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Decomposition of a Diazo Dye in Aqueous Solutions by $KMnO_4$ /UV/H_2O_2 Process

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ABSTRACT

This study examined the photolytic degradation of C.I. Acid Red 73(AR73), in aqueous solution by $KMnO_4$/UV/H_2O_2 process. A continuous circulated photoreactor equipped with a UV lamp was used. (I) Potassium permanganate was used for decolourisation of AR73 dye solution. The stoichiometric amount of potassium permanganate required for 1 mol of AR73 complete color removal was determined (2.79 mol). In the acidic solution, 100% of AR73 color removal and near 10% dye mineralization have been observed in no more than 5 minutes. (II) After decolourisation period, UV/H_2O_2 system was applied for mineralization of the dye solution. Under the best operational conditions, after 180 minutes of UV irradiation, 90% of dye mineralization was observed. III) The results of this method were compared with those of obtained by using UV/H_2O_2 system (without $KMnO_4$). It was found that within the same irradiation time, $KMnO_4$/UV/H_2O_2 process is about 10% more effective for mineralization of AR73 dye solution. Prog. Color Colorants Coat. 5(2012), 41-46. © Institute for Color Science and Technology.

1. Introduction

Due to the large number of aromatics present in the molecules of the synthetic dyes which are widely used in a number of industries such as textile, leather, cosmetics, food and paper printing, most conventional decolorization and mineralization methods are ineffective [1, 2]. For example, the textile industry consumes considerable amounts of water during the dyeing, printing and finishing operations. Dye pollutants from this industry are an important source of environmental contaminations. Azo dyes are an important class of synthetic textile dyes used as coloring agents in the industries, accounting for 50% of all commercial dyes [3]. They are characterized by the presence of one or more azo groups (-N=N-) bound to aromatic rings. However, large amounts of these dyes remain in the effluent after the completion of the dyeing process. Consequently, the textile wastewaters are highly colored. Azo dyes are stable compounds, difficult to destroy or to be decomposed by common treatment in a biological treating station [4]. Homogeneous advanced oxidation

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process (AOP) employing hydrogen peroxide with UV light has been found to be effective in the decolorization and mineralization of dye pollutants [5-9]. The mechanism of dye destruction in AOPs is based on the formation of a very reactive hydroxyl radical ($^{\bullet}OH$) that, with an oxidation potential of 2.80V, can oxidize a broad range of organic compounds. Otherwise, the potassium permanganate ion (MnO_4^-) as a strong oxidizing agent has been applied to oxidize some of the organic compounds [10-12].

In the present study, decolorization and mineralization of AR73 azo dye solution by combined potassium permanganate and one of the AOPs processes (UV/H_2O_2) were studied. In the first step, potassium permanganate solution has been used for decolorization of the dye solution and the effects of reaction conditions on color removal efficiency were examined in batch experiments. In the second step, mineralization of dye solution was studied using UV/H_2O_2 system. Finally, the results of this method ($KMnO_4/UV/H_2O_2$) were compared with UV/H_2O_2 system.

2. Experimental

2.1. Reagents

The 7-Hydroxy-8- (4-phenylazophenylazo)-1, 3-naphthalenedisulfonic acid di sodium salt, commonly named AR73 (70%) was supplied from Aldrich chemicals. Potassium permanganate solutions of the required concentrations were prepared by dissolving $KMnO_4$ (Fluka ≥0.99 %) in ultra pure water. Hydrogen peroxide (30% w/w) was obtained from Prolabo and the pH of the solutions was adjusted using H_2SO_4 and NaOH (Merck).

2.2. Reactors and Methods

Decolorization of AR73 dye was carried out in a stirred batch reactor and for dye mineralization; a continuous photo reactor with a low-pressure mercury lamp (15 W) was used. The reservoir of the reactor was loaded with 4000 ml of the synthetic reaction mixture. A Jasco V-530 spectrometer recording the spectra over the 200-1100 nm range was used for determination of AR73 concentration. Total organic carbon (TOC) of dye solutions was measured by catalytic oxidation followed by IR spectrometry for CO_2 quantification using a Shimadzu TOC-V_{CSN} instrument, equipped with an automatic sample injector. TOC values are the average of three measurements.

In each decolorization experiment, reaction mixtures were obtained by taking an appropriate amount of dye stock solution, adding the different concentrations of potassium permanganate and adjusting the pH value by NaOH or H_2SO_4. The concentration of the residual dye in solution was calculated by Beer Lambert law using the optical density and molar extinction observed at the characteristic wavelength. The stoichiometric amount of $KMnO_4$ required for complete color removal of 1 mol AR73 was 2.79. After decolorization period, desired amount of H_2O_2 was added to reaction mixture, and then UV lamp and circulation pump were turned on. The temperature was kept at 25°C. During the photolysis, sample aliquots were taken from the reactor at regular time intervals. Total carbon organic was determined by TOC analyzer.

The efficiency of color removal and dye mineralization were defined by the following expressions:

$$\text{Decolorization (\%)} = (1 - ([AR73]/[AR73]_0)) \times 100 \quad (1)$$

$$\text{Mineralization (\%)} = (1 - ([TOC]/[TOC]_0)) \times 100 \quad (2)$$

Where: [AR73] and [TOC] are dye and TOC concentrations at time *t*, respectively. $[AR73]_0$ and $[TOC]_0$ are dye and TOC initial concentrations respectively.

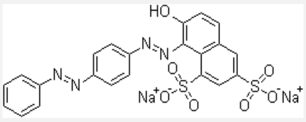
3. Results and discussion

3.1. Decolorization of AR73 by potassium permanganate

The structure of the AR73 and its characteristics were shown in Table 1. The major absorbance of the dye solution are at 510 nm, 345 nm and 245 nm.

According to the previous observations, the best condition for oxidation by potassium permanganate was found at the acidic condition [13]. The amount of permanganate required for complete removal of different dye concentrations is shown in Figure 1. Figure 2 shows the spectral evolution of the dye solution which is decolorized in pH <1.5 using potassium permanganate. As it is shown in Figure 2, complete color removal of AR73 solution (40 mgl^{-1}) has obtained within 5 minutes.

Table 1: Chemical structure and characteristics of AR73.

Name	Structure	Mw($gmol^{-1}$)	Chemical class	C.I. number	λmax (nm)
AR73		556.48	Diazo	27290	510

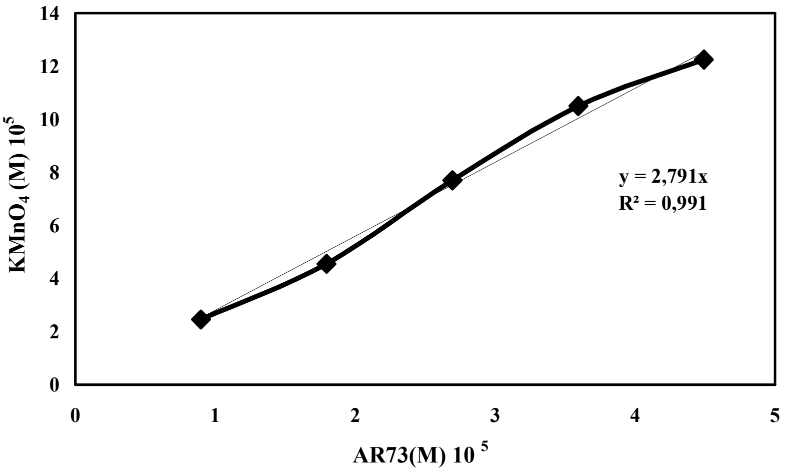


Figure 1: The amount of potassium permanganate required for decolorization of different concentrations of AR73.

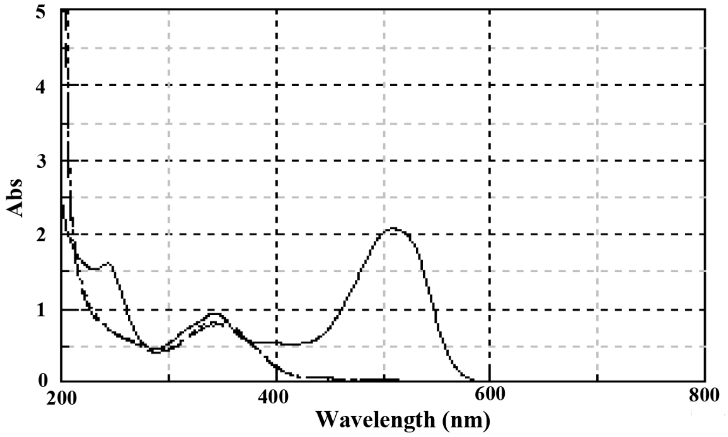


Figure 2: Complete color removal for 4 litre solution of the AR73 (40 mgl^{-1}) (t= 5 min, T=25°C, pH<1.5).

3.2. Effect of the pH on the decolorization efficiency of the dye solutions

The pH influence on the decolorization efficiency was investigated at pH 1-6 and the results are shown in Figure 3. It is observed, at pH: 2, the efficiency of decolorization is more than 97% and the decolorization efficiency decreases with increasing the pH. For the pH > 6, the solutions were not decolorized. The similar results have been obtained in reference [14]. The pH effect depends on the oxidation potential (E°), and it was reported that the pH value determines whether oxidation occurs via one, three, or five electrons exchange [15]. Eq.3 is applied to neutral and alkaline mediate and Eq.4 to acidic conditions.

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^- \quad +0.59V\ (E°) \quad (3)$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad +1.51V\ (E°) \quad (4)$$

Therefore, the more acidic the dye solution, the more powerful the oxidation ability of $KMnO_4$.

3.3. Effect of the temperature on the decolorization efficiency of the dye solutions

The effect of the temperature on the color removal of AR73 solution by potassium permanganate was carried out at 20, 30, 40, 50 and 60°C. The results are presented in Figure 4.

As we can observe, the color removal increases with temperature. Although the increase of temperature enhanced decolorization efficiency, it can also raise the cost of process. After 20 seconds, near 95% color removal of the dye can be obtained at ambient temperature.

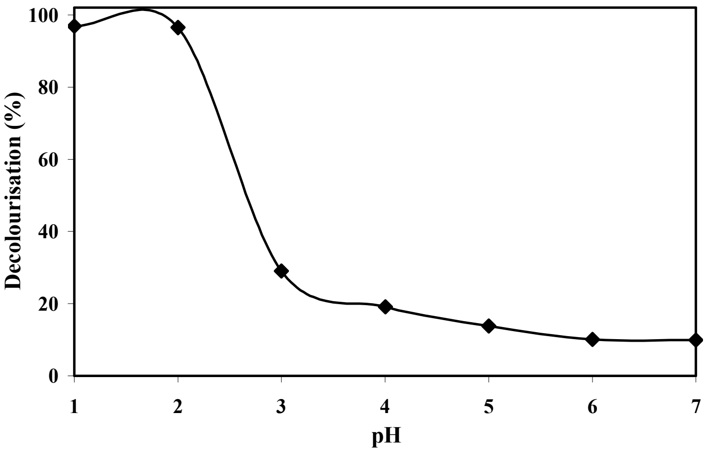


Figure 3: Effect of the pH on the decolorization efficiency ([Dye] = 20 mgl^{-1}, [$KMnO_4$] = 0.04 mol/L, T=25°C, t=20seconds)

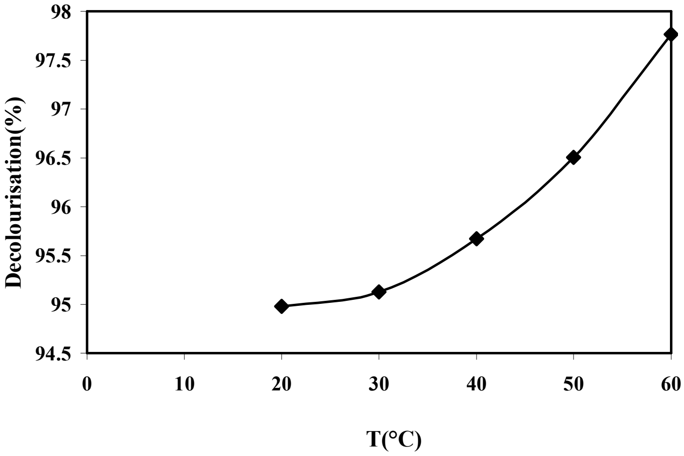


Figure 4: Effect of the temperature on the decolorization efficiency ([Dye] =20mgl^{-1}, [$KMnO_4$] = 0.04 mol/L, pH<1.5, t = 20 seconds).

3.4. Mineralization of AR73

3.4.1. Mineralization of the dye by UV/H_2O_2 process

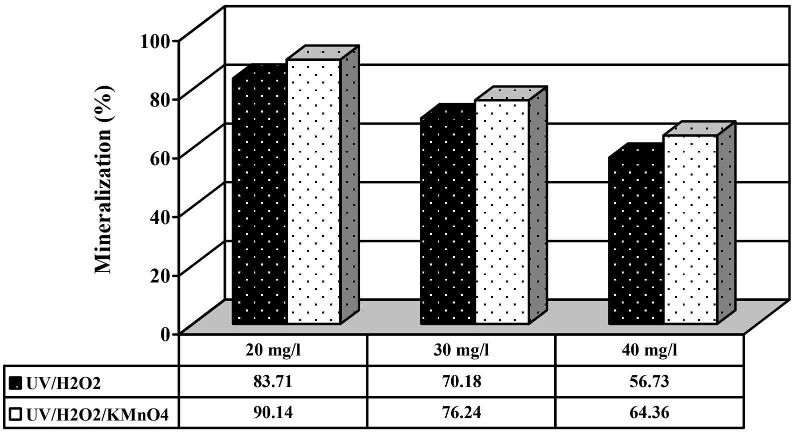
The study of the photochemical treatment of the dye by UV/H_2O_2 process was carried out in the photochemical reactor. There are three important parameters in this method; temperature, H_2O_2 optimum value ([H_2O_2]/ [Dye]) and pH.

Due to Arrhenius equation, the efficiency of the dye mineralization increases by temperature. But, increasing the temperature means more energy and process cost. So, the temperature of the solutions was at room temperature (≈25°C). The effect of H_2O_2 quantity on the dye mineralization was studied when [H_2O_2]/ [Dye] was 20, 30, 50, 60 and 70. The results indicated that the maximum dye mineralization is achieved when [H_2O_2]/ [Dye] =60. It means that there is an optimum value for H_2O_2 quantity while the mineralization efficiency is equal to or less than the optimum value for other H_2O_2 quantities. Then, the effect of pH was studied at room temperature when [H_2O_2]/ [Dye] =60. According to the results, dye mineralization efficiency at original pH of the solutions ($5.5 \leq pH \leq 6.5$) is higher compared to acidic or basic conditions. It means that the best condition of UV/H_2O_2 process is original pH of the dye solutions and [H_2O_2]/ [Dye] =60 at room temperature.

3.4.2. Mineralization of the dye by $KMnO_4$/UV/H_2O_2 process

Total organic carbon of the different Acid Red73 solutions, were followed by TOC analyzer. In the best experimental conditions, nearly 100% of color removal and 10% TOC removal were achieved by oxidative $KMnO_4$ pretreatment within 5 min, while total decolorization of AR73 longs 30 min in UV/H_2O_2 process. As the rate of mineralization increases after completely decolorization, we have combined potassium permanganate pretreatment and UV/H_2O_2 process to minimize the overall time of mineralization. So, in the new process ($KMnO_4$/UV/H_2O_2), potassium permanganate and UV/H_2O_2 process were used for decolorization and mineralization of AR73, respectively. By applying this process, about 90% of dye mineralization was obtained within 180 min while in the best condition of the UV/H_2O_2 process ([H_2O_2]/[Dye] = 60 (w/w)), about 80% of dye mineralization had been achieved within the same process time. Figure 5 shows the comparison of the results, obtained from $KMnO_4$/UV/H_2O_2 and UV/H_2O_2 process for different concentrations of AR73. These results show the high mineralization efficiency after the complete decolorization.

Meanwhile, the complete decolorization is performed only in a few minutes in the combined $KMnO_4$/UV/H_2O_2 process, therefore mineralization efficiency can be obtained at shorter times in comparison with the other processes. So, the combined processes could be recommended for a complete mineralization of the dye.



	20 mg/l	30 mg/l	40 mg/l
■ UV/H2O2	83.71	70.18	56.73
□ UV/H2O2/KMnO4	90.14	76.24	64.36

Figure 5: Comparison of AR73 degradation efficiency using UV/H_2O_2 and $KMnO_4$/UV/H_2O_2 processes, [H_2O_2]/ [Dye] =60 (w/w), [$KMnO_4$] = 0.04 mol/L, T = 25°C, t =180 min.

4. Conclusion

Decolorization and mineralization of the different concentrations of AR73 were studied by applying $KMnO_4/UV/H_2O_2$ and UV/H_2O_2 processes. Total color removal and 10% TOC decrease were obtained after 5 minutes of oxidative pretreatment by potassium permanganate. Although $KMnO_4/UV/H_2O_2$ and UV/H_2O_2 processes gave good results, the $KMnO_4/UV/H_2O_2$ system is considered to be most convenient photodegradation process because it yields higher TOC reduction (near 10%) than UV/H_2O_2 reaction, after the same time of irradiation.

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