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Enhancement of photodegradation of mordant dyes by iron powder and H₂O₂ in presence of UV light

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ABSTRACT

In this study different treatment methods such as H₂O₂/UV, Fenton and photo-Fenton (Fe⁰/H₂O₂/UV) treatments, have been used to investigate the removal of the Mordant red 7 (MR7) azo dye from aqueous solution. In photo-Fenton treatment, iron (Fe) powder was used as a cheap source of Fe²⁺ ions. Complete decolorization of MR7 using H₂O₂/UV process, achieved in less than 60 min. The photodegradation process was mainly effected by different parameters such as initial dye concentrations, [H₂O₂], pH value and presence of different inorganic salts such as carbonate, nitrate and chloride ions. The decrease in the degradation percent was in the order of Carbonate > chloride > nitrate ions. In comparison, the photo-Fenton treatment, using Fe⁰ powder as a source of Fe²⁺ ions, was more efficient in the decolorization of MR7. It was found that complete decolorization of MR 7 obtained in about 30 min. Furthermore, mineralization of MR 7 was investigated using chemical oxygen demand (COD) experiment. The results indicated that, 66.67% of the MR7 dye was mineralized using H₂O₂/UV process in a 3.0 h photoperiod. While photo-Fenton treatment (in presence of Fe⁰ powder), was more efficient and resulted in complete mineralization of MR7 dye in about 2.0 h of photoperiod. © 2010 Trade Science Inc. - INDIA

KEYWORDS

Mordant dyes;
Eriochrome red B;
H₂O₂/UV;
Photo-fenton;
Iron powder.

INTRODUCTION

Advanced oxidation technologies (AOTs) are those processes which involve powerful oxidizing agents such as hydroxyl free radicals (-OH) to efficiently oxidize a wide range of organic pollutants in wastewater at ambient temperature and pressure^[1-4]. The chemical reactions involved in AOTs are faster than oxidation that takes place in the environment. Hydroxyl radical

(-OH) has strong oxidizing potential (E° = +1.8 V at neutral pH to +2.7V in acidic solutions), that lead to effective degradation of a wide variety of aqueous contaminants including azo dyes^[5-7]. Presence of pollutants such as azo dyes in wastewater is of particular environmental concern since they can originate toxic by-products in the environment^[8,9]. Mordant dyes are one class of azo-dyes characterized by the presence of a hydroxyl group *ortho* to the azo-group and are

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colored aromatic compounds which require the presence of a metal (mordant) such as chromium to properly set their color on fabrics by forming an insoluble compound. Synthetic mordant dyes (chrome dyes), representing about 30% of dyes used for wool, are especially useful for black and navy shades. However, mordant dyes are very hazardous to health since improper application of dichromate or incomplete reduction could lead to release of the toxic chromium (VI) salt into the environment^[10]. In general, discharging textile wastewaters contain a high concentration of unfixed dyestuffs that may seriously affect aquatic ecosystems in addition to changing their color. In the same time, less attention was given to the photodegradation of mordant dyes. Thus it is important to treat wastewater containing Mordant red 7 as one class of azo-dyes before discharge^[11]. Effluents containing azo dyes are commonly treated by the combination of biological oxidation and physical-chemical treatment methods^[12]. However, these traditional methods mainly provide a phase transfer of the contaminants from wastewater to solid waste (sludge)^[13]. On the other hand, the decolorization and mineralization of a wide range of dyes to stable inorganic compounds, has been carried out by different AOTs such as homogeneous^[7] and heterogeneous photocatalysis^[14,15]. AOPs refer to a set of different methods leading to the generation of highly oxidative species such as hydroxyl radicals ($\cdot OH$) which are capable of oxidizing the pollutants to such an extent that the treated wastewater may be reintroduced into receiving streams^[16,17]. The strategies for generating the reactive $\cdot OH$ radicals for these oxidation methods include UV photolysis of ozone or hydrogen peroxide, Fenton or photo-Fenton type reactions, and TiO_2 photocatalysis^[18-21]. The main objective of this study was to investigate the photodegradation of the Mordant red 7 azo dye using both UV/ H_2O_2 and photo-Fenton treatment. A cheap source of Fe^{2+} such as iron powder (Fe^0) will be used in the photo-Fenton reaction. Also, to examine the effect of several parameters such as the initial concentrations of both the dye and H_2O_2 and the presence of inorganic anions on the degradation kinetics of the Mordant red 7 azo dye. Mineralization of the dye was studied as indicator of the decrease in the

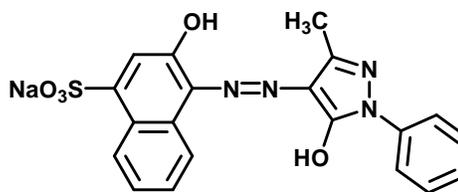


Figure 1 : Chemical structure of Eriochrome red B azo dye (C.I. mono sulphonic Mordant red 7, C₂₀H₁₅N₄NaO₅S) [MR7 dye] chemical oxygen demand (COD).

EXPERIMENTAL

Chemicals

H_2O_2 (30% w/w), iron powder (nominal purity 95.0%), ferrous ammonium sulphate ferrion indicator, mercury (II) sulphate, HNO_3 , NaOH, and potassium dichromate were purchased from BDH Limited, Poole, England and used without further treatment. Target pollutant used in this study was Eriochrome red B (C.I. Mono sulphonic Mordant red 7, C₂₀H₁₅N₄NaO₅S) azo dye (MR7 dye) purchased from Ciba-Geigy LTD Basel, Switzerland. The chemical structure of MR7 is shown in figure 1. All other reagents were analytical grade and used as received. All solutions were prepared with deionized (DI) water.

Methods

Apparatus

Investigations of efficiency of MR7 dye photodegradation were performed in laboratory setup as described elsewhere^[1]. ACE glass photoreactor comprised of a quartz tube surrounded with a water cooling jacket and immersed in a Pyrex cylinder as a solution container. The UV irradiation source was a 20W low-pressure mercury vapor lamp (maximum emission at 254nm). The incident photonic flux was measured by the photolysis of ferrioxalate ($I_0 = 1.46 \times 10^{-6}$ Ein. /L min).

Photodegradation experiments

Aqueous solutions of MR7 dye were prepared in distilled water by dissolving the necessary quantity of the dye and fed into the photoreactor. The content of the photoreactor was mixed with magnetic stirrer and the temperature was maintained at $25 \pm 2^\circ C$ by circulation of water through an internal cooling tube. The pH

of the solution was measured by an Orion pH-Meter and adjusted by using dilute nitric acid or aqueous sodium hydroxide. The lamp was started to initiate the reaction after 3 min of premixing and samples were taken at regular time intervals.

Analysis

Except where noted, analyses was identical to those previously described^[1]. During photodegradation experiments, MR7 dye concentrations were determined and their UV-Vis spectra were recorded with a Perkin Elmer UV-Vis spectrophotometer. Qualitative information related to the degradation of both parent dye and intermediates formed during the photodegradation process was obtained by monitoring the absorbance in the region between 200 and 800 nm. In addition, decolorization of the dye was followed quantitatively by measuring the decrease in absorbance at $\lambda_{\max} = 472\text{nm}$ for the dye chromophore. Chemical oxygen demand (COD), was determined by closed reflux method. Samples were oxidized with a known excess of $\text{K}_2\text{Cr}_2\text{O}_7$ in 50% H_2SO_4 solution. Then the excess of $\text{K}_2\text{Cr}_2\text{O}_7$ was determined by standard solution of ferrous ammonium sulfate in presence of ferrion indicator.

During the photodegradation experiments, remaining % of dye^[22] was calculated as:

$$\text{Remaining (\%)} = \left(\frac{C_t}{C_0} \right) \times 100 \quad (1)$$

where C_0 is the initial MR7 azo dye concentration and C_t is the dye concentration at illumination time t .

RESULTS AND DISCUSSION

Effect of H_2O_2

To investigate the effect of H_2O_2 concentration on the effectiveness of the photodegradation process, aqueous solutions of MR7 dye (0.05mM) were irradiated in the absence and presence of H_2O_2 as shown in figure 2. It was found that while direct photolysis of MR7 dye solution was very slow, dark reaction (dye/ H_2O_2 /dark) was found to have no measurable effect on the decolorization of the dye which was in agreement with the literature^[18]. However, MR7 dye photodegradation was sensitized by the presence of hydrogen peroxide due to the generation of a non-selective and powerful oxidant,

$\cdot\text{OH}$ radicals^[23]. Thus production of $\cdot\text{OH}$ radicals by direct photolysis of added hydrogen peroxide according^[24] to Eq. (1), lead to 96% decolorization of MR7 dye in 50 min.



In addition, the efficiency of the degradation process depends mainly on the concentration of H_2O_2 . Because of the low molar absorptivity of H_2O_2 at 254nm ($18.6\text{-}19.6\text{l/mol-cm}$)^[25], theoretically an excess of H_2O_2 is needed to produce more $\cdot\text{OH}$ radicals. However, it was reported that the concentration of H_2O_2 may either enhance or inhibit the photoreaction rate depending on concentration^[26,27]. Therefore an optimum concentration of H_2O_2 in the reaction course must be reached. At a fixed concentration of dye (0.05mM) at pH = 3.0 and $25 \pm 2^\circ\text{C}$, the effect of the initial concentration of H_2O_2 (2.5×10^{-5} , 2.5×10^{-3} , 2.5×10^{-1} and 5×10^{-1} M) on the photodegradation process was investigated. The photodegradation reaction rate (r) of MR7 dye using H_2O_2 can be represented by the following differential rate law:

$$r = - \frac{d[\text{dye}]}{dt} = k [\text{dye}][\text{H}_2\text{O}_2] \quad (3)$$

In the case of high concentrations of H_2O_2 in this experiment, $[\text{H}_2\text{O}_2]$ is considered constant and a pseudo-first-order rate equation may be used to describe the degradation kinetics:

$$r = - \frac{d[\text{dye}]}{dt} = k_{\text{app}} [\text{dye}] \quad (4)$$

$$\ln \left(\frac{[\text{dye}]_t}{[\text{dye}]_0} \right) = - k_{\text{app}} t \quad (5)$$

where $[\text{dye}]_0$ is the initial dye concentration (0.05mM), $[\text{dye}]_t$ is the concentration of dye after illumination time t , k (min^{-1}) is the true reaction rate constant and k_{app} is the apparent first-order rate constant. A reaction half-

life can be calculated as $t_{1/2} = \frac{0.693}{k_{\text{app}}}$ and the initial rate (R_i , $\text{mg l}^{-1} \text{min}^{-1}$) can be calculated from the half-life and k_{app} as follows:

$$R_i = C_0 k_{\text{app}} \quad (6)$$

Linear regression of first order plots of $\ln \left(\frac{[\text{dye}]_t}{[\text{dye}]_0} \right)$ versus time provides k_{app} from slopes. The results in

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TABLE 1 : Photodegradation kinetics data [half-lives time ($t_{1/2}$), apparent rate constant (k_{app}), the coefficient of determination (R^2) and initial reaction rate for degradation of (2.5×10^{-5} M) MR 7 dye using different concentration (mM) of H₂O₂

[H ₂ O ₂], mM	k_{app} (min ⁻¹)	$t_{1/2}$ (min) = $\ln(2)/k_{app}$	$R_{initial} = C_0 \times k_{app}$ (mol L ⁻¹ min ⁻¹)	R^2
0.25	0.0119	58.24	2.98×10^{-7}	0.9884
2.5	0.0674	10.28	1.69×10^{-6}	0.9958
250	0.0397	17.46	9.93×10^{-7}	0.9934
500	0.021	33.00	5.25×10^{-7}	0.9815

figure 3 indicated that the decrease in dye concentration as a function of exposure time was mainly dependent on the concentration of H₂O₂. The data were in good agreement with the pseudo-first-order kinetic model providing apparent pseudo-first-order rate constants (k_{app} , min⁻¹) for each experiment. Photodegradation kinetics data [half-lives time ($t_{1/2}$), apparent rate constant (k_{app}), the coefficient of determination (R^2) and initial reaction rate for degradation of (0.05mM) MR 7 dye using different concentrations (mM) of H₂O₂ are presented in TABLE 1.

It can be seen that the largest degradation rate of the dye was observed with a H₂O₂ concentration of 2.5mM with apparent rate constant of 0.0674 min⁻¹. Increasing the concentration of H₂O₂ to 500mM inhibited the reaction as noted by more than a 3-fold decrease in the rate constant to 0.021 min⁻¹. Furthermore, the degradation rate constant of the dye at the lower H₂O₂ concentration (0.0119 min⁻¹) was close to the degradation rate at higher concentration (0.021 min⁻¹) indicating the high scavenging rate of ·OH radicals by H₂O₂. Previous reports^[28] have indicated that consumption of ·OH radicals or production of less reactive radicals (such as HO₂·) take place at very high concentration of H₂O₂ due to self-scavenging, competitive reactions such as reaction with HO₂· and dimerization to H₂O₂ according to the following equations:



On the other hand, due to the presence of insufficient ·OH radicals at lower H₂O₂ concentration (0.25mM) the degradation rate constant of the dye decreased to 0.0119 min⁻¹. It is interesting to note that the photodegradation process in the presence of H₂O₂ is more efficient when using the optimum dose of H₂O₂

TABLE 2 : Photodegradation kinetics data [half-lives time ($t_{1/2}$), apparent rate constant (k_{app}), the coefficient of determination (R^2)] for degradation of (2.5×10^{-5} M) MR 7 in the presence of (1.145g/L) different inorganic anions (control = absence of anions)

Anions	k_{app} (min ⁻¹)	$t_{1/2}$ (min) = $\ln(2)/k_{app}$	R^2
Control	0.0637	10.90	0.9948
NO ₃ ⁻	0.0422	16.40	0.9876
Cl ⁻	0.0332	20.90	0.997
CO ₃ ²⁻	0.0202	34.30	0.9935

as reported previously by numerous authors^[29]. Since the highest degradation rate was observed by using 2.5mM H₂O₂, therefore, in all subsequent experiments an initial H₂O₂ concentration of 2.5mM was used.

Effect of pH

Figure 4 presents the pH effect on the MR7 degradation under UV light irradiation in the presence of H₂O₂. Aqueous solutions of MR7 dye (0.05mM) were irradiated at various initial pH (3, 5, 7 and 9) to investigate the effect of initial pH on photodegradation process. It was found that the degree of decolorization of the dye was depending on the value of pH. The results indicate that the decolorization efficiency of MR7 dye at the same dose of H₂O₂ under both acidic and alkaline conditions were different and appear to be dependent on the initial pH. It can be noted that at pH of 3.0 the largest degradation rate was observed with a H₂O₂ concentration of 2.5mM with 92% disappearance of the parent MR7 dye in the first 40 min of photolysis. While increasing the pH value to a strong alkaline medium decreased the photodegradation rate. The lowest rate was observed in alkaline medium as the % disappearance decreased from 92 to 60% at pH9 at the same concentration of H₂O₂ in the same photoperiod as shown in figure 4. This may be due to hydroxyl radicals are generated efficiently with strong oxidizing potential ($E^\circ = 1.8$ V at neutral pH to 2.7 V in acidic solutions under acidic conditions^[26]). Furthermore, photodegradation of MR7 dye was monitored by measurement of the pH within the irradiation time. The pH of the solution decreases slowly at the initial stage of the photooxidation, dropping by about one pH unit (from 5-4.2, 7-5.9 and 9-8.08) except in the case of high pH (pH 3) it remains almost constant within the 60 min of irradiation as shown in figure 5. This slight drop in the

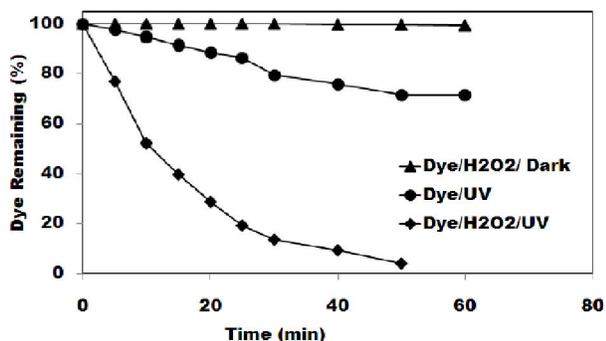


Figure 2 : Photodegradation of 5×10^{-2} mM MR7 dye in the presence of 2.5 mM H_2O_2 at pH 3 and $T = 25 \pm 2^\circ C$

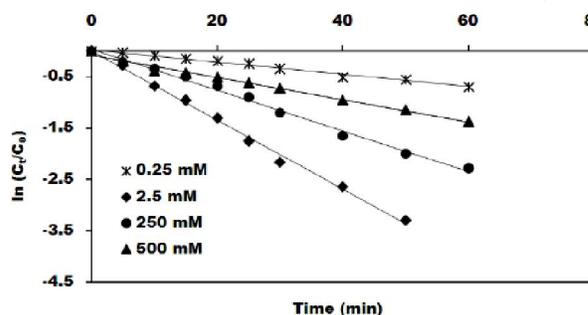


Figure 3 : Effect of H_2O_2 concentration on the degradation of MR7 dye under the conditions: $[dye]_0 = 5 \times 10^{-2}$ mM, pH 3 and $T = 25 \pm 2^\circ C$

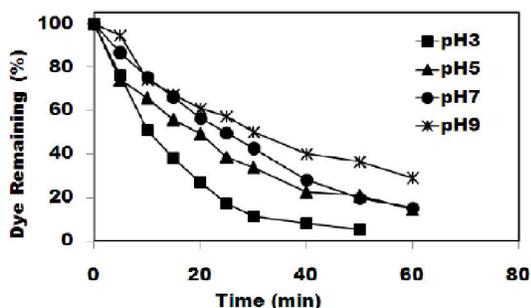


Figure 4 : Effect of pH on MR7 dye degradation under the conditions: $[dye]_0 = 5 \times 10^{-2}$ mM, $[H_2O_2]_0 = 2.5 \times 10^{-3}$ M and $T = 25 \pm 2^\circ C$

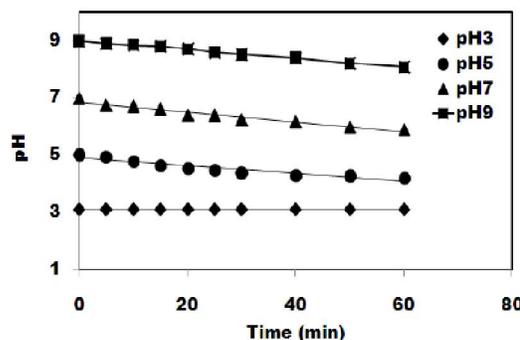


Figure 5 : Change the initial pH of the photodegradation process of MR7 dye during the irradiation time

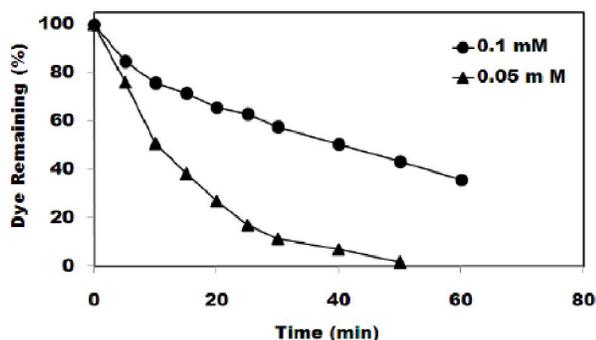


Figure 6 : Effect of initial concentration of the MR7 dye on photodegradation under the conditions: $[H_2O_2]_0 = 2.5 \times 10^{-3}$ M, pH 3 and $T = 25 \pm 2^\circ C$

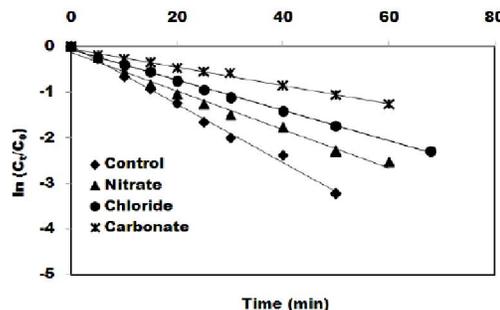


Figure 7 : Effect of (1.145 g/L) different inorganic anions (NO_3^- , Cl^- and CO_3^{2-}) on the photodegradation of MR7 under the conditions: $[dye]_0 = 5 \times 10^{-2}$ mM, $[H_2O_2]_0 = 2.5 \times 10^{-3}$ M, pH 3 and $T = 25 \pm 2^\circ C$

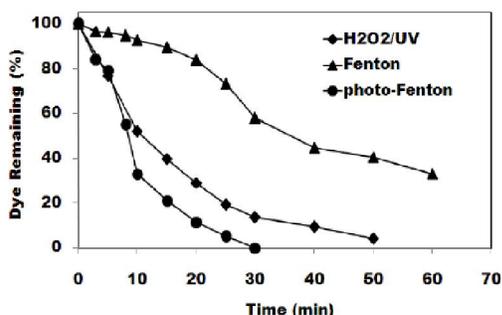


Figure 8 : Effect of photo-Fenton treatment on the photodegradation of MR7 dye under the conditions: $[dye]_0 = 5 \times 10^{-2}$ mM, $[H_2O_2]_0 = 2.5 \times 10^{-3}$ M, iron dosage = 0.11g, pH 3 and $T = 25 \pm 2^\circ C$

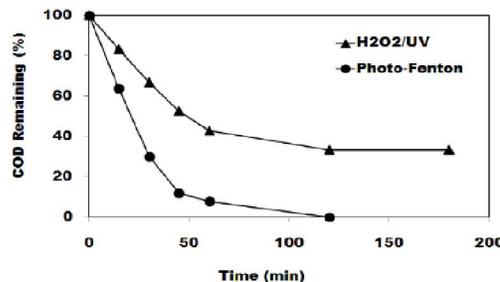


Figure 9 : Mineralization of MR7 dye as indicated by decrease the chemical oxygen demand (COD) during photodegradation by H_2O_2/UV and photo-Fenton processes, under the conditions: $[dye]_0 = 5 \times 10^{-2}$ mM, $[H_2O_2]_0 = 2.5 \times 10^{-3}$ M, iron dosage = 0.11g/L, pH 3 and $T = 25 \pm 2^\circ C$

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pH indicates the formation of organic acid compounds during the degradation process as a result of degradation and cleavage of the azo group in the dye^[30]. Decreasing the pH values during the photodegradation process using H₂O₂ was also observed for different dyes such as Reactive red 120, Reactive black 5, Reactive yellow 84 in aqueous solution^[29]. However, remaining the pH value almost constant at initial high pH (pH 3), indicating that although the organic acid compounds are formed during the degradation process of the dye they are still at such very small concentration supporting the mineralization of MR7 dye under the present conditions.

Since hydroxyl radicals are generated efficiently under acidic conditions^[8], also, the results indicated that MR7 degraded significantly at pH3, subsequent experiments were performed at pH 3.

Effect of initial dye concentration

Production rate of $\cdot\text{OH}$ radicals from the direct photolysis of H₂O₂ is strongly dependent on the incident light. Thus highly absorbing solutions such as dyes may act as filters limiting the penetration of light through the solution^[31]. Therefore, different concentrations (0.1 and 0.05mM) of MR7 dye were used in order to determine the effect of the initial dye concentration on the effectiveness of photodegradation process. Figure 6 presents the results of % remaining of different concentrations (0.1 and 0.05mM) of MR7 dye versus time. The results indicate that at the first 40 min a significant decrease in the decolorization rate resulted at high concentration (0.1mM) of MR7dye with 50% remaining. However, the largest enhancement in the degree of decolorization was observed with a dye concentration of 0.050mM with only 7% of MR7 dye remaining. It was reported that at high concentration of dye most of the UV light will be absorbed by the dye molecules instead of H₂O₂, thus decreasing the generation of $\cdot\text{OH}$ radicals available for photodegradation of MR7^[32]. Also, these results suggest that oxidation occurs on the chromophore rather than on the dye molecular skeleton. Because of this, H₂O₂/UV would be more effective for dilute solutions of the dye.

Effect of inorganic anions

Presence of inorganic anions in the photodegradation

solutions may induce or reduce the rate of photooxidation^[33]. Photodegradation experiments for aqueous solutions of MR7 dye were performed in presence of different inorganic anions. The results of photodegradation in presence of (1.145g/L) nitrate (NO₃⁻), chloride (Cl⁻) and carbonate (CO₃²⁻) ions are presented in figure 7. The kinetic data (TABLE 2) showed that the rate of photodegradation of MR7 was differing in the presence of different inorganic anions. Presence of NO₃⁻ ions lead to slight decrease in the photodegradation rate as shown by increase the half-life (t_{1/2}) of degradation process from 10.90 (in the absence of NO₃⁻) to 16.4 min. Although previous reports^[34] showed that the presence of NaNO₃ had negligible effect on the photodegradation process. This may be attributed to the scavenging of $\cdot\text{OH}$ radicals by NO₃⁻ decreasing the availability of $\cdot\text{OH}$ radicals for the photodegradation process. Furthermore, presence of Cl⁻ ions significantly decreased the decolorization rate constant of dye and the t_{1/2} increased by about 50% (from 10.90 to 20.90 min). However, the rate decreased dramatically from 0.064 min⁻¹ in the absence of CO₃²⁻ to 0.020 min⁻¹ due to the addition of CO₃²⁻ ions which lead to increase the t_{1/2} by 3.4 fold. This behavior may be attributed to $\cdot\text{OH}$ radical scavenging by CO₃²⁻ ion^[35].

Since the experiments were performed at pH 3 under H₂O₂/UV, Carbonate ions were present mainly as H₂CO₃. Presence of bicarbonate ions in the course of photooxidation may decrease the decolorization rate due to scavenging of $\cdot\text{OH}$ by HCO₃⁻ as shown in Eq. (10);



Production of CO₃^{·-} which is less reactive than hydroxyl radical^[36] lowered the levels of $\cdot\text{OH}$ during the course of the reaction hence decreasing the decolorization rate as shown in figure 7. In general, the presence of inorganic anions in the wastewater tends to inhibit the photodegradation of MR7 dye as shown in TABLE 2.

Effect of photo-fenton reaction

Catalytic decomposition of H₂O₂ by ferrous (Fe²⁺) ion in absence of UV light (Fenton's reaction) or in presence of UV light (photo-Fenton reaction) lead to increase the production of $\cdot\text{OH}$ radicals according to the following equation;



Fenton system usually carried out by iron salts as a source of Fe^{2+} ^[9]. However, a source for Fe^{2+} in the Fenton reaction could be Fe° powder that reacts with hydrogen peroxide (Eq. 12) to produce Fe^{2+} which initiates the Fenton reaction (Eq. 11).



To investigate the effect of increased production of OH^\cdot radicals on the photodegradation of MR7 dye, experiments were performed using Fenton and photo-Fenton conditions in presence of Fe° powder as a source for Fe^{2+} ions. It was reported that acidic medium leads to increase the production of OH^\cdot radicals^[9], therefore, the experiments are done at pH 3. The results of photodegradation of MR7 dye using $\text{H}_2\text{O}_2/\text{UV}$ process, Fenton ($\text{H}_2\text{O}_2/\text{Fe}^\circ/\text{dark}$) and the photo-Fenton ($\text{H}_2\text{O}_2/\text{Fe}^\circ/\text{UV}$) conditions are shown in figure 8. It was found that at the first 30 min, the degradation of MR7 dye by Fenton's reaction resulted in about 44% removal and degradation of MR7 by the $\text{H}_2\text{O}_2/\text{UV}$ process resulted in 86% removal. On the other hand, the photo-Fenton reaction resulted in the highest efficiency for degradation of MR7 dye with about 99% disappearance in the first 30 min, indicating that the dominant decolorization mechanism is the photo-Fenton reaction. Furthermore, preliminary investigation of complex formation was performed by following the change in the original color of the dye during the addition of H_2O_2 to Fe powder during experiments under Fenton and photo-Fenton conditions. There was no change in the original color of the dye to indicate complex formation under the conditions of the experiment. Further experiments should be performed to investigate the potential contribution of complex formation to the removal of MR7 dye under these conditions.

Mineralization of MR7 azo dye

Chemical oxygen demand (COD) is the amount of oxygen equivalent to the amount of organic and inorganic matter present in the sample. Decreasing COD is evidence for the oxidation and/or decrease in the carbon content in the sample, hence indicative of the extent of mineralization. The extent of degradation of MR7 dye was determined by measuring the decrease in COD values due to the photodegradation of MR7 dye using $\text{H}_2\text{O}_2/\text{UV}$ and photo-Fenton processes over a 3 h pho-

toperiod as shown in figure 9. The results indicating that the $\text{H}_2\text{O}_2/\text{UV}$ process mineralize about 67% of MR7 dye in period of 3 h, while the photo-Fenton reaction was more efficient leading to 100% mineralization of the dye in only 2.0 h.

CONCLUSION

The results have shown that both $\text{UV}/\text{H}_2\text{O}_2$ process and photo-Fenton treatment can be a suitable pretreatment method for the degradation of MR7 dye. Complete mineralization of MR7 dye was achieved in about 2.0 hr by photo-Fenton reaction in the presence of Fe° powder as a continuous source for Fe^{2+} ions. Among the different processes contributing to the removal of dye, the increasing order of dye decolorization was: photo-Fenton reaction > $\text{H}_2\text{O}_2/\text{UV}$ > Fenton's reaction. Also, the results indicated that presence of inorganic anions such as NO_3^- , Cl^- and CO_3^{2-} ions inhibited the removal of the dye from solution. The decreasing order of dye removal in presence of inorganic anions was: CO_3^{2-} > Cl^- > NO_3^- ions. The investigations should be continued in order to identify the evaluation of the intermediates during the oxidation process.

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