IOP Conf. Series: Materials Science and Engineering **433** (2018) 012039 doi:10.1088/1757-899X/433/1/012039

# Removal of Textile Dye from Aqueous Media Using an Advanced Oxidation Process with UV/$H_2O_2$

***Rasul M. Khalaf*** [1] ***Nagam O. Kariem*** [2] ***Alaa A. M. Khudhair*** [3]

[1]*Asst. Prof., Department of Civil Engineering, University of Mustansiriyah, Baghdad, Iraq, IAHR Member.rasulcon@uomustansiriyah.edu.iq , ORCID 0000-0003-0131-4274*
[2]Asst. Prof., Department of Environmental Engineering, University of Mustansiriyah, Baghdad, Iraq.
ragamob@uomustansiriyah.edu.iq

[3]*Mayoralty of Baghdad, The Design Office, Baghdad, Iraq.*
almuhandis_alaa@yahoo.com

**Abstract.** *This study investigated the treatment of water contaminated with textile dye (Cibacron Red FN-R, reactive red 238) using a UV/H2O2 process. The reaction was influenced by the input concentration of hydrogen peroxide H2O2, pH, temperature, and the concentration of textile dye in the wastewater. Analysis of the experimental results displayed both first order and the second order reactions. The reaction type was found to be of a first order throughout the systems. The removal efficiency of the UV/ H2O2 process at optimal conditions and dosage (H2O2 = 25 mg/L, pH=3, temperature =20 ˚C for 50 mg/L dye concentration) were found to be 80.633% , 97.07%, and 99.43% at 60 min, 120 min, and 180 min, respectively with K1 = 0.0293 min-1 and R2=0.9992%. COD removal was also studied for the UV/H2O2 process and found to be 62.5%.*

**Keywords:** adsorption, coagulation, Advanced Oxidation Processes (AOPs), Destruction of organic and inorganic contaminants, Fenton process, Ozonation process, Hydrogen peroxide.

## 1. INTRODUCTION

### *1.1. Foreword*

The remediation of wastewater from industrial establishments before release must be performed to improve the characteristics of water and to meet administrative prerequisites for environmental protection. The textile industry is one that demands large quantities of water, and thus produces similarly large amounts of wastewater. This effluent is generated from a variety of activities involved in the wet processing of textiles [1].

The existence of dyes in water is easily noticed even at low concentrations. This is not only ugly, but coloration of the water may have a restraining effect on photosynthesising water ecosystems. Dyes might additionally be challenging if they are damaged anaerobically in sediment, as toxic amines are often produced due to incomplete degradation. The breakdown products of dyes are toxic and mutagenic [2]. Figure (1) shows such contamination [3].

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Figure 1. Outlets of Industrial Waste Water

In Iraq, the industrial wastewater released from the textile industry represents a serious environmental problem due to the improper treatment techniques applied for decolorization of this coloured and organic–loaded wastewater. According to data reported by the Iraqi Ministry of Industry and Minerals in 2009, the total amount of industrial wastewater released from the textile industry was 14465.9 $m^3$/day. This relatively large amount of coloured toxic wastewater released into the environment indicates an urgent need for new potential treatment methods [4].

Normal techniques include traditional processes such as adsorption, coagulation, flotation, and sedimentation. Each of these methods is flexible and helpful, but they all end up creating secondary waste items which require further handling [5].

Another arrangement of systems, which is generally more up to date, more effective, and exceptionally encouraging are Advanced Oxidation Processes (AOPs), which have been created and utilised to treat dye-defiled wastewater effluents [6].

Recently, researchers have become interested in the application of Advanced Oxidation Processes (AOPs) for the destruction of organic and inorganic contaminants in water. The literature suggests that many toxic or hazardous chemicals could be removed using this novel procedure. [7]. This approach uses strong oxidizing materials such as HO• radicals produced in situ, which cause a chain reaction to break the macromolecules into minimal and less hurtful molecules. In many situations, the molecules are thus completely mineralized into water and carbon dioxide. The numerous strategies utilised in the AOP approach include the UV photolytic system (UV/H2O2), the Fenton process, the photo-Fenton process, the ozonation process, and sonolysis, all of which encourage declination of dyes [4]. The techniques of dye extermination in AOPs depend on the formation of hydroxyl radicals, HO• , which can oxidise organic compounds [8].

The hydroxyl radical has a rich oxidation potential ($E^0$ = 2.8 V), and can respond to essentially all types of organic compounds, resulting in complete declination of these components, into carbon dioxide, water, and inorganic salts, or at least their transformation into less harmful products ([9]; [10]; [11]; [12]).

## 2. Objectives of the Present Study

The objective of this study is to investigate and test the effectiveness of Advanced Oxidation Processes (AOPs) in the degradation of red textile dye (taken from a textile manufactory) in wastewater. The AOPs considered in this study are homogeneous processes, including photolysis (UV), $H_2O_2$ alone, and UV/$H_2O_2$. In order to achieve the experimental goals, different variables and procedures were invoked throughout the treatment:

Variables invoked throughout the treatment: $H_2O_2$ concentrations, dye concentration, pH, and time.

To determine which kinetic models fit the experimental data, the first order model and second order model were used, and the first order and second order rate constants determined.

## 3. MATERIALS AND METHODS

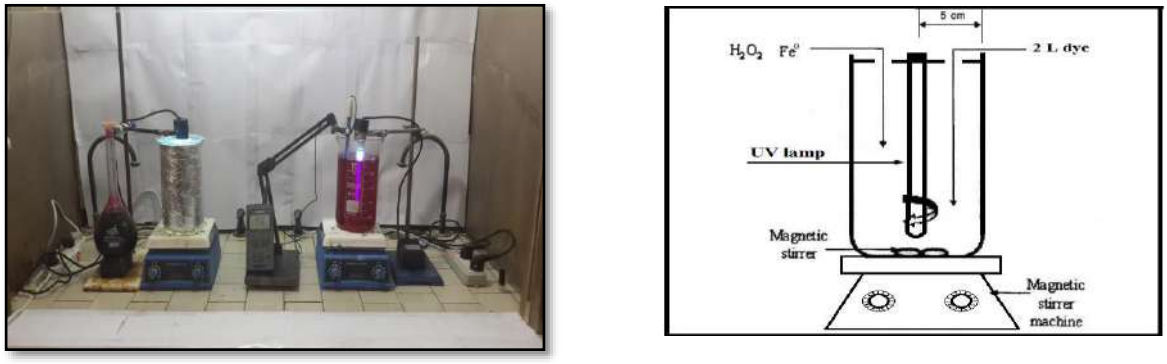
### *3.1. Materials*

All samples were set up by dissolving the requisite amounts of dye in distilled water. Sulfuric acid 98% ($H_2SO_4$) and Sodium hydroxide (NaOH) solutions were used to balance the pH of the solution. Hydrogen peroxide (50% w/w) with a molecular weight 34.01 g/mol, provided by SOLOVOCHEM (UK) was used. The stock solution was diluted to the desired concentration with distilled water. The reactive red dye (cibacron red fn-r) was obtained from Al-Kutt textile factory, south of Baghdad.

### *3.2. Reactor Arrangement*

The experiments were executed in a batch reactor, as shown Figure (2).The reactor consisted of a Pyrex glass cylinder of two litre volume mounted with a magnetic stirrer and a heater (LMS-1003, DAIHAN LAB TECH).

UV radiation with a wavelength of 254 nm was produced using a UV lamp (6 watt 4P-SE, SO SAFE, USA) settled vertically at the highest point of the reactor. The lamp was completely immersed in the barrel shaped reactor and thus was coated in a quartz sleeve for protection (with 20 mm internal diameter, 23 mm external diameter, and 266.7 mm length), as shown in Figure (2). The separation between the light and the reactor sides was at 5 cm to guarantee the most extreme light illumination per [13] and [14].




***(a) The system*** ***(b) General layout***

**Figure 2.** Laboratory-scale batch reactor

The experimental procedures were as follows:

To investigate the best removal conditions, removal efficiency was calculated using the following formula;

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

$C_o$= initial concentration of dye mg/l (before treatment).

$C_t$= Concentration of dye at specified time (after treatment).

The procedure was thus performed as follows:

The desired concentration of dye (10 to 100 mg/L) was prepared and the pH of the solution determined by adding the requisite amounts of $H_2SO_4$ and NaOH solution to the reactor. The solution was blended using a magnetic stirrer at 1,500 rpm for 30 minutes. The heater was set at the desired temperature. Different pH levels (2 to 11) were investigated to find the best pH while other parameters were kept

constant (dye=50, $H_2O_2$=50, and temperature= 10 ˚C). The effects of changes in temperature (10 to 40 ˚C) were investigated, and hydrogen peroxide ($H_2O_2$) concentrations (10, 25, 40, and 50 mg/l) were examined with dye=50 mg/L, pH=3, temperature= 20 ˚C, to test the hydrogen peroxide effects. The dye concentration effect was also studied at different concentration levels of 10, 25, 50, 75, and 100 mg/l. Samples were taken at regular periods of 30 minutes for dye concentration analysis. The investigation of COD removal was also undertaken.

## 4. Analysis

The concentrations of dye in the water samples were measured at the Laboratory of Sanitary in Al-Mustansiriyah University's College of Engineering's Department of Environmental Engineering using a UV-vis spectrophotometer (thermo-genesys 10 UV, USA). The analysis of COD concentrations were undertaken in the Environmental Laboratory of the Ministry of the Environment.

The analysis steps were as listed below:

The desired concentration of textile reactive dye (5 to 150 mg/L) was prepared accurately. The maximum wave length λ (nm) for each dye was measured using a spectrophotometer (thermo-genesys 10 UV, USA), using a survey scan at wavelengths 300 to 900 nm, as seen in Figure (3).

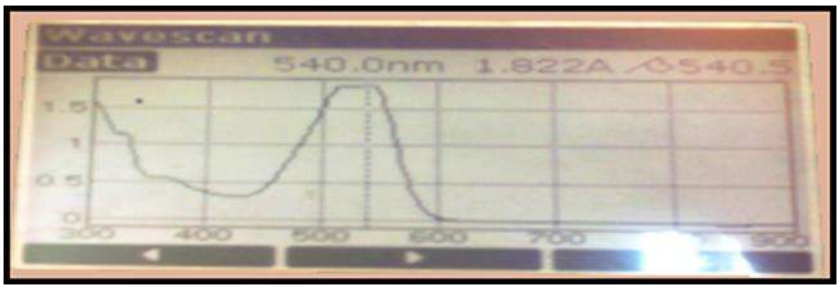



**Figure 3.** Maximum wavelength for Reactive Red dye

Calibration Curve for Analysis: Seven solutions of reactive red dye at concentrations 5, 10, 25, 50, 75, 100, and 150 mg/l were prepared. Absorbance at the maximum wave length (540 nm) was determined using a spectrophotometer (thermo-genesys 10 UV, USA). A linear relationship was plotted between absorbance (at the maximum wavelength of the dye) and each dye concentration, in order to estimate unknown concentrations of dye, as seen in Figure (4).The dye concentration was determined by measuring the absorbance (A) at the dye maximum wave length and by the use of the absorbance coefficient following Beer's law.

**A=KC+E** (2)

where A is absorbance of light at wave length $\lambda$, K is the absorbance coefficient (slope of linear relation), C is the concentration of dye in solution (mg/l), and E is the intercept.

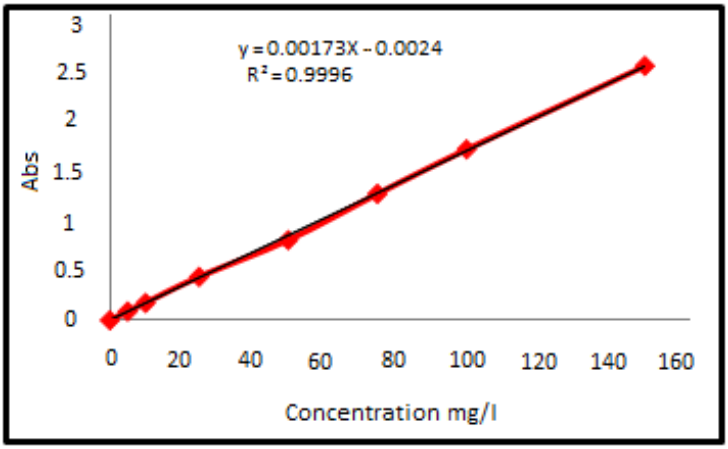



**Figure 4.** Calibration Curves for Reactive Red Dye

## 5. RESULTS AND DISCUSSION

### *5.1. The Effects of pH*

The effects of pH in the UV/$H_2O_2$ processes was tested to discover the pH required to degrade the dye most effectively. In order to obtain the optimum pH at different times, the $H_2O_2$ concentration (50 mg/L), temperature (10 ˚C), and dye concentration (50 mg/L) were fixed in this set of experiments. The outcomes are plotted in Figure (5).

Figure (5) demonstrates the connection between efficiency and reaction time at different initial pH levels, while figure (6) shows the degradation percentage of dye at different initial pH levels with different times. From these figures it can be shown that the removal efficiency of dye increases as the initial pH increases, from 94.134% at PH=2 to 98.72% at PH=3. Figure (6) shows that the maximum removal efficiency occurred at pH=3 after 180 minutes irradiation time; this decreased slightly to 78.806 % at pH =11 for the same irradiation time, which may be due to the increasing number of $OH^-$ ions at high pH values leading to reaction of these ions with generated hydroxide radicals ($HO^\bullet$); $HO_2^-$ anions react with $HO^\bullet$ radicals and the residual $H_2O_2$ consequently lowers the removal efficiency (see equations (3) and (4)). These results are in agreement with results by [15].

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + OH^\bullet \quad (3)$$

$$OH^\bullet + HO_2^- \rightarrow H_2O + O_2^- \quad (4)$$

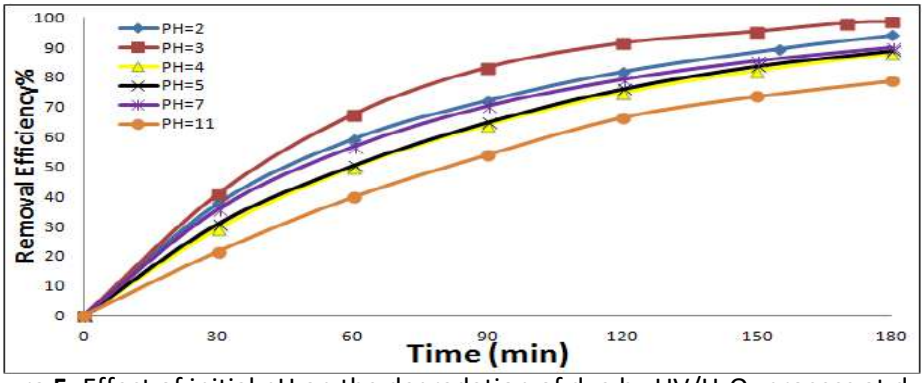



**Figure 5.** Effect of initial pH on the degradation of dye by UV/$H_2O_2$ process at dye con. = 50 mg/L, $H_2O_2$ con. =50 mg/L, and Temp. =10 $^oC$.

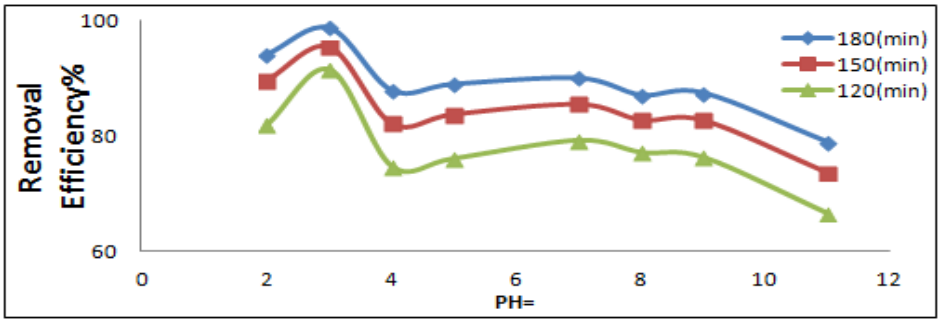



**Figure 6.** Degradation of dye as a function of initial pH by UV/ $H_2O_2$ system at dye con. = 50 mg/L, $H_2O_2$ con. =50 mg/L and Temp. =10 $^oC$, with different irradiation time.

### *5.2. Kinetic Models for UV/$H_2O_2$ process at different pH levels*

To find which kinetic model best fit the experimental data, the first order model (Equation 5) and second order model (Equation 6) were used, with the linear form ($\ln\frac{C_o}{C_t}$) vs. time and ($\frac{1}{C_t}-\frac{1}{C_o}$) vs. time for first and second order models, respectively [16].

$$\ln\frac{[C_0]}{[C_t]} = \mathbf{K_1 t} \quad (5)$$

$$\frac{1}{[C_t]}-\frac{1}{[C_0]} = \mathbf{K_2 t} \quad (6)$$

$C_o$= initial concentration of dye mg/l (before treatment).

$C_t$= Concentration of dye at specified time (after treatment).

t=time in minute.

$k_1$= the first order rate constant ($min^{-1}$).

$k_2$= the second order rate constant ( $Lmg^{-1}min^{-1}$) .

Plots of ($\ln\frac{C_o}{C_t}$) vs. time and ($\frac{1}{C_t}-\frac{1}{C_o}$) vs. time for each experiment created straight lines with slopes $K_1$ and $K_2$, respectively, as shown in figures (7) and (8). From the values of $K_1$, $K_2$, and $R^2$, the first order equation fits the data better than the second order equation (see figures (7) and (8)). This result shows that the rate of degradation directly relative to the concentration of dye.

The relative rate constant ($K_1$) values in figure (9) increased for red dye from 0.0157 $min^{-1}$ to 0.0252 $min^{-1}$ at pH=2 and 3, respectively, then decreased to 0.0088 $min^{-1}$ at PH=11. This is likely due to the anions ($HO_2^-$) reacting with non-dissociated molecules of $H_2O_2$, prompting oxygen and water creation rather than creating hydroxyl radicals under UV radiation. Thus, the concentration of $OH^{\bullet}$ was lower than predicted [17] and [15].

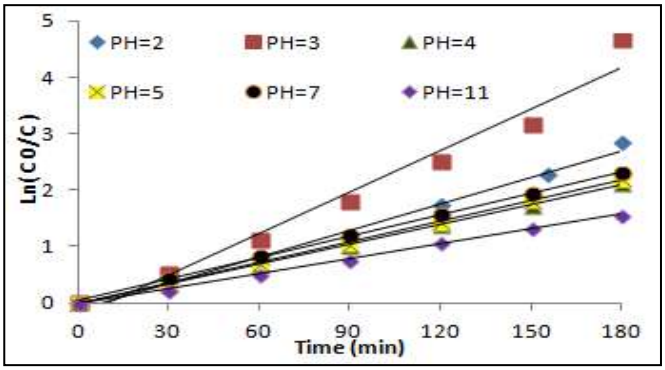



**Figure 7.** First order rate constant at different initial pH for dye degradation by UV/$H_2O_2$ process at dye conc. =50 mg/L, Temp. = 10 ˚C and $H_2O_2$ conc. =50 mg/L.

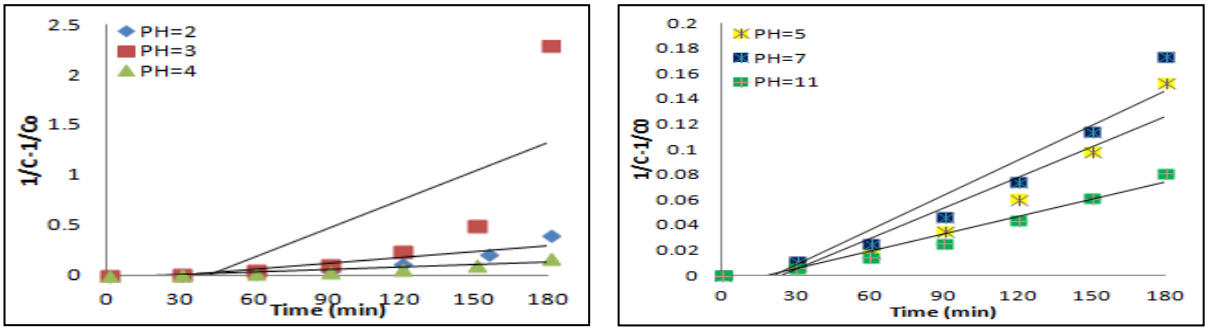



**Figure 8.** Second order rate constant for dye degradation a function at different initial pH by UV/$H_2O_2$ process at dye conc. =50 mg/L, Temp. = 10 ˚C and $H_2O_2$ conc. = 50 mg/L.

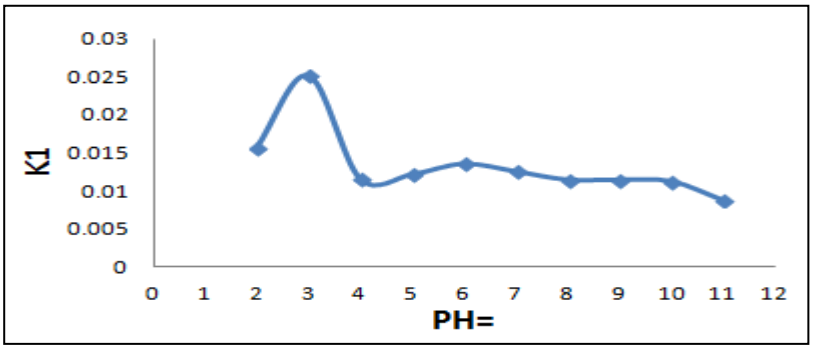



**Figure 9.** First order rate constant for dye degradation as a function of initial pH using the UV/$H_2O_2$ process at dye conc. = 50 mg/L, Temp. =10 ˚C and $H_2O_2$ conc.= 50 mg/L.

*5.3. Effect of Initial $H_2O_2$ Concentration*

The effect of initial concentration of $H_2O_2$ on the UV/ $H_2O_2$ process was explored by performing experiments with various concentrations of $H_2O_2$ (10, 25, 40, and 50 mg/L). The optimum pH (3) from the previous investigation stage was applied in these tests. The dye concentration of 50 mg/L and the temperature of 20 ˚C were also preserved. The results are shown in figures (10) and (11). These figures demonstrate that the removal efficiency of dye distinctly increases with increasing quantities of $H_2O_2$ till it reaches its ultimate value (99.43% removal) at 25 mg/L after about 180 min of irradiation time; it then starts to decrease gradually, and the addition of further $H_2O_2$ above this amount had a negative result, reaching only 96.64% removal at 50 mg/L $H_2O_2$.

Many investigators offer several explanations for these phenomena; one of the most famous is that hydroxyl radicals produced from the direct photolysis of hydrogen peroxide are the fundamental capable species in the degradation process. Thus, increasing the concentration of $H_2O_2$ too far will reduce the rate of degradation due to the reaction of hydrogen peroxide with these radicals, and hence act as an inhibiting agent due to self-scavenging of $HO^{\bullet}$ by $H_2O_2$, (Equation 7). However, if the $H_2O_2$ dose is too low, the $HO^{\bullet}$ arrangement will likewise be low, diminishing treatment efficiency. Thus, the correct balance of $H_2O_2$ concentration must be sought [18].

Figures (12) and (13) show that the first order kinetic model best fits the experimental data for different $H_2O_2$ concentrations, with $R^2$ ranging from 0.845 to 0.9992 for Reactive Red dye. These results indicate that the rate constant ($K_1$ in the first order case) increases from 0.0043 $min^{-1}$ to 0.0293 $min^{-1}$ for red dye at $H_2O_2$ concentrations from 10 to 25 mg/L; then, the $K_1$ value decreases to 0.0189 $min^{-1}$ for $H_2O_2$ concentrations of 50 mg/L, due to the excess $H_2O_2$ producing excess $HO^{\bullet}$ radicals.. Figure (14) shows representative samples taken from the reactor at different times at optimum conditions: $H_2O_2$ con. =25, dye con. =50, Temp. =20 ˚C, and pH**=3.**

$$H_2O_2 + \mathrm{OH}^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \qquad (7)$$

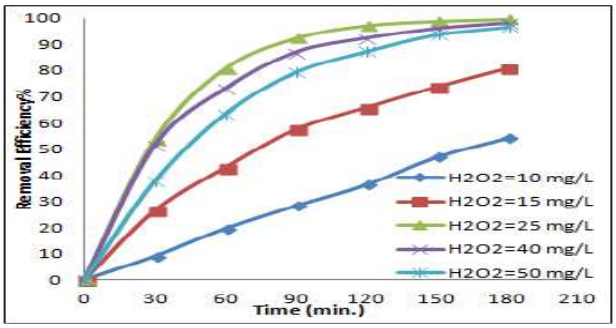



**Figure 10.** Effect of initial $H_2O_2$ concentrations on the degradation of dye by UV/ $H_2O_2$ process at pH=3, dye conc. =50 mg/L and Temp. =20 ˚C.

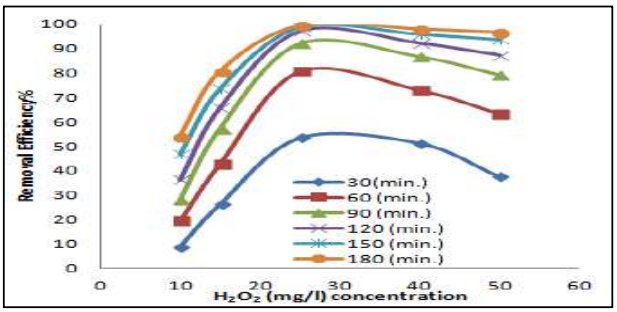



**Figure 11.** Degradation of dye as a function of H2O2 initial concentration by UV/ H2O2 process at pH=3, dye conc.=50 mg/l , Temp.=20 ˚C and different irradiation time.

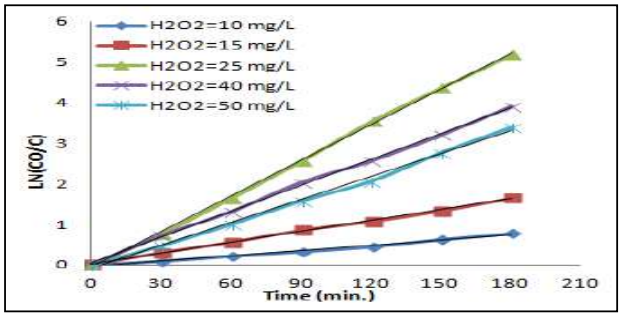



**Figure 12.** First order rate constant for dye degradation by UV/$H_2O_2$ system at dye conc. =50 mg/l, Temp. =20 ˚C and pH=3.

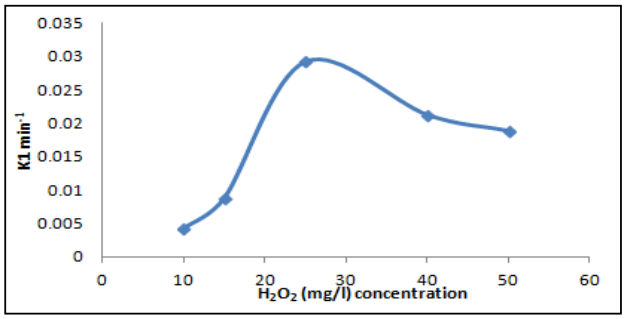



**Figure 13.** First order rate constant for dye degradation as a function of initial H2O2 concentration by UV/H2O2 process, dye con. =50 mg/l, Temp. = 20 ˚C and pH=3.

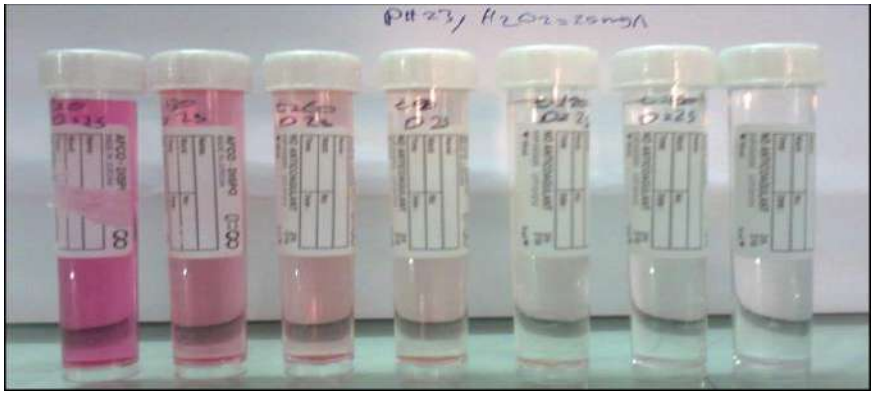


**Figure 14.** Reactive red textile dyes taken from reactor at times 0, 30, 60, 90, 120, 150, and 180 min.

*5.4. Impact of Temperature*

The solution temperature is another significant parameter that influences the degradation of dye. Various temperatures (10, 20, and 40 ˚C) were studied to investigate their effects on the removal efficiency of dye. The doses of reagents and other parameters were held constant(dye= 50 mg/L, $H_2O_2$= 25 mg/L, and pH=3). The results were plotted as in figures (15) and (16). These figures show that the removal efficiency of dye increases from 88.95997% at 10 ˚C to 99.43094 % at 20 ˚C, while above 20 ˚C there was a slight decrease with increasing temperature. The increase in temperature accelerated the decomposition of $H_2O_2$ thus expanding the generation of HO radicals, improving the decay procedure.

The results show that only a marginal effect on degradation performance was obtained, however. Above 40 ˚C, the efficiency of hydrogen peroxide exploitation reduced due to the quickened decay of hydrogen peroxide into water and oxygen, as specified by [19]. Figures (17) and (18) show that the analyses is suitable for a first order reaction. The reaction rate constant reaches its ultimate value of 0.0293 $min^{-1}$ at 20 ˚C.

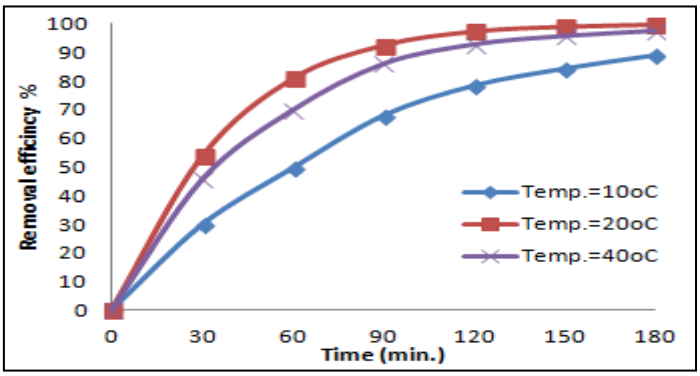



**Figure 15.** Effect of different temperatures on degradation of dye during UV/ $H_2O_2$ process at $H_2O_2$ con. =25 mg/L, pH=3, and dye con. =50.

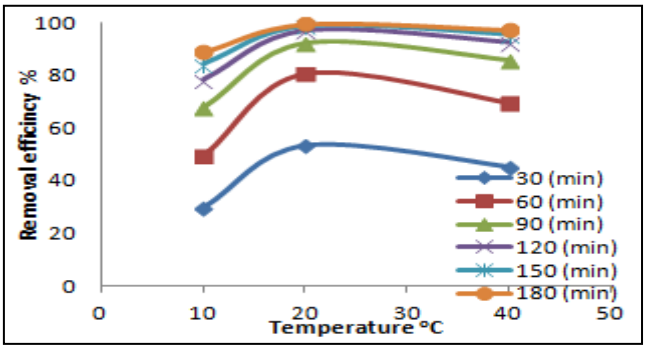



**Figure 16.** Degradation of dye as a function of temperature during UV/ $H_2O_2$ process at pH=3, dye con. =50 mg/L and, $H_2O_2$ con. =25 mg/L with different irradiation time.

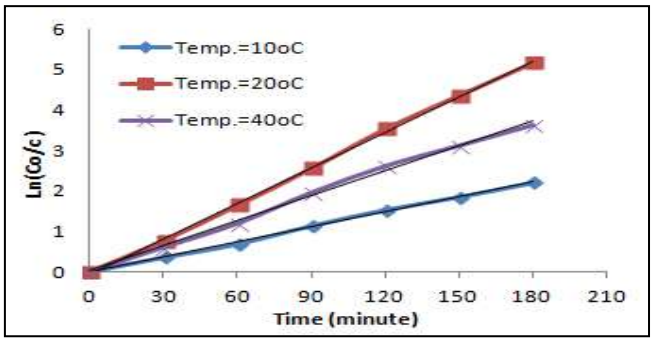



**Figure 17.** First order rate constant for dye degradation at deference temperature during UV/ H2O2 process at pH=3, dye con. =50 mg/L and H2O2 con. = 25 mg/L.

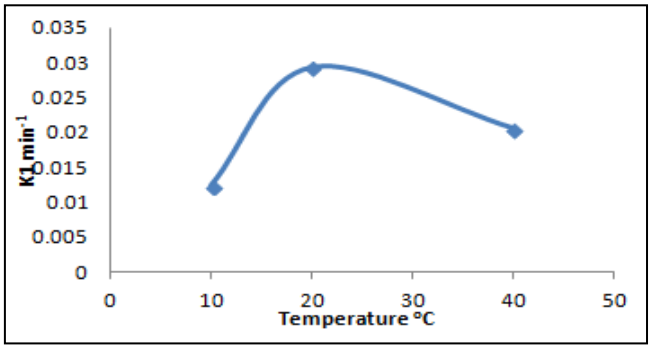



**Figure 18.** First-order rate constant for dye degradation as a function of temperature during UV/$H_2O_2$ process at pH=3, dye con. =50 mg/L and $H_2O_2$ con. = 25 mg/L.

*5.5. Effect of Initial Dye Concentration*

Different concentrations of dye (10, 25, 50, 75, and 100) mg/L were used at $H_2O_2$ concentration = 25 mg/L, pH= 3 and temperature =20 ˚C. The results are plotted in figures (19) and (20). From these figures it can be seen that the removal efficiency diminishes from 100% to 60.33% as the concentration of dye increases from 10 to 100 mg/L.

Increasing the initial concentration decreases the colour removal efficiency from 100% to 60.33455 % for Red dye after a 180-minute irrigation time. This can be attributed to the reduction of light photon penetration, which leads to a lowering of hydroxyl radical concentrations [4]. Figures (21) and (22) show that the data appears most suitable for a first order reaction. The reaction rate constant reaches its most extreme value (0.072 $min^{-1}$) at 10 mg/L.

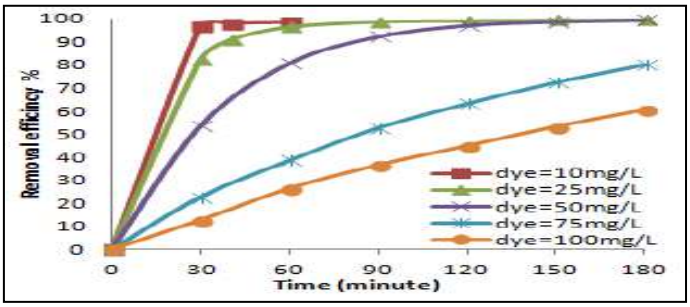



**Figure 19.** Effect of different dye concentrations on the degradation of dye by UV/ $H_2O_2$ process at pH=3, and Temp. = 20 ˚C. $H_2O_2$ con. = 25 mg/L.

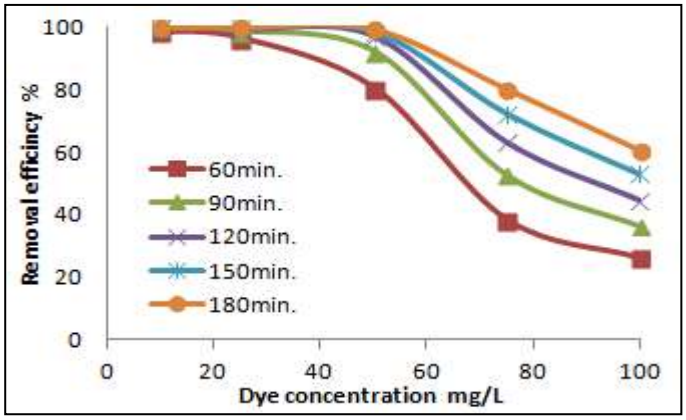



**Figure 20.** Degradation of dye as a function of different dye concentrations by UV/ H2O2 process at pH=3, and Temp. =20 ˚C at H2O2 con. =25 mg/L and different irradiation time.

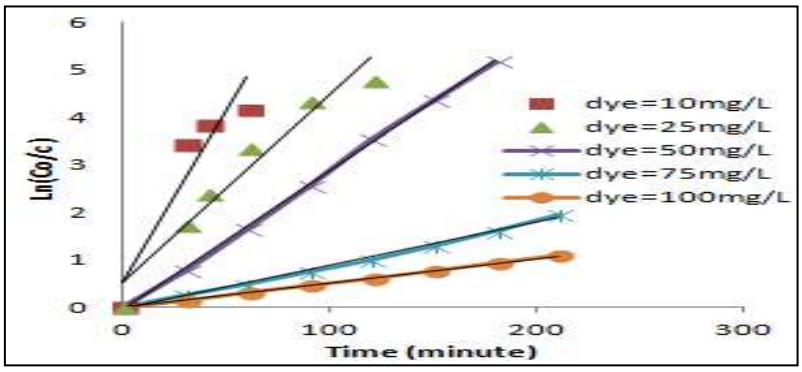



**Figure 21.** First order rate constant for dye degradation at different concentrations of dye by UV/ $H_2O_2$ process at pH=3, $H_2O_2$ con. =25 mg/L and Temp. = 20 ˚C.

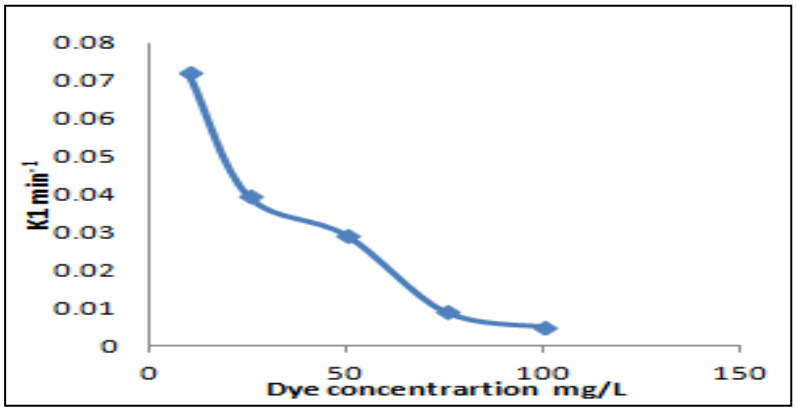



**Figure 22.** First order rate constant for dye-water degradation as a function of different concentration by UV/ $H_2O_2$ process at pH=3, dye conc. =50 mg/L, $H_2O_2$ con. =25 mg/L and Temp. =20 ˚C.

## 6. CONCLUSIONS

The results show that the AOP technique is a potentially effective approach for textile wastewater treatment. The optimal concentration of $H_2O_2$ for UV/$H_2O_2$ was found to be equal to 25 mg/L; the optimal temperature was found to be 20 ˚C; and the optimum irradiation time was found to be 120 minutes. The optimal pH for UV/$H_2O_2$ was found to be 3. COD removal was achieved by means of degradation of the dye during the process of decolourisation. Colour removal can be considered the first stage, followed by COD removal; at 180 minutes, colour removal efficiency is 99.65% and COD removal is 62.5% for Reactive Red Dye using the UV/$H_2O_2$ process. Removal efficiency increases with a decrease in dye concentration and increases with $H_2O_2$ dosage till reaching a maximum; it then decreases with increasing $H_2O_2$ dosage. The first order kinetic model was found to be most suitable for this process because of its higher coefficient of determination as compared to the second order kinetic model.

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## 8. *ACKNOWLEDGMENTS*

The authors are thankful to the Environmental Laboratory staff of the Ministry of the Environment for their cooperation and provision of materials, and for allowing the use of their laboratory during the period of the research.