



Decolorization of Mordant red 73 azo dye in water using H₂O₂/UV and photo-Fenton treatment

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ABSTRACT

Decolorization of the Mordant red 73 (MR73) azo dye in water was investigated in laboratory-scale experiments using UV/H₂O₂ and photo-Fenton treatments. Photodegradation experiments were carried out in a stirred batch photoreactor equipped with a low-pressure mercury lamp as UV source at 254 nm. The effect of operating parameters such as pH, [H₂O₂], [dye] and the presence of inorganic salts (NaNO₃, NaCl and Na₂CO₃) were also investigated. The results indicated that complete dye decolorization was obtained in less than 60 min under optimum conditions. Furthermore, results showed that dye degradation was dependent upon pH, [H₂O₂] and initial dye concentration. The presence of chloride ion led to large decreases in the photodegradation rate of MR73 while both nitrate and carbonate ions have a slight effect. The photo-Fenton treatment, in the presence of Fe powder as a source of Fe²⁺ ions, was highly efficient and resulted in 99% decolorization of the dye in 15 min. Mineralization of MR73 dye was investigated by determining chemical oxygen demand (COD). In a 3 h photoperiod “65%” of the dye was mineralized by the H₂O₂/UV process, while the photo-Fenton treatment was more efficient producing 85% mineralization over the same 3-h period.

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1. Introduction

Large amounts of different anthropogenic compounds are produced annually due to the rapid growth of industry in most countries. Many of these compounds are toxic and/or carcinogenic and may affect the environment in different ways [1]. Anthropogenic dyes, such as azo-dyes produced from textile and other industries, have low biodegradability under aerobic conditions leading to concern over industrial discharges [2–7]. Azo-dyes account for some 60–70% of the 10,000 commercial dyes currently in use [8–10]. Azo-dyes contain the azo chromophoric group (–N=N–) in addition to aromatic systems and auxochromes (such as OH, NH₂, CO₂H, –SO₃ and Cl) [9]. Mordant dyes are one class of azo-dyes characterized by the presence of a hydroxyl group *ortho* to the azo-group and are 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 [11].

Although some azo-dyes themselves have a minor environmental effect, their precursors and degradation products such as aromatic amines are considered highly carcinogenic [12]. In addition, effluents of textile dyeing industries are known to contain significant amounts of suspended solids, inorganic salts, chlorinated organics, surfactants and some heavy metals and to have variable pH [13]. In general, discharging textile wastewaters contain a high concentration of unfixed dye stuffs 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 73 as one class of azo-dyes before discharge [8]. Effluents containing azo-dyes are commonly treated by the combination of biological oxidation and physical–chemical treatment methods [14]. However, these traditional methods mainly provide a phase transfer of the contaminants from wastewater to solid waste (sludge) [15]. Alternatively, advanced oxidation processes (AOPs) such as homogeneous and heterogeneous photocatalysis are promising technologies which aim at the decolorization and mineralization of a wide range of dyes to stable inorganic compounds or, at least, their transformation into biodegradable or harmless products [16–19]. AOPs refer to a set of different methods leading to the generation of highly oxidative species such as hydroxyl radicals (*OH) which are capable of oxidizing the pollutants to such an extent that the treated wastewater may be reintroduced into receiving streams [8,12,16–20]. The use of homogeneous photodegradation systems such as H₂O₂/UV and Fe⁰/H₂O₂/UV

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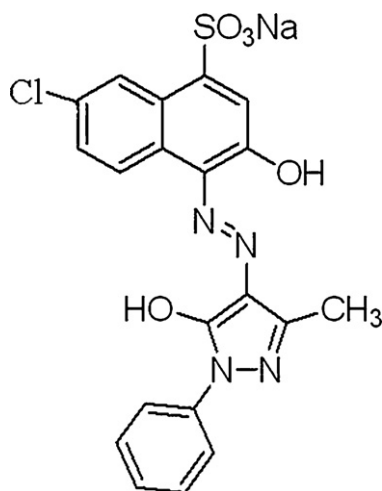


Fig. 1. Chemical structure of Eriochrome red 3B azo dye (C.I. mono sulphonic Mordant red 73) [MR73 dye].

(photo-Fenton) have attracted much attention due to their high efficiency in the oxidation of different pollutants including dyes [21–25]. The main objective of this work was to study several parameters that affect the degradation kinetics of the Mordant red 73 azo dye by both UV/H₂O₂ and Fe/H₂O₂/UV systems. Iron powder (Fe⁰) has been used as a cheap source of Fe²⁺ in the photo-Fenton reaction. Chemical oxygen demand (COD) removal was used as an indicator of mineralization and hence the effectiveness of the water treatment process.

2. Materials and methods

2.1. Reagents

Eriochrome red 3B (C.I. Mono sulphonic Mordant red 73) azo dye (MR73 dye) used in the present work (see Fig. 1) was purchased from Ciba-Geigy LTD Basel, Switzerland. This dye was used without further purification. H₂O₂ (30% w/w), HNO₃, NaOH, ferrous ammonium sulphate, ferrion indicator, mercury (II) sulphate and potassium dichromate were purchased from BDH Company. Iron powder (nominal purity 95.0%) was supplied by BDH Limited, Poole, England and used without further treatment. All other reagents were analytical grade and used as received. All solutions were prepared with deionized (DI) water.

2.2. Methods

2.2.1. Photoreactor and actinometry

Photoreactions were carried out in an 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 container has inlets for feeding reactants and ports for measuring temperature and withdrawing samples. The UV irradiation source was a 20 W low-pressure mercury vapor lamp (maximum emission at 254 nm). The incident photonic flux was measured by the photolysis of ferrioxalate ($I_0 = 1.46 \times 10^{-6}$ Ein./L min).

2.2.2. Photodegradation procedure

The photoreactor was operated with an initial working volume of 250 ml. Solutions were prepared by dissolving the necessary quantity of the dye and H₂O₂ in distilled water and fed into the photoreactor. The aqueous solutions were magnetically stirred and the temperature was maintained at 25 ± 2 °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

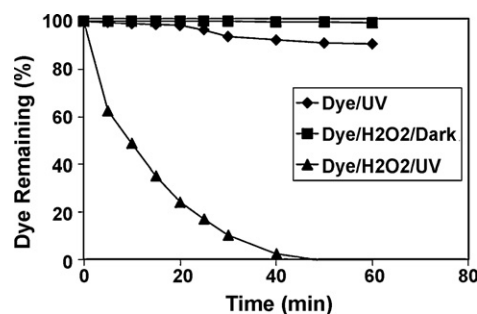


Fig. 2. Photodegradation of 5×10^{-2} mM MR73 dye in the presence of 2.5 mM H₂O₂ at pH 3 and $T = 25$ °C.

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.

2.2.3. Analytical procedures

Solutions withdrawn from the photoreactor were analyzed for decolorization and chemical oxygen demand (COD). UV–Vis spectra were recorded during photodegradation using a Perkin Elmer UV–Vis spectrophotometer. Monitoring the absorbance in the region between 200 and 800 nm provided qualitative information that was related to the degradation of both parent dye and intermediates formed during the photodegradation process. In addition, decolorization of the dye was followed quantitatively by measuring the decrease in absorbance at $\lambda_{\text{max}} = 492$ nm for the dye chromophore. Chemical oxygen demand (COD) was determined using the closed reflux method to oxidize samples with a known excess of K₂Cr₂O₇ in 50% H₂SO₄ solution. A standard solution of ferrous ammonium sulfate was used for the titration of excess K₂Cr₂O₇. The color removal (%) of MR73 azo dye was calculated as [26]:

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

where C_0 is the initial MR73 azo dye concentration and C_t is the dye concentration at illumination time t .

3. Results and discussion

The typical UV–Vis spectrum of MR73 azo dye presents absorption bands at 492, 360 and 285 nm. The band at 492 nm (attributed to $n \rightarrow \pi^*$ transitions of N=N, C=N and C=O chromophore groups) is responsible for the color of the dye solution and is thus used to monitor the rate of decolorization of the dye. Absorbance bands at 360 and 285 nm ($\pi \rightarrow \pi^*$ transition in aromatic rings) represent aromatic character of the dye, hence decreases in absorbance at these wavelengths correspond to loss of aromaticity of the dye during photodegradation [27].

3.1. Effect of H₂O₂

Solutions of dye (5×10^{-2} mM) were irradiated in the absence and presence of H₂O₂ as shown in Fig. 2. H₂O₂ alone in the absence of UV irradiation (dye/H₂O₂/dark) was found to have no measurable effect on the decolorization of the dye. In the absence of H₂O₂, direct photolysis of the dye (dye + $h\nu \rightarrow$ products) was slow and resulted in less than 10% azo bond degradation in 60 min which was in agreement with the literature [12]. However, generation of a non-selective and powerful oxidant, •OH radicals [28,29] by direct photolysis of added hydrogen peroxide (H₂O₂ + $h\nu \rightarrow 2 \bullet\text{OH}$) significantly enhanced the degradation of the dye, since complete decolorization (dye + •OH \rightarrow products) was obtained in less than

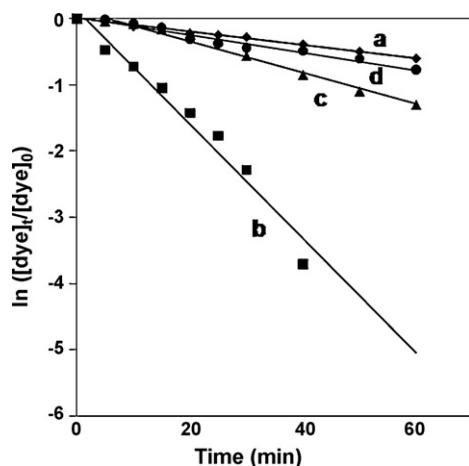


Fig. 3. Effect of H_2O_2 concentration (a) 0.025 mM, (b) 2.5 mM, (c) 250 mM and (d) 500 mM on the degradation of MR73 dye under the conditions: $[\text{dye}]_0 = 5 \times 10^{-2}$ mM, pH 3 and $T = 25^\circ\text{C}$.

50 min. However, 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 254 nm (18.6–19.6 l/mol cm) [30], theoretically an excess of H_2O_2 is needed to produce more $\cdot\text{OH}$ radicals. However in our previous work [31], in addition to other reports [32,33], we observed that the concentration of H_2O_2 may either enhance or inhibit the photoreaction rate depending on concentration. Therefore an optimum concentration of H_2O_2 in the reaction course must be reached. 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 efficiency of the system was investigated using fixed concentrations of dye (5×10^{-2} mM) at pH 3.0 and $25 \pm 2^\circ\text{C}$. The photodegradation reaction rate (r) of MR73 dye using H_2O_2 can be represented by the following differential rate law:

$$r = -\frac{d[\text{dye}]}{dt} = k[\text{dye}][\text{H}_2\text{O}_2] \quad (2)$$

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:

$$r = -\frac{d[\text{dye}]}{dt} = k_{\text{app}}[\text{dye}] \quad (3)$$

$$\ln\left(\frac{[\text{dye}]_t}{[\text{dye}]_0}\right) = -k_{\text{app}}t \quad (4)$$

where $[\text{dye}]_0$ is the initial dye concentration (5×10^{-2} mM), $[\text{dye}]_t$ 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 $t_{1/2} = 0.693/k_{\text{app}}$ 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:

$$R_i = C_0 k_{\text{app}} \quad (5)$$

Linear regression of first-order plots of $\ln([\text{dye}]_t/[\text{dye}]_0)$ versus time provide k_{app} from slopes. The results in Fig. 3 indicated that the decrease in dye concentration as a function of exposure time was mainly dependent on the concentration of H_2O_2 . 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.

The enhancement and/or inhibitory effects of H_2O_2 concentration on the degradation rate of the dye is represented by plotting the logarithm of k_{app} against the logarithm of the peroxide concentration as shown in Fig. 4. The largest degradation rate of the

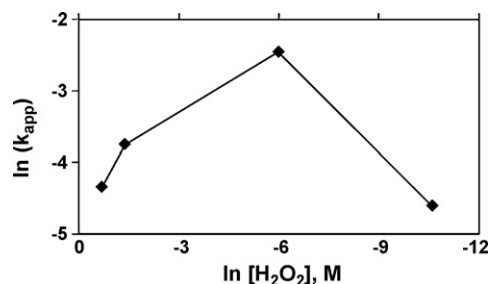


Fig. 4. Effect of H_2O_2 concentration on the pseudo-first-order photodegradation rate constant (k_{app}) under the conditions: $[\text{dye}]_0 = 5 \times 10^{-2}$ mM, pH 3 and $T = 25^\circ\text{C}$.

dye was observed with a H_2O_2 concentration of 2.5×10^{-3} M with apparent rate constant of 0.0863 min^{-1} . Increasing the concentration of H_2O_2 to 5×10^{-1} M inhibited the reaction as noted by a 6-fold decrease in the rate constant to 0.0103 min^{-1} . Furthermore, the degradation rate constant of the dye at the lower H_2O_2 concentration (0.01 min^{-1}) was similar to the degradation rate at higher concentration (0.0103 min^{-1}) indicating the high scavenging rate of $\cdot\text{OH}$ radicals by H_2O_2 .

Previous reports [34] have indicated that consumption of $\cdot\text{OH}$ radicals or production of less reactive radicals (such as $\text{HO}_2\cdot$) take place at very high concentration of H_2O_2 due to self-scavenging ($\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2\cdot + \text{H}_2\text{O}$), competitive reactions such as reaction with $\text{HO}_2\cdot$ ($\text{HO}_2\cdot + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$) and dimerization to H_2O_2 ($2\cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$). On the other hand, due to the presence of insufficient $\cdot\text{OH}$ radicals at lower H_2O_2 concentration (2.5×10^{-5} M) the degradation rate constant of the dye decreased to 0.01 min^{-1} . Therefore, in all subsequent experiments an initial H_2O_2 concentration of 2.5×10^{-3} M was used.

3.2. Effect of pH

To investigate the effect of initial pH, solutions of MR73 dye were irradiated at various initial pHs (2, 3, 5, and 9). The results (Fig. 5) showed small differences in the degree of decolorization of the dye at different pH values. For example, in the case of 10 min reaction times, the decolorization efficiencies were 38.9%, 33.5%, 37.3% and 35.4% at initial pH of 2, 3, 5 and 9 "respectively". At 50 min reaction times the decolorization efficiencies changed slightly (94.3%, 98.9%, 94.5% and 96.5%) for initial pHs of 2, 3, 5 and 9 "respectively". The results indicate that the decolorization efficiency of MR73 dye at the same dose of H_2O_2 under both acidic and alkaline conditions were very similar and appear to be independent of the initial pH. On the other hand, pH decreased in alkaline medium from 8.7 to 6.50 and in weak acidic medium from 5.16 to 4.24, while under strong acidic conditions (pH 3) there was no observed change in pH during the degradation reaction. This may be due to the production of the corresponding weak acidic intermediates as a result

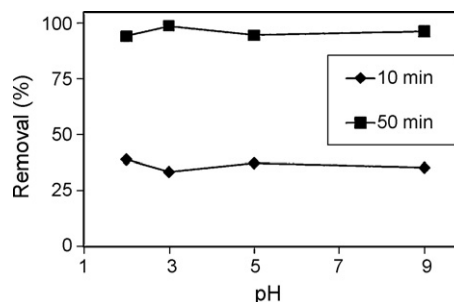


Fig. 5. Effect of pH on MR73 dye degradation at 10 and 50 min exposure times under the conditions: $[\text{dye}]_0 = 5 \times 10^{-2}$ mM, $[\text{H}_2\text{O}_2]_0 = 2.5 \times 10^{-3}$ M, and $T = 25^\circ\text{C}$.

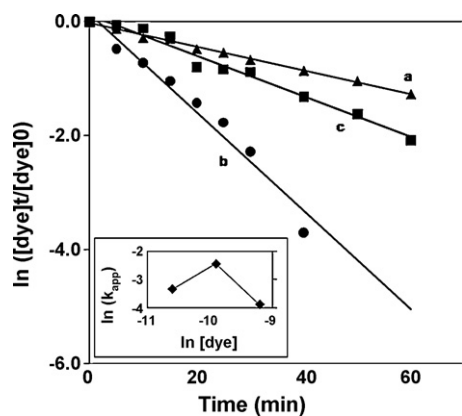


Fig. 6. Effect of initial concentration of the MR73 dye (a) 0.1 mM, (b) 0.05 mM and (c) 0.025 mM on dye photodegradation under the conditions: $[\text{H}_2\text{O}_2]_0 = 2.5 \times 10^{-3}$ M, pH 3 and $T = 25^\circ\text{C}$. Inset shows the relation between the k_{app} and $[\text{dye}]$ on a logarithmic scale.

of degradation and cleavage of the azo-group in the dye [35]. Since hydroxyl radicals are generated efficiently under acidic conditions [31], also, the results indicated that MR73 degraded significantly at pH 3, subsequent experiments were performed at pH 3.

3.3. Effect of initial dye concentration

The above results indicated that the photodegradation rate of MR73 dye was enhanced only in the presence of H_2O_2 . While the rate of photolysis of H_2O_2 is strongly dependent on the incident light, highly absorbing solutions such as dyes may act as filters limiting the penetration of light through the solution [36]. Therefore, the effect of the dye concentration on its photodegradation rate was examined. Fig. 6 shows the pseudo-first-order plot for different concentrations (0.1, 0.05, 0.025 mM) of MR73 dye. The results indicate that while the decolorization rate was slow at lower concentration (0.025 mM) with apparent rate constant of 0.0357 min^{-1} , a significant decrease in the decolorization rate ($k_{\text{app}} = 0.0209 \text{ min}^{-1}$) resulted at high concentration (0.1 mM) of dye. The largest enhancement in the degree of decolorization was observed with a dye concentration of 0.050 mM (see inset in Fig. 6). At high concentration of dye most of the UV light will be absorbed by the dye molecules instead of H_2O_2 , thus decreasing the generation of $\bullet\text{OH}$ radicals available for photodegradation of MR73 [37]. Furthermore, since the dye is the limiting reagent in the photodegradation process, low concentrations of dye would reduce the rate of decolorization. Also, these results suggest that oxidation occurs on the chromophore rather than on the dye molecular skeleton. Because of this, $\text{H}_2\text{O}_2/\text{UV}$ would be more effective for dilute solutions of the dye.

3.4. Effect of inorganic anions

Inorganic anions occur naturally in wastewater (e.g. NO_3^-) or may be added to facilitate the dyeing process (e.g. Cl^- , CO_3^{2-}). The presence of inorganic anions in textile wastewaters plays an important role in the photooxidation kinetics of different dyes. Inorganic anions may induce or reduce the rate of photooxidation. For example, formation of $\bullet\text{OH}$ radicals during the irradiation of nitrate ion may induce the rate of photooxidation [38], while scavenging of hydroxyl radicals by chloride and carbonate ions [39–41] reduces the reaction rate. Furthermore, the degree of aggregation ($2\text{Dye} - \text{SO}_3\text{Na} \leftrightarrow [\text{Dye} - \text{SO}_3\text{Na}]_2$) and ionization ($\text{Dye} - \text{SO}_3\text{Na} \leftrightarrow [\text{Dye} - \text{SO}_3^- \text{Na}^+]$) of dyes may significantly decrease the photooxidation rate [42]. It has been reported that the “common ion effect” due to the presence of inorganic anions led to

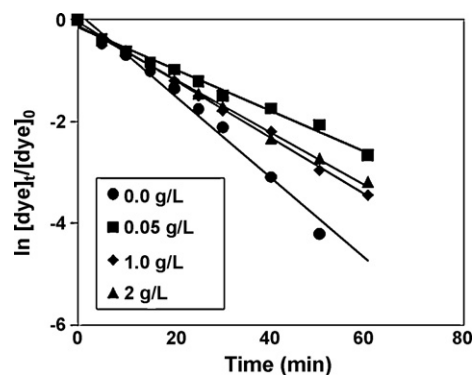
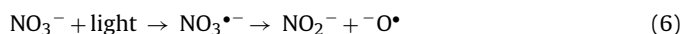


Fig. 7. Effect of concentration of NaNO_3 on the photodegradation of MR73 under the conditions: $[\text{dye}]_0 = 5 \times 10^{-2}$ mM, $[\text{H}_2\text{O}_2]_0 = 2.5 \times 10^{-3}$ M, pH 3, $T = 25^\circ\text{C}$.

decreased π -electron (electrostatic) repulsion between two ionic dyes hence increasing the degree of aggregation [43]. It is known that solubilization and ionization of dyes, which affect their attack by $\bullet\text{OH}$ radicals, decreased by increasing the aggregation degree. Thus the tendency for reaction between $\bullet\text{OH}$ radicals and the dye is expected to decrease as the dye undergoes greater aggregation [42]. A series of experiments were performed to investigate the influence of these inorganic anions (with concentrations similar to operation conditions) on the photodegradation process.

3.4.1. Influence of NaNO_3 on the photodegradation of MR73

Fig. 7 shows the pseudo-first-order degradation of MR73 at different concentrations of NaNO_3 under UV irradiation. Although previous reports [14,44] showed that the presence of NaNO_3 had negligible effect on the photodegradation of ethanol and 2-propanol under UV light irradiation, these results indicated that in the presence of 0.05 g/L NO_3^- , the rate constant decreased by about 50% from 0.081 (in the absence of NO_3^-) to 0.041 min^{-1} . This may be attributed to the scavenging of $\bullet\text{OH}$ radicals by NO_3^- decreasing the availability of $\bullet\text{OH}$ radicals for the photodegradation process. However, increasing the concentration of NO_3^- from 0.05 to 1 and 2 g/L, respectively, increased the photodegradation rate constant to 0.057 and 0.053 min^{-1} . As discussed previously, irradiation of NO_3^- ion [38] may produce $\bullet\text{OH}$ radicals due to the rapid protonation of produced $^-\text{O}^\bullet$ as follows:



It appears that at low NO_3^- concentration the scavenging effect (Eq. (8)) by photochemically generated NO_2^- (Eq. (6)) is predominant while at higher concentration competition reactions become prominent leading to production of $\bullet\text{OH}$ radicals (Eqs. (6) and (7)) which contribute to enhanced decolorization rates.

3.4.2. Effect of sodium chloride

The pseudo-first-order plot of MR73 at different concentrations of NaCl under UV irradiation is shown in Fig. 8. It is clear that the decolorization rate constant of dye decreased dramatically from 0.081 min^{-1} in the absence of Cl^- to 0.021 min^{-1} due to the addition of 1.0 g/L NaCl . This behavior may be attributed to OH^\bullet radical scavenging by Cl^- ion. Cl^- is known to react with $\bullet\text{OH}$ radical (forming $\text{OHCl}^{\bullet-}$ radical) [45,46] with a reported rate constant of $3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at pH 2–3. The $\text{OHCl}^{\bullet-}$ radical generated is less reactive than the OH^\bullet radical leading to slower degradation of MR73 dye. A further decrease in the rate of decolorization ($k_{\text{app}} = 0.0147 \text{ min}^{-1}$) was observed when the concentration of Cl^- increased to 6 g/L which may be attributed to an increase in both

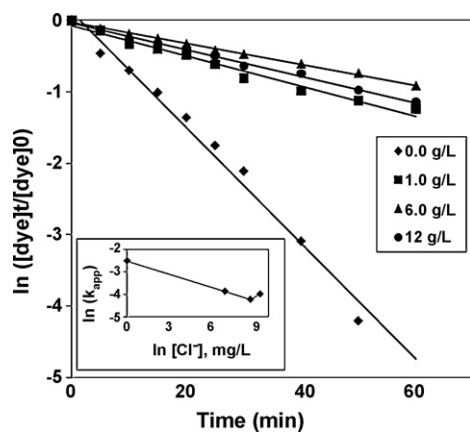


Fig. 8. Effect of concentration of NaCl: (a) 0.0 mg/L, (b) 1000 mg/L, (c) 6000 mg/L and (d) 12,000 mg/L on the photodegradation of MR73 under the conditions: $[dye]_0 = 5 \times 10^{-2}$ mM, $[H_2O_2]_0 = 2.5 \times 10^{-3}$ M, pH 3 and $T = 25^\circ\text{C}$. Inset shows the relation between k_{app} and $[Cl^-]$ on a logarithmic scale.

scavenging rates and the degree of aggregation of the dye as discussed previously. However, in the presence of even higher levels of Cl^- (12 g/L) the reaction rate is observed to increase slightly (to $k_{app} = 0.0186 \text{ min}^{-1}$). This may be attributed to either the dissociation of the $OHCl^{\bullet-}$ radical to OH^\bullet and Cl^- or conversion of $OHCl^{\bullet-}$ to Cl^- and H_2O in the acidic medium [47]. Therefore, under the experimental conditions (pH 3), competition reactions for scavenging and formation of OH^\bullet may take place which would lead to increased decolorization rates in the presence of 12 g/L Cl^- as shown in the inset in Fig. 8 (plot of $\ln[Cl^-]$ and $\ln k_{app}$).

3.4.3. Influence of Na_2CO_3 on the photodegradation of MR73

Different concentrations of Na_2CO_3 were used to study the effect of carbonate ions on the photooxidation of MR73. Carbonate ions were present mainly as H_2CO_3 , since the experiments were performed at pH 3 under H_2O_2/UV . Presence of bicarbonate ions in the course of photooxidation may decrease the decolorization rate due to scavenging of OH^\bullet by HCO_3^- ($HCO_3^- + OH^\bullet \rightarrow CO_3^{\bullet-} + H_2O$). Production of $CO_3^{\bullet-}$ which is less reactive than hydroxyl radical [48] lowered the levels of OH^\bullet during the course of the reaction hence decreasing the decolorization rate as shown in Fig. 9. It was observed that the decolorization rate constant (0.081 min^{-1}) in the absence of carbonate ions decreased to 0.048 min^{-1} due to the presence of 1×10^{-4} M Na_2CO_3 . On the other hand, the inhibition effect of Na_2CO_3 on the rate of dye degradation at concentrations greater than 1×10^{-4} M was negligible, possibly due to competition between scavenging reactions and formation of $CO_3^{\bullet-}$ which

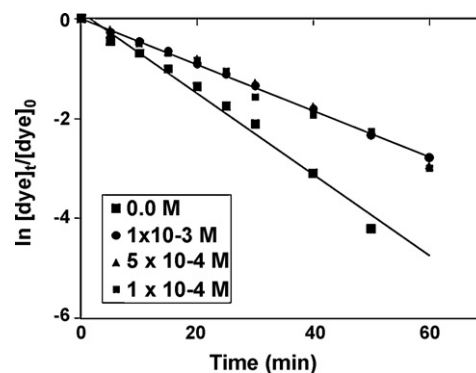


Fig. 9. Effect of concentration of Na_2CO_3 (carbonic acid) on the photodegradation of MR73 under the conditions: $[dye]_0 = 5 \times 10^{-2}$ mM, $[H_2O_2]_0 = 2.5 \times 10^{-3}$ M, pH 3 and $T = 25^\circ\text{C}$.

may act as a selective photooxidant for this dye especially at high concentrations of CO_3^{2-} .

In general, the presence of inorganic anions in the wastewater tends to inhibit the photodegradation of MR73 dye. As shown in Table 1, the lowest rate constant was observed in the case of chloride ion corresponding to the greatest increase in the half-life from 8.56 min (at 0.0 g/L Cl^-) to 47 min (at 6 g/L Cl^-). The presence of nitrate and carbonate ions led to relatively small retardation of photodegradation rates, with half-lives increasing to the range of 12–17 and 14–15 min, respectively. Furthermore, it was found that for each inorganic anion when $t_{1/2}$ increased, $R_{initial}$ decreased as shown in Table 1.

3.5. Effect of photo-Fenton reaction

As described above, the photodegradation of MR73 dye was mainly initiated by the production of OH^\bullet radicals resulting from the direct photolysis of H_2O_2 . Photodegradation experiments using photo-Fenton conditions were studied to investigate the effect of increased production of OH^\bullet radicals by catalytic decomposition of H_2O_2 in the presence of Fe^{2+} . Generally, iron salts are used as a source of Fe^{2+} [7] in the photo-Fenton process. However, a source for Fe^{2+} in the Fenton reaction could be Fe^0 powder that reacts with hydrogen peroxide (Eq. (9)) to produce Fe^{2+} which initiates the Fenton reaction [7]



Since the reaction in Eq. (9) is enhanced in strong acidic medium [7], the experiment was done at pH 3. It was reported [7] that removal of dyes by using Fenton's reaction (H_2O_2/Fe^{2+}) in the pres-

Table 1
Decoloration rate constants (k) and half-lives ($t_{1/2}$) of MR73 dye during aqueous photolysis in the presence of various amounts of inorganic anions in the UV/ H_2O_2 process, with $[MR73]_0 = 5 \times 10^{-2}$ mM, $[H_2O_2]_0 = 2.5$ mM, pH 3 and $T = 25 \pm 2^\circ\text{C}$.

Anion	Conc. (g/L)	k_{app} (min^{-1})	$t_{1/2}$ (min)	$R_{initial} = C_0 k_{app}$ ($\text{mol}^{-1} \text{min}^{-1}$)	R^2
Control	0.0	8.1×10^{-2}	8.56	4.1×10^{-6}	0.985
NO_3^-	1	4.11×10^{-2}	16.86	2.1×10^{-6}	0.988
	2	5.66×10^{-2}	12.24	2.8×10^{-6}	0.997
	3	5.28×10^{-2}	13.13	2.6×10^{-6}	0.996
Cl^-	1	2.1×10^{-2}	33.00	1.1×10^{-6}	0.979
	2	1.47×10^{-2}	47.14	7.4×10^{-7}	0.997
	3	1.86×10^{-2}	37.26	9.3×10^{-7}	0.994
CO_3^{2-}	1	4.8×10^{-2}	14.44	2.4×10^{-6}	0.988
	2	4.7×10^{-2}	14.62	2.4×10^{-6}	0.993
	3	4.6×10^{-2}	15.03	2.3×10^{-6}	0.999

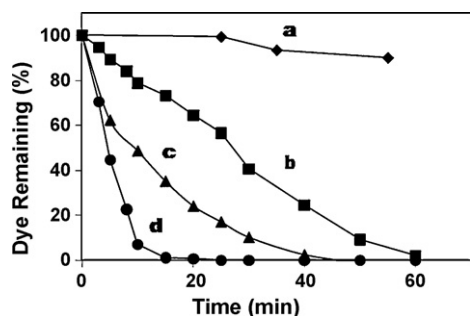


Fig. 10. Removal of MR73 dye from aqueous solution by (a) adsorption, (b) the Fenton reaction, (c) $\text{H}_2\text{O}_2/\text{UV}$ conditions and (d) the photo-Fenton reaction under the conditions: $[\text{dye}]_0 = 5 \times 10^{-2}$ mM, $[\text{H}_2\text{O}_2]_0 = 2.5 \times 10^{-3}$ M, iron dosage = 0.11 g, pH 3 and $T = 25^\circ\text{C}$.

ence of Fe powder may involve one or more of three processes, namely adsorption of dyes on the surface of Fe powder, complex formation (via released Fe^{2+} bonded to N and O atoms present in the dye structure) and degradation by $\cdot\text{OH}$ radicals formed from Fenton's reaction. In addition to these three processes the removal of MR73 dye in this study proceeded via the photo-Fenton reaction ($\text{H}_2\text{O}_2/\text{Fe}^0/\text{UV}$). To investigate the contribution of each process on the removal of MR73 dye from aqueous solution several experiments were performed separately. Fig. 10 demonstrates the removal of MR73 dye using adsorption, the Fenton reaction, $\text{H}_2\text{O}_2/\text{UV}$ and the photo-Fenton reaction. Adsorption of the dye on the surface of Fe^0 powder resulted in about 1% removal in 15 min. Over the same time the degradation of dye by Fenton's reaction ($\text{H}_2\text{O}_2/\text{Fe}^0/\text{dark}$) resulted in about 27% removal and degradation of MR73 by the $\text{H}_2\text{O}_2/\text{UV}$ process resulted in 65% removal. On the other hand, the photo-Fenton reaction ($\text{H}_2\text{O}_2/\text{Fe}^0/\text{UV}$) resulted in the highest efficiency for degradation of MR73 dye with about 99% disappearance in 15 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 MR73 dye under these conditions.

3.5.1. Effect of iron dose

Fig. 11 illustrates the effect of the dose of Fe powder on the photodegradation of MR73 dye. The results showed that the removal rate of the dye increased when the added iron dose increased from 0.056 to 0.11 g/L Fe. This may be attributed to increased production of $\cdot\text{OH}$ radicals with increased iron dose leading to enhanced

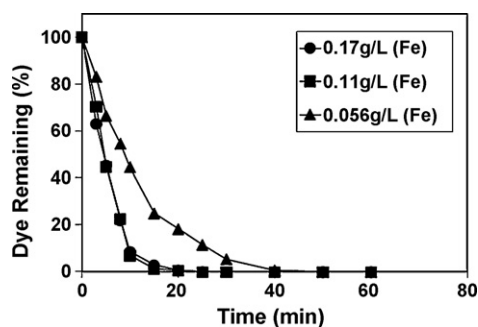


Fig. 11. Effect of the amount of Fe powder on removal of MR73 dye under the conditions: $[\text{dye}]_0 = 5 \times 10^{-2}$ mM, $[\text{H}_2\text{O}_2]_0 = 2.5 \times 10^{-3}$ M, pH 3 and $T = 25^\circ\text{C}$.

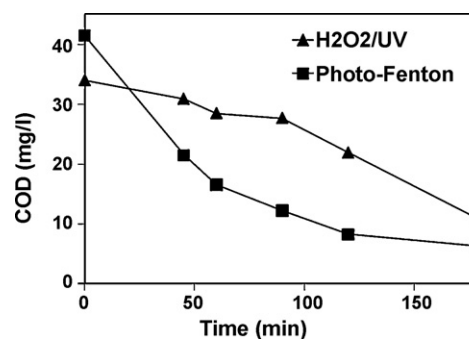


Fig. 12. Changes in the chemical oxygen demand (COD) during photodegradation of MR73 dye by $\text{H}_2\text{O}_2/\text{UV}$ and photo-Fenton processes, under the conditions: $[\text{dye}]_0 = 5 \times 10^{-2}$ mM, $[\text{H}_2\text{O}_2]_0 = 2.5 \times 10^{-3}$ M, iron dosage = 0.11 g/L, pH 3 and $T = 25^\circ\text{C}$.

photodegradation rates. On the other hand, further increases in the amount of Fe powder to 0.17 g/L did not result in appreciable increases in the rate of degradation. Increasing the amount of Fe powder would result in excess Fe^{2+} ions which may scavenge $\cdot\text{OH}$ radicals formed [7].

3.6. Mineralization of MR73 azo dye

As discussed previously, decrease the absorption band of MR73 dye at 492 nm is used to monitor the rate of decolorization of the dye, while decreases in absorbance at 360 and 285 nm indicate the degradation of the aromatic portion of the dye [30]. A rapid decrease in the intensities of the bands at 492, 360 and 285 nm (data are not shown) were observed suggesting that both the chromophore and the aromatic part of the MR73 azo dye were breaking down. In addition, 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 MR73 dye was determined by measuring the decrease in COD values due to the photodegradation of MR73 dye using $\text{H}_2\text{O}_2/\text{UV}$ and photo-Fenton processes over a 3 h photoperiod. The results (see Fig. 12) indicate that the $\text{H}_2\text{O}_2/\text{UV}$ process resulted in 69% mineralization of the dye in 3 h, while the photo-Fenton reaction was more efficient leading to 85% mineralization of the dye over the same time.

4. Conclusion

The experimental data demonstrated that both $\text{H}_2\text{O}_2/\text{UV}$ and photo-Fenton processes are promising techniques for the degradation of MR73 dye from aqueous solution. Using Fe powder as a continuous source for Fe^{2+} ions in the photo-Fenton reaction increased the production of $\cdot\text{OH}$ radicals and led to 85% mineralization of the dye in 3 h. 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 > adsorption. On the other hand, removal of the dye from solution was inhibited by the presence of inorganic anions, with the highest effect in the case of chloride ions which produced an increase in the half-life from 8.56 to 47 min.

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