions were carried out to examine the effect of some anions namely chloride, nitrate, phosphate and sulphate ions. These anions are generally present in the dye discharge of many industrial effluents [12]. Thus it would be necessary to monitor the effect of such anions on the rate of decoloration of the dye. The results of such studies are presented in Table 3.

Table 1
The effect of $[H_2O_2]$ on photolytic decoloration of Neutral Red

$[H_2O_2]$ (mM)	$k \times 10^{-2}$ (min^{-1})	% Decoloration
1.7	3.0	60
3.3	5.0	79
6.7	6.3	84
13.2	9.0	92
20	10	94

Concentration of dye = 65 μM.

Table 2
The effect of Neutral Red [NR] concentration on photolytic decoloration

[NR] (μM)	$k \times 10^{-2}$ (min^{-1})	% Decoloration
133	2.5	53
65	6.3	84
32.5	9.0	92
16.25	15	95

$[H_2O_2] = 6.7$ mM.

It can be seen from this table that all the ions had some significant effect on the rate of decoloration. Both nitrate and phosphate resulted in as much as 30% decrease in the rate of decoloration, whereas chloride and sulphate ions decreased the rate by 20%. Thus, these ions should be removed from the dye solution prior to photolytic decoloration.

In order to compare the efficiency of dye decoloration by using another advanced oxidation processes, we chose the Fenton process. In general, the Fenton's reagent generates ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals, which are strong oxidizing reagents, to react with the dye solution and degrade it [13,14].

$$H_2O_2 + Fe^{+2} \rightarrow {}^{\bullet}OH + OH^- + Fe^{+3} \quad k = 70\ M^{-1}\ s^{-1} \tag{1}$$

The hydroxyl radical propagates the reaction by reacting with the organic dye (RH) to produce further radicals, which can then react in many different steps.

$${}^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet} \quad k = 10^9 - 10^{10}\ M^{-1}\ s^{-1} \tag{2}$$

$$R^{\bullet} + H_2O_2 \rightarrow ROH + HO^{\bullet} \tag{3}$$

Additionally many other reactions are also possible, which include the radical–radical reaction or the reaction of the OH radical with H_2O_2

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{4}$$

$${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad k = 3.3 \times 10^7\ M^{-1}\ s^{-1} \tag{5}$$

The peroxide radicals ($HO_2^{\bullet}$) produced in the above case can further oxidize other species present in the solution.

Table 3
The effect of ions (0.5 mg/ml) on photolytic decoloration of Neutral Red

Ions	$k \times 10^{-2}$ (min^{-1})	% Decoloration
–	6.3	84
$NaNO_3$	4.3	72
Na_3PO_4	4.3	73
Na_2SO_4	5.0	76
NaCl	5.0	78

[Dye] = 65 μM, $[H_2O_2] = 6.7$ mM.

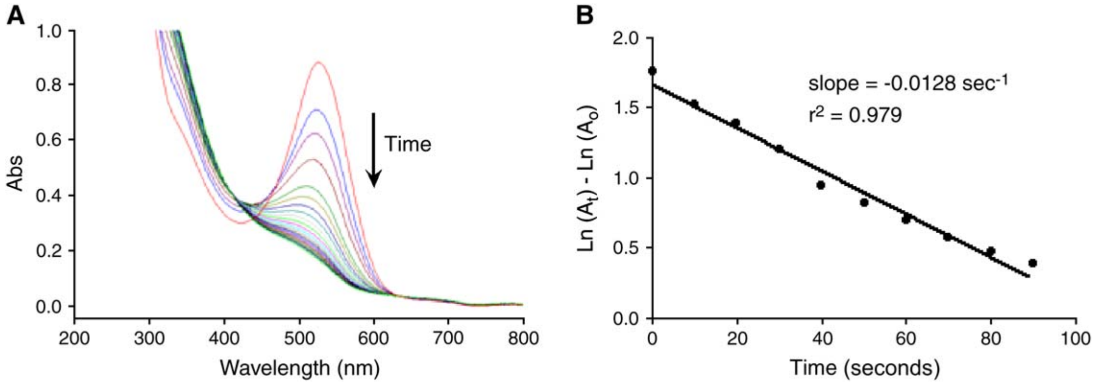

Fig. 4. Time-dependent decoloration of Neutral Red by the Fenton process. (A) UV/vis scan of dye solution after exposure to Fe^{2+}/H_2O_2. Scans were taken at 10 s intervals for 5 min. (B) First-order curve fitting of the Neutral Red decoloration data.

$$HO_2^{\bullet} + Fe^{+3} \rightarrow O_2 + Fe^{+2} + H^{+} \quad k = 1.26 \times 10^{6}\ M^{-1}\ s^{-1} \tag{6}$$

The rapid consumption of H_2O_2 that is often observed with Fenton's reagents is probably due to combined effect of reactions (1)–(4). However, since reaction (2) has the highest rate constant, it is mainly responsible for the degradation of the dye. Furthermore, it is possible for Fe^{2+} to be auto-regenerated in this system, and acts as a catalyst [15].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^{+} + HO_2^{\bullet} \tag{7}$$

Fig. 4 shows the time-dependent decoloration of Neutral Red upon exposure to Fenton's reagent. Like the photolytic oxidation of the dye, the Fenton decoloration was also found to fit to the first-order kinetics. However, it is obvious that the decoloration rate with Fenton was much faster than observed with photolytic process. A systematic optimization study was carried out to find the optimum set of condition for decoloration of Neutral Red using the Fenton process.

Table 4 shows the effect of varying Neutral Red concentration on the apparent rate of decoloration as well as % decoloration. Just like in the photolytic process, we found 65 μM Neutral Red to be the best choice for this process.

Likewise, the effect of H_2O_2 concentration was also studied, as shown in Table 5. Higher concentration of H_2O_2, in general, resulted in faster decoloration rate; however, it was

Table 4
The effect of dye concentration on Neutral Red decoloration by Fenton's reagent

[NR] (μM)	$k \times 10^{3}$ (min^{-1})	% Decoloration (in less than 5 min)
133	5.8	60
65	13	88
32.5	24	96
16.25	54	99

$[H_2O_2] = 0.17$ mM, $[Fe^{2+}] = 0.34$ mM.

Table 5
The effect of H_2O_2 concentration on Neutral Red decoloration by Fenton's reagent

$[H_2O_2]$ (mM)	$k \times 10^{-3}$ (s^{-1})	% Decoloration (in less than 5 min)
0.17	13	88
0.33	34	97
0.67	65	98
1.3	89	98
2.0	77	92

[Dye] = 65 μM, $[Fe^{2+}] = 0.34$ mM.

Table 6
The effect of Fe^{2+} concentration on Neutral Red decoloration by Fenton's reagent

$[Fe_2SO_4]$ (mM)	$k \times 10^{-3}$ (s^{-1})	% Decoloration (in less than 5 min)
0.04	2.0	52
0.08	3.5	74
0.16	5.0	83
0.34	13	88
0.67	17	88
1.34	15	52

[Dye] = 65 μM, $[H_2O_2] = 1.6$ mM.

Table 7
The effect of various ions in Fenton process mediated decoloration of Neutral Red

Ions	$k \times 10^{3}$ (min^{-1})	% Decoloration (in less than 5 min)
–	13	88
Na_2SO_4	9.0	77
NaCl	6.7	74
$NaNO_3$	11	87
Na_3PO_4	5.5	77

[Dye] = 65 μM, $[Fe^{2+}] = 0.34$ mM, $[H_2O_2] = 0.17$ mM, [ions] = 0.5 mg/ml.

Table 8
Comparison of the effects of ions on dye decoloration by photolytic oxidation and the Fenton processes

Anions	Change in relative apparent rate (%)	
	Photolytic process	Fenton process
–	100	100
Nitrate	68	85
Phosphate	68	42
Sulphate	79	69
Chloride	79	52

interesting to note that beyond 1.3 mM of H_2O_2, both the decoloration rate and the % dye decoloration decreased.

Examination of varying the Fe^{2+} concentration on dye decoloration also showed a similar pattern. As can be seen in Table 6, added increasing concentrations of Fe^{2+} resulted in both the rate and the % decoloration to increase to an optimum level; however, beyond 0.67 mM Fe^{2+}, both these values started to decrease.

Lastly, the decoloration of Neutral Red by Fenton process was also investigated in the presence of the same four anions (chloride, nitrate, phosphate and sulphate ions) which were tested for the photolytic oxidation process of Neutral Red. Each of these added ions caused a certain change in % degradation of the dye solution. In the absence of these salts, the dye degraded by 88% in less than 5 min at room temperature. However, with the addition of these salts to the dye solution, some additional changes were observed (Table 7). The maximum decrease in degradation rate was 60% which was observed in the case of phosphate. Chloride ions also caused a significant change of 52%. The mechanism of decoloration inhibition in the presence of chloride ions has been reported elsewhere [16]. Other anions that were tested also showed inhibitory effects.

Table 8 shows the comparison of the effects of various anions on the decoloration rate of Neutral Red by the two processes. As can be seen from the table, the ions had different affects on the rate of decoloration, depending on the AOP being used. For example, chloride and phosphate ions inhibited the Fenton process more than the photolytic process; whereas, nitrate appeared to affect the photolytic process more.

4. Conclusion

In summary, we have reported a comparative study on the efficiency of photolytic oxidation and Fenton process for the decoloration of Neutral Red. Our results show that the Fenton process is much more efficient than the photolytic process for decolorizing this dye. Examination of the effects of various ions showed that most of the anions tested inhibited both the processes; however, there were pronounced differences in the effects of these ions depending on the AOP being used.

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