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Homogeneous photodegradation of dye aqueous solution with H_2O_2/UV process: The effects of inorganic anions and temperature

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ABSTRACT

Photodegradation of aqueous solution of Mordant red17 (MR17) azo dye in UV/H_2O_2, advanced oxidation process was investigated in this study. Results show that MR17 dye decolorization rate was mainly effected by different parameters such as solution pH, H_2O_2 concentration, initial dye concentrations and presence of different inorganic anions such as NO_3^-, Cl^-, CO_3^{2-} ions. The degradation percent of the dye decreased by the presence of inorganic anions in the order of $CO_3^{2-} > Cl^- > NO_3^-$ ions. While increase the temperature of the solution medium from 283 to 318K led to increase the decolorization rate of MR17 dye from 0.048 to 0.164 min^{-1}. The low value of the apparent activation energy E_a (24.91 kJ mol^{-1}) indicates that decolorization process of MR17 dye is achieved easily using H_2O_2/UV process. This results further proved by presence of 100% decolorization of MR17 dye in about 50 min and about 85.57% mineralization in a 3.0 h photoperiod.

KEYWORDS

Mordant dyes;
Eriochrome red B;
H_2O_2/UV;
Photo-fenton;
Iron powder.

INTRODUCTION

Dyes are used in different fields such as textile, tannery, paper and pulp, in addition to food, pharmaceutical, and cosmetic industries[1]. The wide use of dyes has resulted in an increase in the volume and complexity of the wastewater discharged to the environment. It was reported that there is a big amount of dyes are lost in the effluent during the dyeing process[2]. The greatest environmental concern with colored substances such as dyes in the surface water is their absorption and reflection of sunlight entering the water. Thus causing interferes with the growth of bacteria and plants and disturbance the ecology of the receiving water[3]. Also, most dyes have low biodegradability and toxic nature such as azo dyes can originate toxic by-products in the environment[4]. 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[5].

In the same time, less attention was given to the photodegradation of mordant dyes. Thus it is important to treat wastewater containing Mordant red 17 as one class of azo-dyes before discharge[6]. Effluents containing azo dyes are commonly treated by the combination of biological oxidation and physical-chemical treatment methods[7]. However, these traditional methods mainly provide a phase transfer of the contaminants from wastewater to solid waste (sludge)[8]. On the other hand, the decolorization and mineralization of a wide range of dyes to stable inorganic compounds, has been carried out by different advanced Oxidation Processes (AOPs)[9] such as homogeneous[10,11] and heterogeneous photocatalysis[12,13].

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[14,15]. The strategies for generating the reactive •OH radicals for these oxidation methods include UV photolysis of ozone or hydrogen peroxide[16], Fenton or photo-Fenton type reactions, and TiO_2 photocatalysis[17].

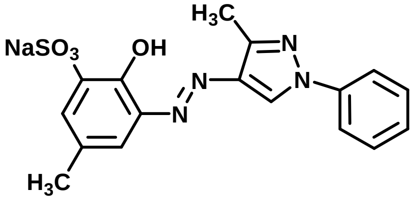
This study aimed to investigate UV/ H_2O_2 process for the photodegradation of the Mordant red 17 azo dye. Also, to examine the effect of several parameters such as the initial concentrations of both the dye and H_2O_2 and the presence of inorganic anions on the degradation kinetics of the dye. The effect of temperature of the solution medium on the decolorization rate was investigated. In addition the effect of Mineralization of the dye was studied as indicator of the decrease in the chemical oxygen demand (COD).

EXPERIMENTAL

Chemicals

H_2O_2 (30% w/w), 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 G azo dye (C.I. mono sulphonic Mordant red 17) azo dye (MR17 dye) purchased from Ciba-Geigy LTD Basel, Switzerland. The chemical structure of MR17 is shown in TABLE 1. All other reagents were analytical grade and used as received. All solutions were prepared with deionized (DI) water.

TABLE 1 : Characteristics of eriochrome red G azo dye (Mordant red 17 azo dye or MR 17).

Chemical Structure	Molecular Formula	λ max (nm)	Mw (g/mol)
	$C_{17}H_{16}N_4NaO_5S$	430	411.39

Methods

Apparatus

Photochemical reactor

The photoreactor used for the photodegradation of MR17 dye was purchased from ACE glass. 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.

Radiation source

A 20W low-pressure mercury vapor lamp (maximum emission at 254 nm) was the UV irradiation source. The lamp was surrounded with a water-cooling jacket to remove the heat and to maintain a constant temperature. The lamp tube was immersed in the reaction solution. The incident photonic flux (light intensity) was measured by the photolysis of ferrioxalate as an actinometer. The value of the incident photonic flux was determined as ($I_o = 1.46 \times 10^{-6}$ Ein. /L min).

Procedures

Experiments of photodegradation of MR17 dye were performed as described elsewhere[13]. Aqueous solutions of MR17 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 ± 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 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

As mentioned previously[18], the change in the concentrations of MR17 dye due to the photodegradation 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 λ_{max} = 430 nm for the dye chromophore. The decolorization ratio, expressed as a percentage, (%) was calculated by[19] the following Equation:

$$\text{Decolorization}(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (1)$$

where C_0 is the initial concentration of MR17 dye in the solution and C_t is the final concentration of MR17 at time t.

Chemical oxygen demand (COD), was determined by closed reflux method. Samples were oxidized with a known excess of $K_2Cr_2O_7$ in 50% H_2SO_4 solution. Then the excess of $K_2Cr_2O_7$ was determined by standard solution of ferrous ammonium sulfate in presence of ferrion indicator.

RESULTS AND DISCUSSION

The primary step in these experiments was the determination of the maximum absorbance (λ_{max}) for MR17 dye using different concentrations. At pH 3 (at which the experiments were carried out) the spectrum of MR17 dye represents absorption bands at 430 and 260 nm. The band at 430 nm (attributed to n > π^* 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 band at 260 nm ($\pi > \pi^*$ transition in aromatic rings) represent aromatic character of the dye, hence decreases in the absorbance at this wavelength correspond to loss of aromaticity of the dye during photodegradation[20]

The effect of pH of the dye solution on decolorization efficiency

Changing the solution pH has an important effect on the structure and characteristics of the dyes[19]. Thus the degradation of (0.05 mM) MR17 was studied at various initial pHs (3, 5, 7 and 9) to investigate its effect on the decolorization process as shown in Figure 1. The results indicate that the decolorization efficiency of MR17 dye at the same dose of H_2O_2 under both acidic and alkaline conditions were different and appear to be dependent on the initial pH. It can be noted that the largest decolorization rate with almost 100% disappearance of the parent MR17dye in the first 50 min of photolysis was observed at pH 3.0 with a H_2O_2 concentration of 2.5 mM.

While increasing the pH value to a strong alkaline medium decreased the decolorization (%). The lowest degradation rate was observed in alkaline medium as the decolorization (%) decreased from 100 to 73.4% at pH9 at the same concentration of H_2O_2 in the same photoperiod as shown in Figure 1. This may be due to the efficient generation of hydroxyl radicals with strong oxidizing potential (E^0 = 1.8 V at neutral pH to 2.7 V in acidic pH) under acidic conditions[21,16].

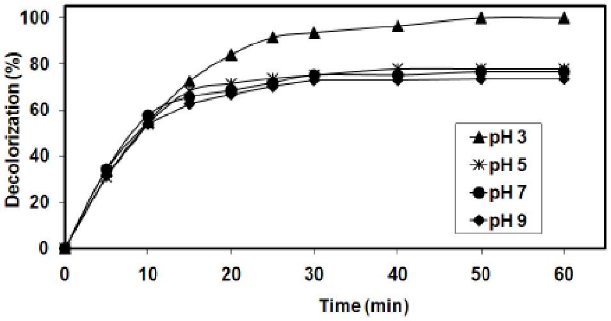


Figure 1 : Dependence of the decolorization (%) on the pH value of MR17 dye under the conditions: $[dye]_0 = 5\times10^{-2}$ mM, $[H_2O_2]_0 = 2.5\times10^{-3}$ M and T = 25 ± 2°C.

Furthermore, decolorization (%) of MR17 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 less than one pH unit in acidic medium (from 5.00 - 4.61) while the neutral and alkaline medium lead to dropping by more than one pH unit (7.00 - 5.15 and 9.00 - 7.40) except in the case of high pH (pH3) it remains almost constant within the 60 min of irradiation as shown in Figure 2. This slight drop in the 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[22]. Decreasing the pH values during the photodegradation process using H_2O_2 was also observed for different dyes such as Reactive red 120, Reactive black 5, Reactive yellow 84 in aqueous solution[6]. However, remaining the pH value almost constant at initial high pH (pH3), 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 MR17 dye under the present conditions. Since hydroxyl radicals are generated efficiently under acidic conditions[23], also, the results indicated that MR17 degraded significantly at pH3, subsequent experiments were performed at pH 3.

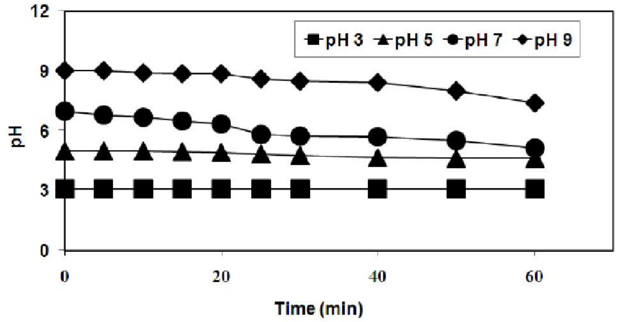


Figure 2 : Change the initial pH of the photodegradation process of MR17 dye during the irradiation time, under the conditions: $[dye]_0 = 5\times10^{-2}$ mM, $[H_2O_2]_0 = 2.5\times10^{-3}$ M and T = 25 ± 2°C.

Effect of initial hydrogen peroxide (H_2O_2) concentration

Photodegradation process is mainly dependent on the amount of $^{\bullet}$OH radicals. However, production of $^{\bullet}$OH radicals is a function of the concentration of H_2O_2. Several experiments were performed to investigate the effect of H_2O_2 concentration on the effectiveness of the photodegradation of MR17 dye. Aqueous solutions of MR17 dye (0.05mM) were irradiated in the absence and presence of H_2O_2 as shown in Figure 3. It was found that while direct photolysis (in the absence of H_2O_2) of MR17 day solution was very slow and resulted in about 5% of dye decolorization in 60 min. Also, in the same period of the experiment, dark reaction (MR17dye/H_2O_2/dark) was found to have about 5% of dye decolorization which was in agreement with the literature[24].

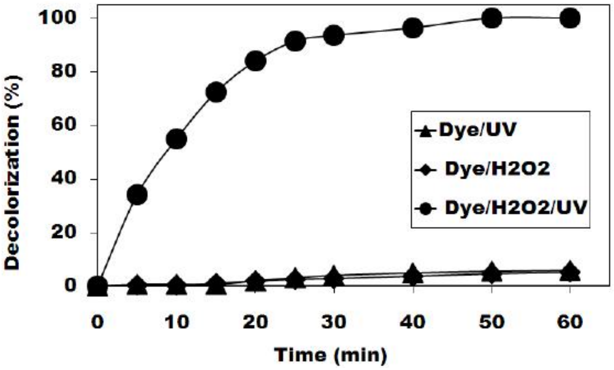


Figure 3 : Dependence the decolorization (%) of 5x10-2 mM MR17 dye on the presence of H_2O_2 under the conditions: $[dye]_0 = 5\times10^{-2}$ mM, $[H_2O_2]_0 = 2.5\times10^{-3}$ M, pH 3 and T = 25 ± 2°C.

However, MR17 dye photodegradation was sensitized by the presence of hydrogen peroxide due to the generation of a non-selective and powerful oxidant, $^{\bullet}$OH radicals[25]. Thus production of $^{\bullet}$OH radicals by direct photolysis of added hydrogen peroxide[26] according to Eq. 2, resulted in 100% decolorization of MR17 dye in the first 50 min.

$$H_2O_2 + h\nu\ 2\,{}^{\bullet}OH \qquad (2)$$

It was reported that the dosage of H_2O_2 is a critical parameter of advanced oxidation processes (AOPs)[27]. Also, the results of the decolorization of MR17 depends mainly on the concentration of H_2O_2. When H_2O_2 reacts with dye molecules, theoretically an excess of H_2O_2 is needed to produce more $^{\bullet}$OH radicals. However, increase both the concentration of H_2O_2 and $^{\bullet}$OH radicals result in competitive reactions, which would inhibit the decolorization rate of MR17 according to Eq. 3-7[19]

$$\bullet OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \qquad (3)$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow {}^{\bullet}OH + H_2O + O_2 \qquad (4)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \qquad (5)$$

$$2\,HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (6)$$

$$2\,{}^{\bullet}OH \rightarrow H_2O_2 \qquad (7)$$

The previous reactions show that $^{\bullet}$OH radicals consumed by reactions (3), (5) and (7). Therefore an optimum concentration of H_2O_2 in the reaction course must be reached. As described previously[13], a pseudo-first-order rate equation can be used to illustrate the photodegradation reaction rate (r) of MR17 dye using different concentrations of H_2O_2 (2.5x10^{-5}, 2.5x10^{-3}, 2.5x10^{-1} and 5x10^{-1}M). Linear regression of first-order plots of ln C_0/C_t versus time provide k_{app} from slopes. The results in Figure 4 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.

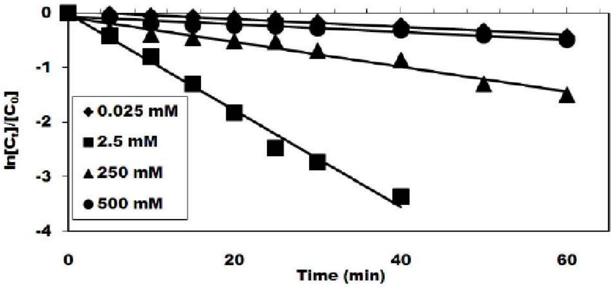


Figure 4 : Dependence of the decolorization (%) of MR17 dye on the H2O2 concentration under the conditions: [dye]0 =5×10-2 mM, pH 3 and T=25 ± 2°C.

Photodegradation kinetics data [half-lives time ($t_{½}$), apparent rate constant (k_{app}), the coefficient of determination (R^2) and initial reaction rate for degradation of (0.05 mM) MR17 dye using different concentrations (mM) of H_2O_2 are presented in TABLE 2.

TABLE 2 : Photodegradation kinetics data [half-lives time ($t_{½}$), apparent rate constant (k_{app}), the coefficient of determination (R^2) and initial reaction rate for degradation of (5 x10^{-5} M) MR 17 dye using different concentration (mM) of H_2O_2.

$[H_2O_2]$, mM	k_{app} (min^{-1})	t ½ (min)	$R_{initial}$ (mol L$^{?1}$ min$^{?1}$)	R^2
0.025	0.007	99	1.75E-07	0.9884
2.5	0.088	7.87	2.2E-06	0.9958
250	0.022	31.5	5.5 E-07	0.9934
500	0.007	99	3.5E-07	0.9815

It can be seen that the largest degradation rate of the dye was observed with a H_2O_2 concentration of 2.5 mM with apparent rate constant of 0.088 min^{-1}. Increasing the concentration of H_2O_2 to 500 mM lead to high inhibition of the reaction as noted by more decrease in the rate constant to 0.007 min^{-1}. Furthermore, the degradation rate constant of the dye at the lower H_2O_2 concentration (0.007 min^{-1}) was the same as the degradation rate at higher concentration (0.007 min^{-1}). At lower H_2O_2 concentration (0.025 mM), the decolorization rate decreases due to the presence of insufficient $^{\bullet}$OH radicals. While increasing the concentration of H_2O_2 to 500 mM, resulted in high scavenging rate of high reactive $^{\bullet}$OH radicals by H_2O_2 to produce less reactive radicals such as $HO_2^{\bullet}$ (Eq. 3). It is interesting to note that the photodegradation process in the presence of H_2O_2 is more efficient when using the optimum dose of H_2O_2 as reported previously by numerous authors[27]. Since the highest degradation rate was observed by using 2.5 mM H_2O_2, therefore, in all subsequent experiments an initial H_2O_2 concentration of 2.5 mM was used.

Effect of dye initial concentration (C_o) on efficiency of the process

Effect of initial dye concentration on the photodegradation rate was investigated by irradiation of solutions with different initial concentrations (0.1 and 0.05 mM) of MR17 dye. pseudo-first-order kinetic model was used to represent the data as shown in Figure 5.

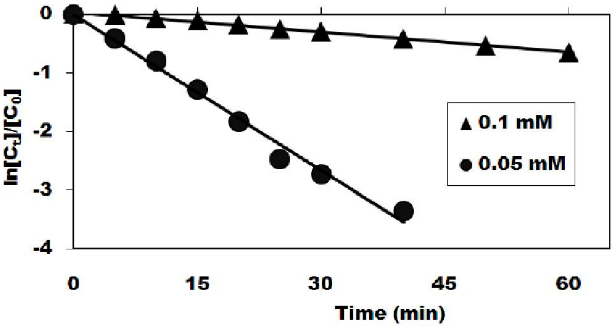


Figure 5 : Effect of initial concentration of the MR17 dye on photodegradation under the conditions: $[H_2O_2]_0$ = 2.5x10^{-3}M, pH 3 and T= 25 ± 2 °C.

The kinetic data such as apparent rate constant (k_{app}, min^{-1}), half-lives time ($t_{½}$), and the coefficient of determination (R^2) for degradation of MR17 dye are presented in TABLE 3.

TABLE 3 : Kinetics data for effect of initial dye concentrations on photodegradation of MR17 dye using 2.5x10^{-3} M $[H_2O_2]$, pH 3 and T= 25 ± 2 °C.

[MR17 dye], mM	k_{app} (min-1)	$t_{½}$ (min)	R^2
0.1	0.0115	60.27	0.9944
0.05	0.0884	7.840	0.9888

Results indicated that the lowest decolorization rate (50%) was observed at high concentration of dye (0.1 mM) in the first 40 min with apparent rate constant of 0.0115 min^{-1} and half-life of 60.27 min. However, using low initial concentration of the dye (0.05 mM) resulted in large enhancement in the degree of decolorization to reach 93% which lead to increase the apparent rate constant more than 7 times to be 0.0884 min^{-1} and the half-life decreased to 7.84 min. This is due to the absorption of major illuminated light by dye molecules, at high initial concentrations, which act as filters limiting the penetration of light through the solution[28] thus decreasing the generation of $^{\cdot}OH$ radicals available for photodegradation of MR17 dye[29]. Also, these results suggest that oxidation occurs on the chromophore rather than on the dye molecular skeleton. Because of this, H_2O_2/UV would be more effective for dilute solutions of MR17 dye.

Effect of inorganic anions on photodegradation process

To investigate the effect of inorganic anions on the decolorization of MR17 dye, experiments were performed in presence of (1.145 g/L) nitrate (NO_3^-), chloride (Cl^-) and carbonate (CO_3^{-2}) ions. TABLE 4 presented the results of varies the decolorization % at different times with the studied inorganic anions.

TABLE 4 : Effect of (1.145 g/L) different inorganic anions (NO_3^-, Cl^- and CO_3^{-2}) on the photodegradation of MR17 under the conditions: $[dye]_0 = 5x10^{-2}$ mM, $[H_2O_2]_0 = 2.5x10^{-3}$ M, pH 3 and T = 25 ± 2°C, (control = absence of anions).

Time (min)	Decolorization (%)			CO^{-2}_3
	Control	NO^-_3	Cl^-	
0	0.00	0.00	0.00	0.00
5	34.00	29.77	31.51	16.28
10	55.00	46.51	42.92	26.98
15	72.50	66.05	64.38	41.40
20	84.00	75.81	76.71	46.98
25	91.50	83.72	86.30	61.86
30	93.50	90.70	89.95	69.77
40	96.50	96.28	94.52	79.53
50	100.00	100.00	96.80	86.98
60	100.00	100.00	98.17	90.23

It was reported that presence of inorganic anions in the photodegradation solutions may induce or reduce the rate of photooxidation[30]. The kinetic data (TABLE 5) showed that the rate of photodegradation of MR17 was differ in the presence of different inorganic anions. Presence of NO_3^- ions lead to slight decrease in the photodegradation rate as shown by increase the half-life ($t_{1/2}$) of degradation process from 7.88 (in the absence of NO_3^-) to 8.45 min. Although previous reports[31] showed that the presence of $NaNO_3$ had negligible effect on the photodegradation process. This may be attributed to the scavenging of $^{\cdot}OH$ radicals by NO_3^- decreasing the availability of $^{\cdot}OH$ radicals for the photodegradation process. Furthermore, presence of Cl^- ions significantly decreased the decolorization rate constant of dye and the $t_{1/2}$ increased from 7.88 to 10.19 min. However, the rate decreased dramatically from 0.088 min^{-1} in the absence of CO_3^{2-} to 0.040 min^{-1} due to the addition of CO_3^{2-} ions which lead to increase the $t_{1/2}$ by 2.2 fold (from 7.88 to 17.33 min). This behavior may be attributed to $^{\cdot}OH$ radical scavenging by CO_3^{2-} ion[32].

TABLE 5 : Photodegradation kinetics data [apparent rate constant (k_{app}), half-lives time ($t_{½}$) and the coefficient of determination (R^2)] for degradation of (2.5 x10^{-5} M) MR17 in the presence of (1.145 g/L) different inorganic anions (control = absence of anions).

Anions	k_{app} (min^{-1})	t ½ (min) = ln (2)/k_{app}	R^2
Control	0.088	7.88	0.988
NO_3^-	0.082	8.45	0.992
Cl^-	0.068	10.19	0.990
CO_3^{2-}	0.040	17.33	0.989

Since the experiments were performed at pH 3 under H_2O_2/UV, carbonate ions were present mainly as H_2CO_3. Presence of bicarbonate ions in the course of photooxidation may decrease the decolorization rate due to scavenging of $^{\cdot}OH$ by HCO_3^- as shown in Eq. 8.

$$HCO_3^- + OH^{\cdot} \rightarrow CO_3^{\cdot-} + H_2O \qquad (8)$$

Production of $CO_3^{\cdot-}$ which is less reactive than hydroxyl radical[33] lowered the levels of $^{\cdot}OH$ during the course of the reaction hence decreasing the decolorization rate as shown in TABLE 4. In general, the presence of inorganic anions in the wastewater tends to inhibit the photodegradation of MR17 dye as shown in TABLE 5.

Effect of temperature of aqueous medium

Effect of temperature on MR17 dye degradation was investigated. Figure 6 represent the effect of temperature on the decolorization rate of MR17 dye at 273, 298, 308 and 318K. Apparently, temperature showed significant positive influence on the rate of degradation of the dye. The results obtained in Figure 6 indicate that the decolorization rate of the MR17 dye increases with the increase in the temperature. Thus when the temperature increased from 283 to 318K, the decolorization rate increased from 0.048 to 0.164 min^{-1}. This increase in the decolorization rate may be due to both increase the reaction activity of $^{\bullet}OH$ radicals[33] and the increase in collision frequency of molecules in the solution[34], which enhances the reaction between MR17 dye molecules and $^{\bullet}OH$ radicals.

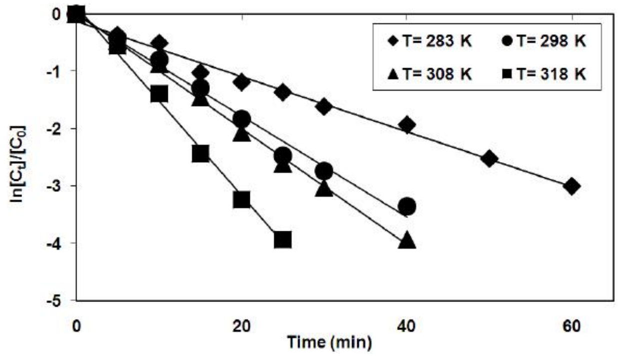


Figure 6 : Effect of temperature on photodegradation of the MR17 dye under the conditions: $[H_2O_2]_0 = 2.5\times10^{-3}$M, $[dye]_0$ = 5 mM and pH 3.

According to the apparent kinetic rate constants at different temperatures, the apparent activation energy E, for the decolorization of MR17 dye by H_2O_2/UV was computed with Arrhenius Equation:

$$k = A\exp\left(-\frac{E}{RT}\right) \qquad (9)$$

Taking the natural logarithm of both sides yields:

$$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right) \qquad (10)$$

where, *A* is the pre-exponential (or frequency) factor; E_a is the apparent activation energy (J mol^{-1}), R is the ideal gas constant (8.314 $Jmol^{-1}$ K^{-1}) and T is the reaction absolute temperature (K). The Arrhenius plot of ln *k* versus 1/T for MR17 (Figure 7) has a linear relationship and allow to obtain E_a from its slope. The apparent activation energy E_a, obtained from the Arrhenius type plot in Figure 7 was found to be 24.91 kJ mol^{-1}. Generally, the reaction activation energy of ordinary thermal reactions is usually between 60 kJ mol^{-1} and 250 kJ mol^{-1}[33], the result implies that the decolorization of MR17 dye in aqueous solution by H_2O_2/UV process requires lower activation energy (E_a) and can be easily achieved.

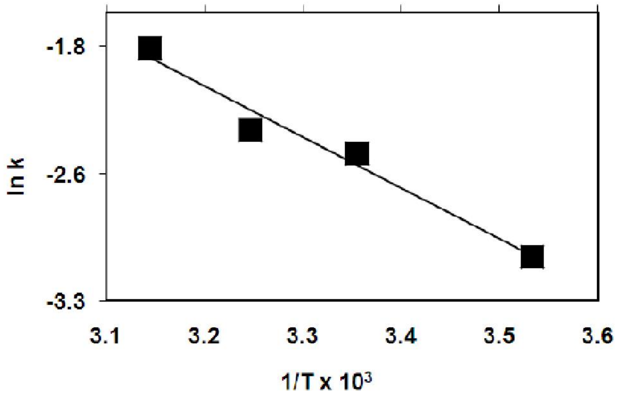


Figure 7 : The arrhenius plot of ln k versus 1/*T* of the decolorization of MR17 by H_2O_2/UV process under the conditions: $[H_2O_2]_0 = 2.5\times10^{-3}$ M, $[dye]_0$ = 5mM and pH 3.

Mineralization of MR7 azo dye

The extent of the mineralization of the dye was determined on the basis of chemical oxygen demand (COD) measurements. The mineralization efficiency was calculated by Eq.11.

$$\text{Mineralization}(\%) = \frac{COD_0 - COD_t}{COD_0}\times 100 \qquad (11)$$

where COD_0 corresponds to the initial value of COD and COD_t is the value of COD obtained at time t.

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 car-

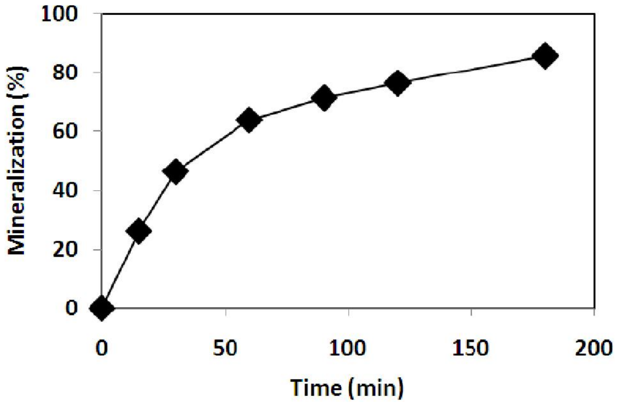


Figure 8 : Mineralization of MR17 dye as indicated by decrease the chemical oxygen demand (COD) during photodegradation by H_2O_2/UV process, under the conditions: $[dye]_0 = 5\text{x}10^{-2}$mM, $[H_2O_2]_0 = 2.5\text{x}10^{-3}$ M, pH 3 and T= 25 ± 2°C.

bon content in the sample, hence indicative of the extent of mineralization. The extent of degradation of MR17 dye was determined by measuring the decrease in COD values due to the photodegradation of MR17 dye using H_2O_2/UV over a 3.0 h photoperiod as shown in Figure 8. The results indicating that the H_2O_2/UV process was very efficient and mineralizes about 85.57% of MR17 dye in period of 3.0 h.

CONCLUSION

The results have shown that UV/H_2O_2 treatment is very effective and can be a suitable pre-treatment method for the degradation of MR17 dye. Using a 20W low-pressure mercury vapor lamp in presence of 2.5×10^{-3} M H_2O_2 lead to about 100% decolorization in the first 50 min and 85.57% mineralization of MR17 dye in about 3.0 hr. 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 decolorization rate was found to increase by increasing the temperature of aqueous medium from 283 to 318K. The lower value of E_a obtained from the slope of the linear relationship of Arrhenius Equation indicated that the decolorization of MR17 dye in aqueous solution by H_2O_2/UV process requires lower activation energy and can be easily achieved. The investigations should be continued in order to identify the evaluation of the intermediates during the oxidation process.

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