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Degradation of Methyl Red using Fenton's reagent and the effect of various salts

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Abstract

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. In this study, degradation of Methyl Red, an azo dye, was studied using the ferrous-hydrogen peroxide system. The oxidation and subsequent degradation of the dye was found to be dependent on both the amount of Fe^{2+} ions as well as hydrogen peroxide. In order to study the effect of other salts that are normally present in textile waste streams, a systematic study was carried out using 10 different salt solutions. Some of the ions tested enhanced the rate and extent of degradation of the dye, whereas some had an inhibitory effect. The rates of degradation were found to fit to first-order kinetics.

Keywords: Methyl Red; Fenton's reagent; Dye degradation; Decolourization; Textile waste; Hydrogen peroxide

1. Introduction

There are numerous types of synthetic dyes like azo, vat, nitro, indigo etc., which are widely used for different purposes in paper and pulp manufacturing, and printing and textile industry [1–3]. The effluents from these industries cause the water bodies not only to become colored, but also cause an environmental damage to the living organisms by stopping the re-oxygenation capacity of water and also blocking sunlight, thereby, causing a disturbance in the natural growth activity of aquatic life [4]. Furthermore, some of these dyes on passage to drinking water cause damage to human life as some of these dyes are carcinogenic in nature [5,6]. It is, therefore, essential to remove these dyes from water bodies or treat them in such a way so as to minimize the damage to the environment and also decolorize the water.

Many different approaches have been suggested to tackle the removal of dyes from aqueous solution. Among the widely used ones are the adsorption methods, biological degradation, coagulation processes and the ozone and hypochlorite treatment of dye waste effluents [7–9]. All these methods are either costly, inefficient or result in the production of secondary waste product. Recent progress on this frontier has led to study the feasibility of using advanced oxidation processes, AOP [10]. Among the promising methods in this category, utilizes a reagent which is a mixture of H_2O_2 and Fe^{2+}, commonly known as the Fenton's reagent [11]. There are quite a few studies on the usage of this reagent with the aim to degrade a particular species under consideration [12–14]. Additionally, Fenton's reagent in the presence of UV radiation, a process called as photo-Fenton reaction, has also been studied and has shown promising results [15]. This paper reports the findings of the degradation of Methyl Red using the Fenton's reagent. The effect of various additives on the degradation of the dye solution

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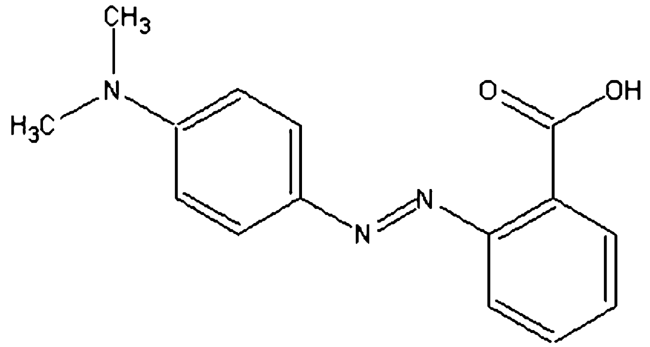

Fig. 1. Structure of Methyl Red.

was also studied and a plausible explanation is given with regard to the stability of the dye in their presence.

2. Materials and methods

2.1. Reagents

Methyl Red (FW = 269.31) was procured from Fluka and used as such. Deionized water was used to make the dye solutions of desired concentration. Hydrogen peroxide (35% w/w) was obtained from Merck and used at a final concentration of 5 mM. $FeSO_4$ was prepared as a 0.1 M solution in 1 mM H_2SO_4 solution. Methyl Red used in all the experiments was at a concentration of 50 μM in water. UV/VIS studies were carried out using a CARY 50 UV/VIS spectrophotometer, using a 1 cm quartz cell. The kinetic constants reported here were obtained by using the Cary WinUV software suite.

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 50 μM Methyl Red solution was mixed with 30 μl of 0.1 M $FeSO_4$/1 mM H_2SO_4. The Fenton chemistry reaction was started by the addition of 15 μl of 1 M H_2O_2. Immediately after the addition of H_2O_2, scans were collected every 6 s, for a total of 2 min. For experiments, examining the effects of different ions on the degradation of Methyl 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 Methyl Red spectra in the absence of H_2O_2.

3. Results and discussion

This paper deals with the degradation of Methyl Red with Fenton's reagent. The structure of the dye is given in Fig. 1. The dye has an absorption maximum at 440 nm in

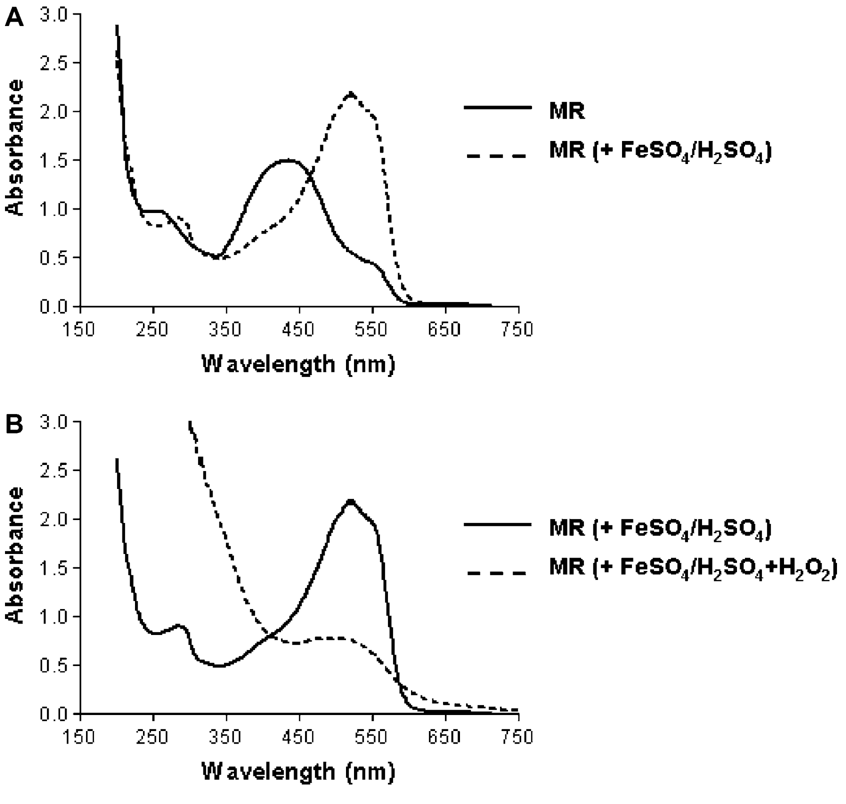

Fig. 2. (A) Shifting of MR spectra when $FeSo_4$/H_2SO_4 is added (dashed line). (B) Degradation of Methyl Red using the Fenton Reagent (dashed line).

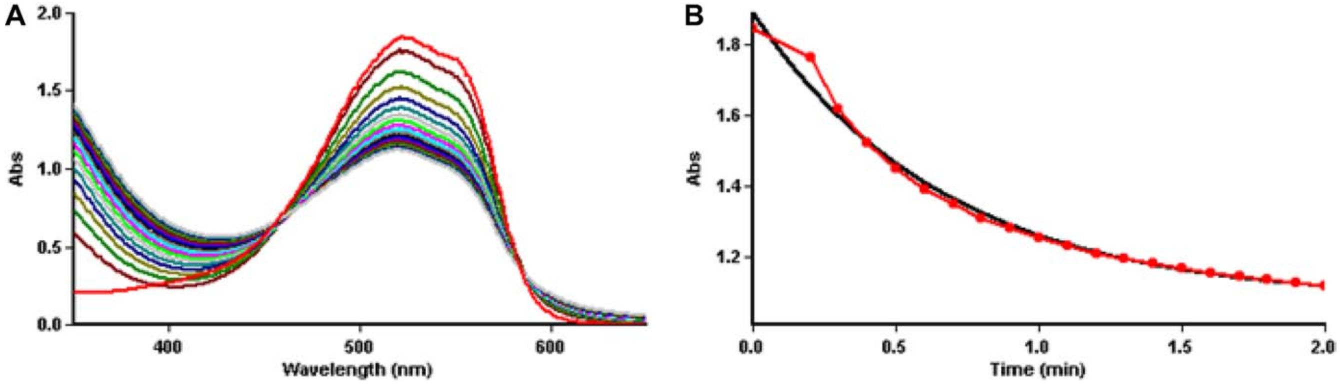

Fig. 3. (A) Time-dependent degradation of Methyl Red with Fenton's reagent. (B) First-order kinetic of the degradation of MR, solid circles = experimental data, solid line = theoretical curve for first-order kinetics.

aqueous solution. This maximum is shifted towards higher wavelength in the presence of acidic $FeSO_4$. Fig. 2 depicts the change in absorption maxima of the dye solution. For degradation studies, the decrease in the shifted peak at 520 nm was monitored. The degradation of this dye in the presence of H_2O_2 and acidic $FeSO_4$ (Fenton's reagent) was carried out. Initially, experiments were carried out in the absence and presence of either Fenton's reagent or H_2O_2 alone. The results showed no degradation in such individual cases. However, when the two reagents were mixed together in the dye solution, rapid and significant dye degradation was observed. The change in absorption value of the dye solution with time is shown in Fig. 3, along with the experimental and the theoretical curve fitting of the change in absorbance values with time. Both of these agree within acceptable limits of experimental conditions. The absorption data of the dye solution were fitted to the first-order rate equation. The rate constant value for the degradation of the dye and was found to be 1.48 min^{-1}.

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.

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

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.

Table 1
Comparison of various ions in municipal water and textile waste streams [17]

Ion	Concentration in normal municipal water (mg/l)	Concentration in textile waste stream (mg/l)
K^+	20	40
Cl^-	7.6	17.5
Na^+	4.2	139.5
PO_4^{-3}	0.02	16.4

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

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

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

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

$${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad k = 3.3 \times 10^7\ M^{-1}\ s^{-1} \qquad (3)$$

The peroxide radicals ($HO_2^{\bullet}$) produced in the above case can further oxidize other species present in the solution [16]

$$HO_2^{\bullet} + Fe^{2+} \rightarrow O_2 + Fe^{3+} + H^+ \quad k = 1.26 \times 10^6\ M^{-1}\ s^{-1} \qquad (4)$$

The rapid depletion of H_2O_2 that is often observed with Fenton's reagents is probably due to combined reactions (1)–(4). However, since reaction (2) has the highest rate constant, it is responsible for the degradation of the dye.

Table 2
Effect of various salts on the degradation of Methyl Red

Added salt	Rate constant[a], k (min^{-1})	% Dye degradation[a]
–	1.48	42
NaCl	1.22	47
$NaIO_3$	2.34	26
$CaCl_2$	0.99	44
$CuSO_4$	1.61	29
Na_2SO_4	1.61	40
$CrK(SO_4)_2$	2.44	57
$Ca_3(PO_4)_2$	1.25	92
$Mg(NO_3)_2$	1.30	45
$Co(NO_3)_2$	1.53	45

[a] Obtained by fitting the discoloration data to first-order kinetics.

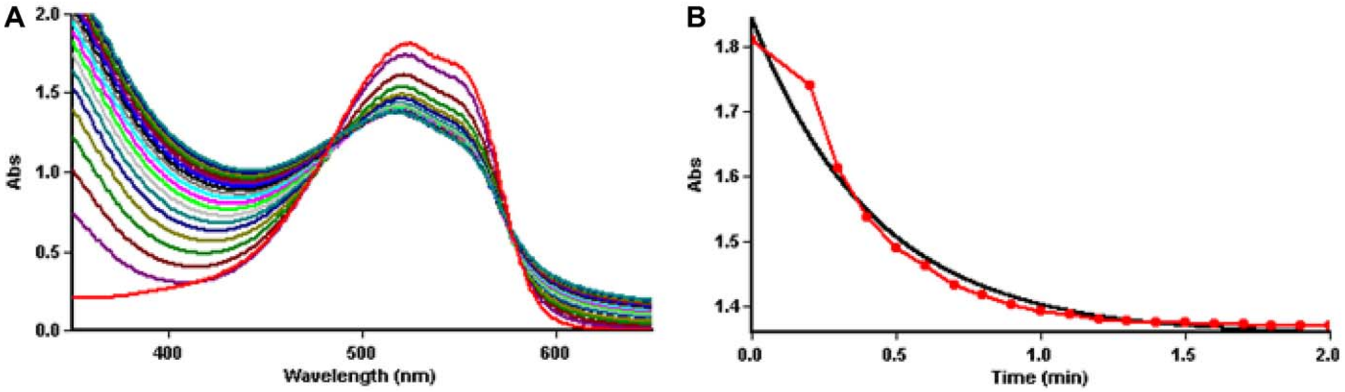

Fig. 4. (A) Inhibition of degradation of Methyl Red with Fenton's reagent in the presence of $NaIO_3$. (B) First-order kinetic of the degradation of MR, solid circles = experimental data, solid line = theoretical curve for first-order kinetics.

Also, it is possible for Fe^{2+} to be auto-regenerated in this system, and act as a catalyst [11]

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \quad (5)$$

In addition to dyes, textile waste streams also have elevated levels of other salts and ions. Table 1 compares the presence of some common ions in the municipal streams and the textile effluents [17]. One can see a substantial increase in the concentration of such ions in the effluents, which can further complicate dye degradation and removal efforts. All these ions in the effluents are well beyond the acceptable limits and are also of concern in many different ways.

The degradation of Methyl Red was investigated in the presence of certain salts which were added to the dye solution in fixed quantities along with the Fenton's reagent. The other experimental conditions were kept the same as for neat Methyl Red degradation study. Among the salts chosen for this purpose were NaCl, $NaIO_3$, $CaCl_2$, $CuSO_4$, Na_2SO_4, $CrK(SO_4)_2$, $Ca_3(PO_4)_2$, $Mg(NO_3)_2$ and $Co(NO_3)_2$. Each of these added salts caused a certain change in % degradation of the dye solution. In the absence of these salts, the dye degraded by 42% in less than 2 min at room temperature, however, with the addition of these salts to the dye solution, the change either became less or more. The maximum change in degradation of 92% was observed in the case of $Ca_3(PO_4)_2$, whereas the least change corresponding to a value of 26% was observed in the case of $NaIO_3$. Perhaps, iodate ions can react with either H_2O_2 to decrease the amount of H_2O_2 available for OH radical production, or quench the OH radicals directly. Other salts that were tested showed intermediate effects between the two extremes. The results are shown in Table 2, along with the calculated values of the rate constants in each case. The trend is also shown diagrammatically in Figs. 4 and 5 for two selective salts that had opposite effects. In the presence of chloride ions, the % change in absorption was found to be 46%. Although this change is not substantial, but it has a certain finite value. This change can be explained on the basis of the following chemical reaction involving chloride ions [13]

$$Cl^- + {}^{\bullet}OH \rightarrow ClOH^{\bullet -}$$

$$ClOH^{\bullet -} + Fe^{2+} \rightarrow Cl^- + OH^- + Fe^{3+}$$

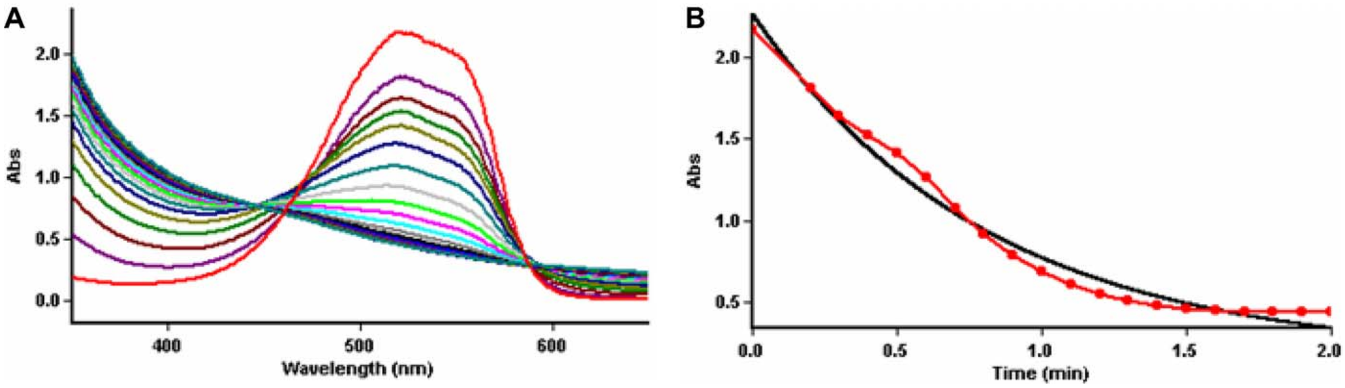

Fig. 5. (A) Enhancement of degradation of Methyl Red with Fenton's reagent in the presence of $CaPO_4$. (B) First-order kinetic of the degradation of MR, solid circles = experimental data, solid line = theoretical curve for first-order kinetics.

The maximum change in absorption value of 92% was observed in the presence of phosphate ions. Since the main step in terms of dye degradation comes from the reaction of OH radicals with the dye, therefore, an increased rate of dye degradation probably indicates presence of more OH radicals. In our case the phosphate ions are perhaps involved in many reactions which lead to the production of more OH radicals, thereby enhancing the dye degradation.

4. Conclusion

The present study describes the degradation of Methyl Red (MR) using the Fenton's reagent. This approach was found to degrade MR rapidly and efficiently. The discoloration of the dye solution was monitored spectrophotometrically and was found to fit to first-order equation. It is suggested that the photolytic oxidation of the dye is due to the reaction of the dye with the hydroxyl radicals generated in solution. Our study also examined the effect of various ions that are generally found in textile waste stream, on the decolorization of MR. Interestingly, we found that $NaIO_3$ adversely affected the discoloration of MR by Fenton reagent, whereas $Ca_3(PO_4)_2$ significantly increased the discoloration rate of the dye. Thus some ions and salts that may be present in textile waste streams have the potential to significantly affect the dye degradation rates and should always be included in such studies.

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