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A comparative study of Neutral Red decoloration by photo-Fenton and photocatalytic processes

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Abstract

Neutral Red was subjected to two different advanced oxidative processes, namely the photo-Fenton process and the photocatalytic process. The dye was found to undergo substantial and rapid decoloration by both the methods, however, the photo-Fenton-mediated decoloration of the dye was much more efficient. Conditions were optimized in both set of experiments to achieve the most efficient dye decoloration. Additionally the effects of added anions on photocatalytic and photo-Fenton-mediated dye decoloration were examined and compared to our previously published results with photolytic and Fenton-mediated Neutral Red decoloration. Most of the ions tested had an inhibitory effect on photo-Fenton process, but unexpectedly enhanced the photocatalytic process, except for chloride, which inhibited both the processes. The kinetics data in both the cases fitted well to the first-order equation. Comparison of the results among the four different advanced oxidation processes shows that Neutral Red is most efficiently degraded by photo-Fenton process, followed by Fenton process, then photolytic, and then with photocatalytic process.

Keywords: Neutral Red; Comparative decoloration; Fenton's reagent; Photocatalysis; Titanium oxide

1. Introduction

Synthetic dyes are widely used in many industries such as leather, paper, textile, etc. to impart fast colors to the desired products. Many of these dyes are complex organic molecules consisting of substituted sites or linkages. On exposure to environmental conditions, the effluent discharge of these industries containing these dye molecules pose a potential threat to living organisms and to water bodies at large which are the ultimate source of life for all the living species [1–5]. Since most of these dye molecules are water soluble, their removal from water effluent by conventional means is not easy. Various methods have been suggested to handle the dye removal from water; these include biodegradation, coagulation, adsorption, advanced oxidation (AOP) and the membrane process [6–10]. All these processes have some advantages or disadvantages over the other method. A balanced approach is therefore needed to look into the worthiness on choosing an appropriate method which can be used to degrade the dye in question. On the contrary, very little literature is available in terms of comparative studies of dye degradation for a specific dye. In our earlier studies we have reported a comparative study on the efficiency of photolytic oxidation and Fenton process for the decoloration of Neutral Red (belonging to the quinone-imine class of dyes) [11]. Our results showed that the Fenton process was 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. In this paper we are extending our work by looking at the comparative study of Neutral Red decoloration by two photo-induced phenomena namely the photo-Fenton oxidation of this dye with UV in the presence of H_2O_2, and the photocatalytic decoloration of the dye. Both the processes have a common denominator of a photon injection; however, they differ widely

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in the sense that the former has an added amount of H_2O_2 which causes the production of OH radicals which are responsible for further reaction in the media. On the other hand, the latter process is in the presence of a catalyst (TiO_2 in this case), which causes the release of electrons on irradiation. These electrons can then take part in further reactions as discussed later in this paper. 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 based on the merits of both the processes.

2. Materials and methods

2.1. Reagents

Neutral Red (FW = 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, the samples were irradiated with a UV lamp with an output at 254 nm. For the decoloration processes, Neutral Red stock solution of 1.2×10^{-2} M was prepared in 100 mL of deionized water in a 250 mL flask. Necessary dilutions of this stock were done with deionized water.

2.2. Preparation of samples and discoloration/degradation studies using photo-Fenton process

All the experiments reported were carried out in a 4 mL quartz cuvette. Briefly, 3 mL of Neutral Red solution was mixed with $FeSO_4/H_2SO_4$ and H_2O_2 (Fenton's reagent) and then exposed to UV radiation. Scans were collected at regular intervals of time after irradiation. 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 were added to the cuvette before the addition of $FeSO_4/H_2SO_4 + H_2O_2$ and UV light.

2.3. Preparation of samples and discoloration/degradation studies using photocatalytic process

A 50 mg/50 mL of the catalyst (titanium oxide) was added to an appropriately diluted Neutral Red solution. The contents of the dye solution were allowed to equilibrate for 30 min in the dark before irradiating the solution with a UV light of 254 nm for a given period of time. During irradiation, the contents of the solution were agitated continuously so as to maintain a homogeneous environment. A series of such solutions were taken in different beakers and subjected to UV radiation. After a certain time interval, 3 mL of the sample was withdrawn, filtered through a 0.45 μm filter and the absorbance of the filtrate was monitored using a spectrometer. The absorbance value obtained in each case was plotted against time to obtain the order of discoloration rate.

3. Results and discussion

Waste effluents from textile industries are a major source of water pollution. These waste streams contain numerous toxic dyes, which are resistant to natural breakdown and degradation. Therefore, there is a need to find economical and bio-friendly methods to degrade textile dyes. Numerous approaches have been taken to clean up and degrade these dye pollutants, however, the most promising among them are the Advanced Oxidative Processes (AOP). Among the most promising of these AOP include generation of hydroxyl radicals from H_2O_2 using either of the following: (1) UV radiation (photolysis), (2) Fe^{2+} ions (Fenton's reagent), (3) combination of UV and Fe^{2+} (UV peroxidation), or (4) using TiO_2 (TiO_2 photocatalysis). Extensive work has been done on the use of these approaches to degrade dyes; however, comprehensive comparative studies comparing the efficiencies of these processes on the same dye are very few. Previously, we had reported on a comparative decoloration study of Neutral Red using the photolytic and the Fenton processes [11].

In this study we wanted to compare the efficiencies of two additional photo-induced AOP, namely photo-Fenton oxidation and the photocatalytic process, to degrade Neutral Red (a quinine-imine dye). The structure of this dye is given in Fig. 1. Both photo-Fenton and the photocatalytic processes resulted in efficient time-dependent decoloration of the dye, which fits first-order rate decay and could be used to extract apparent rate constants (Figs. 2 and 3). However, we were interesting in examining the various parameters to find the optimized conditions for the most efficient degradation of Neutral Red. Furthermore, we wanted to study the effects of various salts on these oxidative processes.

3.1. Photo-Fenton studies on Neutral Red

The Fenton reaction has been commonly used for non-biodegradable waste effluents [12]. However, they have a likely disadvantage of producing large sludge containing iron and also that the reaction is generally slow in its application [13]. Illumination of the Fenton's system by a UV/vis light was suggested to overcome these problems [14]. The photoreduction causes the production of ferrous ions and other radical species such as $^{\bullet}OH$, $HO_2^{\bullet}$ and $O_2^{-\bullet}$. Since many operational

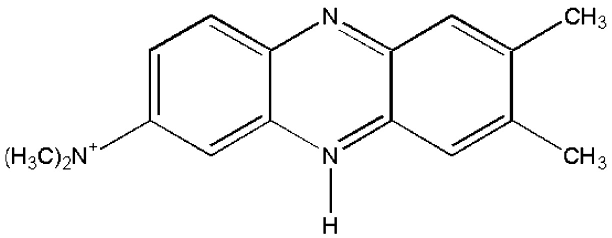

Fig. 1. Chemical structure of Neutral Red used in the present study.

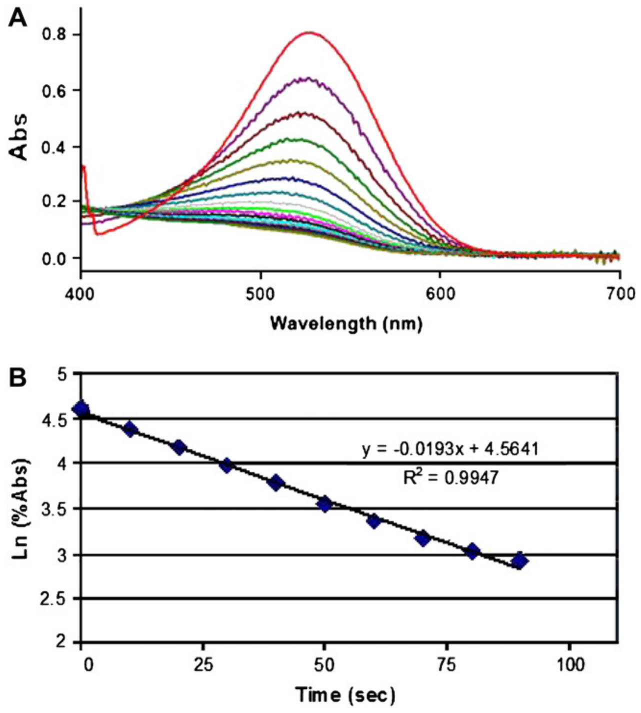

Fig. 2. Time-dependent decoloration of Neutral Red by the photo-Fenton process. (A) UV/vis scans of the dye solution after exposure to $Fe^{2+}/H_2O_2 + UV$. Scans were taken at 10 s intervals. (B) First-order curve fitting of the photo-Fenton-mediated Neutral Red decoloration.

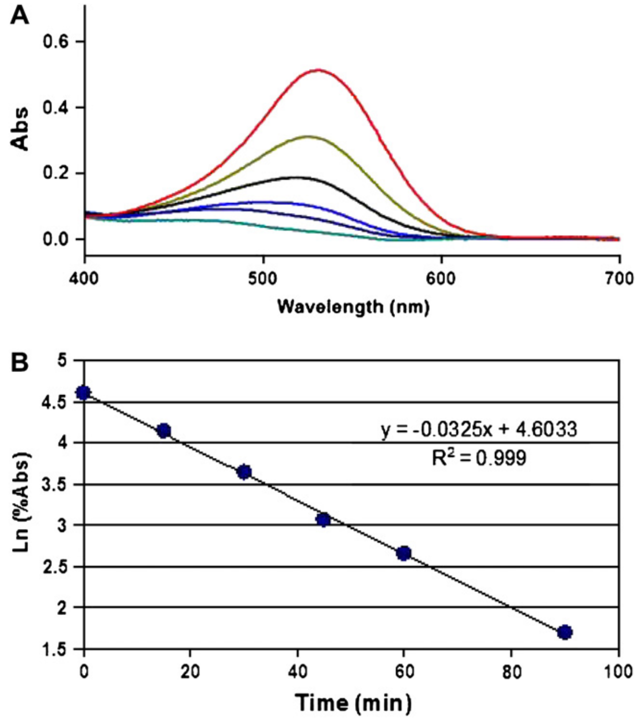

Fig. 3. Time-dependent decoloration of Neutral Red by the photocatalytic process. (A) UV/vis scans of the dye solution after exposure to $TiO_2 + UV$. Scans were taken at 0,15, 30, 45, 60, and 90 min. (B) First-order curve fitting of the photocatalytic-mediated Neutral Red decoloration.

Table 1
The effect of $[Fe^{2+}]$ on photo-Fenton oxidation of Neutral Red

$[Fe^{2+}]$ (μM)	k (s^{-1}) × 10^{-3}	% Decoloration (in 2 min)
42	5.3	51
83	6.9	66
167	12	84
333	20	82
667	18	75
1333	15	62

[Dye] = 65 μM; H_2O_2 = 1.67 mM.

parameters are involved in this scheme, it was therefore necessary to optimize the conditions of maximum degradation by varying the experimental conditions. These included the concentration of the Fenton's reagent (specifically, Fe^{2+}), the amount of H_2O_2 and the irradiation time.

In order to find the optimum concentration of the Fenton's reagent in the photo-Fenton studies, a fixed concentration of dye solution and H_2O_2 was subjected to UV radiation with increasing amounts of Fenton's reagent. The % decoloration was calculated in a usual manner and the results are depicted in Table 1 and Fig. 4. An optimized concentration of 0.3 mM of the Fe^{2+} was found from this set of experiments.

Similarly, the effect of H_2O_2 concentration on the decoloration was examined by fixing the dye concentration and Fe^{2+}. The % degradation of Neutral Red at fixed concentration of H_2O_2 in this case is shown in Table 2. Unlike the Fenton process, where higher concentrations of H_2O_2 resulted in the inhibition of the AOP, in the photo-Fenton process, we did not see this effect even at very high H_2O_2 concentrations (Table 2). Furthermore, comparing the Fenton [11] and the photo-Fenton processes, it appears that the latter is a more efficient process for the decoloration of Neutral Red.

Likewise, dye concentration was altered in the experiment while keeping the values of the Fenton's reagent constant. Like the previously published Fenton study, the optimized value for dye concentration in the photo-Fenton process was found to be 65 μM (Table 3).

The effect of some additional ions on the dye coloration (apparent rate constant as well as % dye degradation) was also studied. These ions are generally present in the waste effluent and can thus cause a considerable effect on dye

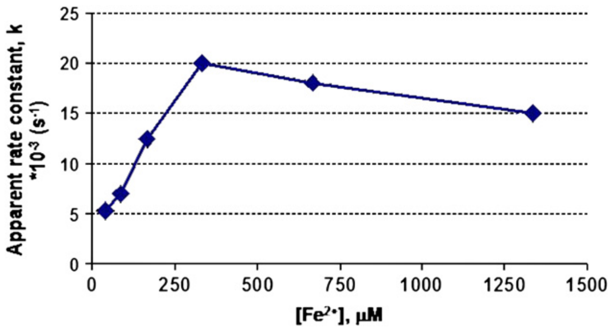

Fig. 4. Effect of Fe^{2+} concentration on photo-Fenton-mediated oxidation of Neutral Red ([dye] = 65 μM and $[H_2O_2]$ = 1.67 mM).

Table 2
The effect of $[H_2O_2]$ Neutral Red [NR] degradation in a photo-Fenton process

$[H_2O_2]$ (mM)	k (s^{-1}) × 10^{-3}	% Decoloration (in 2 min)
0.17	26	76
0.33	25	93
0.67	42	93
1.3	82	93
2.7	110	97

$[Fe^{2+}] = 0.33$ mM; [NR] = 65 μM.

Table 4
The effect of ions on Neutral Red decoloration in a photo-Fenton process

Ions	k (s^{-1}) × 10^{-3}	% Decoloration (in 2 min)
–	20	82
$NaNO_3$	17	85
Na_3PO_4	15	70
Na_2SO_4	15	73
NaCl	10	58

[Dye] = 65 μM; $[Fe^{2+}] = 333$ μM; $[H_2O_2] = 1.67$ mM.

degradation. The salts of these ions were added in a fixed quantity to the reaction mixture before adding the other ingredients in solution. No change in absorbance value of the dye solution was noted in the sole presence of these ions. The salts selected were NaCl, $NaNO_3$, Na_3PO_4 and Na_2SO_4 (Table 4). All the four salts were found to inhibit the photo-Fenton process, with chloride ions having the greatest inhibitory effect (50% inhibition). The observed effect of the ions was very similar to what we had seen earlier with the Fenton study [11].

3.1.1. Reaction scheme for dye degradation using the photo-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 [15]

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

Additional amounts of ${}^{\bullet}OH$ radicals are also produced from the direct photolysis of H_2O_2

$$H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH$$

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

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

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

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 ($HO_2^{\bullet}$) can produce H_2O_2 and O_2 through disproportionation reaction or can react with Fe^{2+}

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad k = 8.3 \times 10^5\ M^{-1}\ s^{-1} \tag{6}$$

$$HO_2^{\bullet} + Fe^{2+} + 2H^+ \rightarrow Fe^{3+} + H_2O_2 \quad k = 1.26 \times 10^6\ M^{-1}\ s^{-1} \tag{7}$$

Since reaction (2) has the highest rate constant, it is mainly responsible for degrading the dye.

Table 3
The effect of Neutral Red [NR] concentration on % degradation in a photo-Fenton process

[Dye] (μM)	k (s^{-1}) × 10^{-3}	% Decoloration (in 2 min)
133	12	68
65	20	82
32.5	26	92
16	51	94

$[Fe^{2+}] = 333$ μM; $[H_2O_2] = 1.67$ mM.

3.2. Photocatalytic studies on Neutral Red

Photocatalytic decoloration of Neutral Red was studied by using Titanium (IV) oxide (TiO_2) together with UV light to degrade an aqueous solution of the dye. A significant adsorption of the dye is observed when the dye and the catalyst (TiO_2) are incubated together (in the dark), however, this adsorption levels off after 30 min. Thus all photocatalytic experiments were done after this equilibration time of 30 min. When the dye is exposed to UV radiation in the absence of any catalyst, no decoloration of the dye is observed. However, exposure of the dye to both TiO_2 and UV light resulted in immediate decoloration of the dye, which follows a first-order decay rate (Fig. 3).

The Neutral Red concentration in solution was varied to see the effect of dye concentration on the photocatalytic decoloration. It was noted that both the % decoloration and the apparent rate constant had an inverse relationship with the dye concentration, with the highest decoloration rate being observed at the lowest dye concentration (32.5 μM) tested (Table 5). This can be rationalized on the basis that at high concentrations of the dye, the photons (from UV light) are not able to enter the solution, and thus the generation of hydroxyl radicals is slowed down (as discussed below).

Table 5
The effect of Neutral Red concentration on its % decoloration in a photocatalytic process

[Neutral Red] (μM)	k (min^{-1}) × 10^{-3}	% Decoloration (in 15 min)
133	12	22
65	33	38
32.5	148	89

$[TiO_2] = 50$ mg/mL.

3.2.1. Reaction scheme for dye degradation using the photocatalytic process

When a catalyst such as TiO_2 is exposed to UV radiation, electrons are promoted from the valence band to the conduction band. As a result of this, an electron–hole pair is produced [16]

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb} \tag{8}$$

where, e^-_{cb} and h^+_{vb} are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both these entities can migrate to the catalyst surface, where they can enter in a redox reaction with other species present on the surface. In most cases h^+_{vb} can react easily with surface bound H_2O to produce OH radicals, whereas, e^-_{cb} can react with O_2 to produce superoxide radical anion of oxygen

$$H_2O + h^+_{vb} \rightarrow OH^{\bullet} + H^+ \tag{9}$$

$$O_2 + e^-_{cb} \rightarrow O_2^{-\bullet} \tag{10}$$

This reaction prevents the combination of the electron and the hole which are produced in the first step.

The $OH^{\bullet}$ and $O_2^{-\bullet}$ produced in the above manner can then react with the dye to form other species and is thus responsible for the decoloration of the dye

$$O_2^{\bullet}- + H_2O \rightarrow H_2O_2 \tag{11}$$

$$H_2O_2 \rightarrow 2^{\bullet}OH \tag{12}$$

$$OH^{\bullet} + \text{dye} \rightarrow \text{dye}_{ox} \quad k = 10^9\text{–}10^{10}\ M^{-1}\ s^{-1} \tag{13}$$

$$\text{Dye} + e^-_{cb} \rightarrow \text{dye}_{red} \tag{14}$$

Lastly, the decoloration of Neutral Red by photocatalytic process was also investigated in the presence of the same four anions namely chloride, nitrate, phosphate and sulphate ions, which were tested for the photo-Fenton oxidation process of Neutral Red, as well as for the previously published photolytic and Fenton processes [11]. 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 37% in 15 min at room temperature. However, with the addition of these salts to the dye solution, some additional changes were observed (Table 6). Nitrate, phosphate and sulphate ions all caused increased in the decoloration of the dye, with phosphate enhancing the decoloration the most (apparent rate constant increased by almost 230%). Chloride ions caused a significant inhibition of the dye decoloration process. The mechanism of decoloration in the presence of chloride ions has been reported elsewhere [17]. The dramatic enhancement of decoloration by phosphate, nitrates, and sulphate ions was much unexpected. We hypothesize that these ions are somehow enhancing the process by which hydroxyl radicals are generated from TiO_2 thereby leading to enhanced dye degradation. Further research is needed to elucidate the exact mechanism of this effect.

Table 6
The effect of ion concentration on Neutral Red decoloration in a photocatalytic process

Ions	k (min^{-1}) × 10^{-3}	% Decoloration (in 15 min)
–	33	37
$NaNO_3$	76	61
Na_3PO_4	79	76
Na_2SO_4	59	53
NaCl	25	33

[Dye] = 65 μM; [TiO_2] = 50 mg/mL.

Table 7
Comparison of the effects of ions on dye decoloration by photolytic, Fenton, photo-Fenton, and photocatalytic processes

Anions	Relative change in apparent rate (%)			
	Photolytic	Fenton	Photo-Fenton	Photocatalytic
–	100	100	100	100
Nitrate	68	85	85	230
Phosphate	68	42	75	239
Sulphate	79	69	75	179
Chloride	79	52	50	76

A comparison of the effect of these ions on the apparent rate constants of dye decoloration by the four AOPs, photolytic, Fenton, photo-Fenton, and photocatalytic is shown in Table 7. As can be seen from the data, the ions had differing effects on the decoloration process. For example, phosphate, nitrate, and sulphate ions all inhibited the photolytic, Fenton, and photo-Fenton processes, but unexpectedly they caused dramatic enhancement in the photocatalytic process. On the other hand, chloride ions had an inhibitory effect on all the four AOPs. These different effects of the ions highlight the importance of testing various ions when optimizing a specific AOP for degrading a specific compound or dye.

4. Conclusion

In this study we have reported a comparative study on the efficiency of photo-Fenton oxidation and photocatalytic process for the decoloration of Neutral Red. Our results show that the photo-Fenton process is much more efficient than the photocatalytic process for decolorizing this dye. Comparison of previously published data with the current study leads to the following rank order for the AOPs for efficient degradation of NR: photo-Fenton > Fenton > photolytic > photocatalytic. Examination of the effects of various ions showed that they had significant and varying effects on the dye decoloration, depending on the AOP being used.

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