



## UV-ClO<sub>2</sub> assisted decolorization of methylene blue

H. A. Habeeb Alshamsi and H. A. Khayoon Al Shdood

Chemistry Department, College of Education, University of Al-Qadisiya, Diwaniya, Iraq

### ABSTRACT

*This research investigates the efficiency of UV in combination with chlorine dioxide (UV/ClO<sub>2</sub>) for decolorizing of aqueous solution textile dyes methylene Blue. All the experiments have been done by using photoreactor provided with ultraviolet source of low pressure mercury-lamp (LPML). The study included the investigating the effects of dye concentration, temperature, rate flow of gas and light intensity. A complete degradation has been achieved in a somewhat short period alternatively 60 min. The maximum removal of color was found at higher temperature(318 K). The results showed that the rate of removal increased with decrease of initial dye concentration, and also the ratio of removal increased with increase in temperature. The activation energy for degradation of aqueous solution of methylene blue was found 16.577kJ/Mole. Moreover, it was noticed that with the increase of both air flow velocity and incident light intensity, increases the ratio of methylene blue removal. The decolorization reaction was found to follow pseudo first order kinetics with respect to the dye concentration. All of the important previous effects have been applied on chemical oxygen demand (COD). The ratio of COD removal associates positively with the ratio of decolorization rate of methylene blue.*

**Keywords:** methylene blue, decolorization, ClO<sub>2</sub>/UV, COD

### INTRODUCTION

The decolorization of wastewater is still a major environmental concern as result of expanding of textile industry in many countries and a high quantity of textile industry production is lose during the dying process via discharge of their effluents into aquatic system [1-3]. Synthetic dyes used in textile industry, are resist the biodegradation and may be causes a series of environmental problems.

There are more than 100,000 different synthetic dyes produced in over 700,000 tons yearly worldwide[4]. Wastewater generated by the dye production industry and many other industries which use dyes and pigments is high in both color and organic content and these dye chemical substances which are produced are considered toxic and even carcinogenic and mutagenic [5]. That is why there is a need to develop effective methods for the degradation of organic pollutants, either to less harmful compounds or to their complete mineralization[6].

Treatment methods are based primarily on efficiency and economic cost[4]. Divided methods remove contaminants into three kinds: a biological, chemical and physical ones[7]. Biological methods are conventional treatment, which have become ineffective to remove the color, for example, the process of aerobic treatment leads to the production of large amounts of mud or sludge biological. The same is applicable for methods of conventional chemical treatment. If the liquid waste was not handled properly, it will be a serious threat to all vital species on earth. Because the decomposition of these pollutants in the environment can produce a great deal of toxic substances[8]. There are many ways to treat liquid waste that accompany these methods, which may vary depending on the type and volume of waste and the degree of treatment required[9]. Examples of oxidizing agents that used efficiently in the treatment of contaminated water is hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ozone (O<sub>3</sub>) and advanced oxidation processes that include: O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub> and Fenton reagent Fe<sup>2+</sup> / H<sub>2</sub>O<sub>2</sub>[10]. The method adopted in

this study is the use of UV and chlorine dioxide (UV/ClO<sub>2</sub>) as a technique for mineralization of methylene blue dye (Figure 1) from aqueous solution.

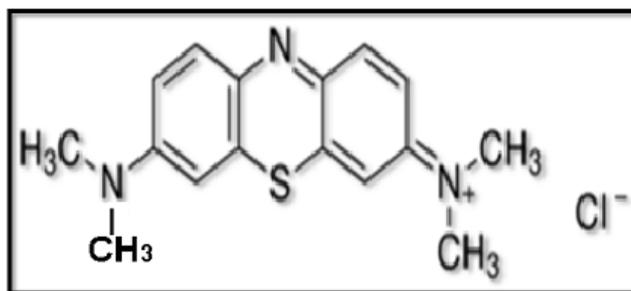


Figure 1 . Structural formula of methylene blue

## EXPERIMENTAL SECTION

### 2.1. Materials

Sulphuric acid (98%) and sodium chlorite were supplied from B.D.H. Methylene Blue dye (product of USA.MSDS) was purchased from Omega. All the other solutions were prepared with double distilled water.

### 2.2. Instruments

UV-Visible 1650 spectrophotometer (Shimadzu, Japan) was used to record the absorption spectra of aqueous solutions of dye. The temperature was adjusted by used regulator water bath WB (Optima). COD was measured by (Lovibond, Vario LR) and a Thermoreactor TR 300 (Merck, Germany). The equipment of chlorine dioxide preparation is locally collected .

### 2.3. Photo reactor setup

The photoreactor shown in Figure 2 [11,12], was fitted with a fixed low-pressure mercury lamp (4,6,8,and 12W) with the higher intensity light emitted at 254 nm . The UV lamp was put in the side of reactor and the quartz sleeve was enclosed. The photoreactor was fitted with a regulator water bath to maintain the temperature and a circulation pump to continuous feed and collection of dye solution in a 1L flask . A syringe was fitted with photoreactor to withdraw dye solution samples in mean time.

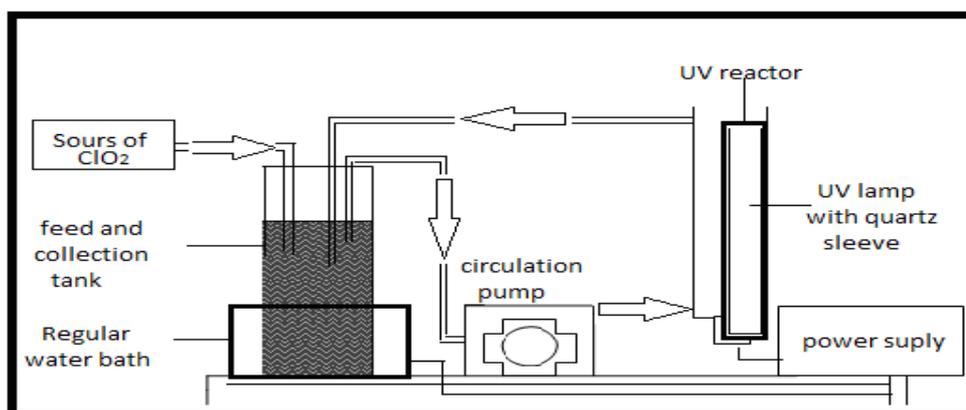


Figure 2. Photoreactor setup

### 2.4. Preparation of Chlorine Dioxide

A pure solution of chlorine dioxide is prepared by adding slowly the dilute sulfuric acid to a sodium chlorite solution, removing any contaminants such as chlorine by sodium chlorite scrubber, and passing the gas into distilled water by a steady steam of air. The experimental setup to generate the chlorine dioxide is described in Figure 3 [13].

### 2.5. Procedure

The irradiation time for all experiments were fixed at 60min. Due to the primary experiments indicated that the most dye molecules are degraded and the dye solution become colorless at the time similar to this period. COD was measured according to the Standard Methods [13]. Control experiments were

carried out under UV irradiation with  $\text{ClO}_2$  in the solutions. In all experiment the lamp was warming for 10 min prior to initiation of reaction. Determination of dye concentration was carried out by using the calibration curve shown in Figure 4. The absorbance of dye was measured at maximum absorption  $\lambda=664$  nm as Figure 5 shows.

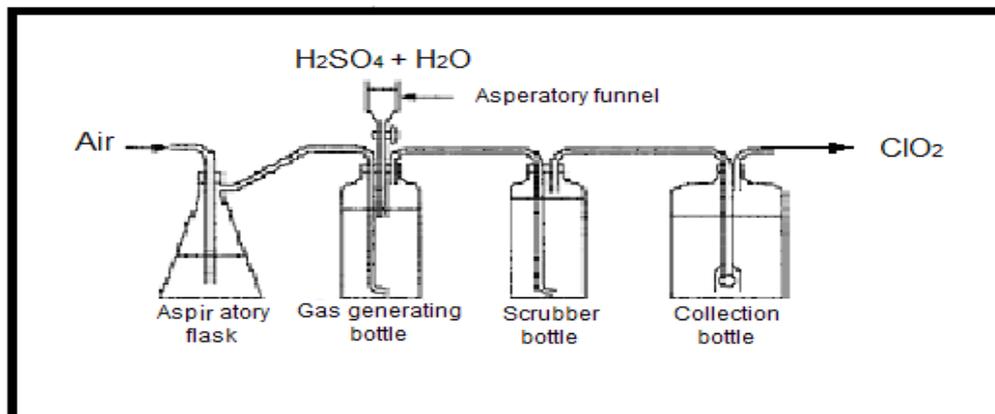


Figure 3 . Chlorine dioxide generation and absorption system

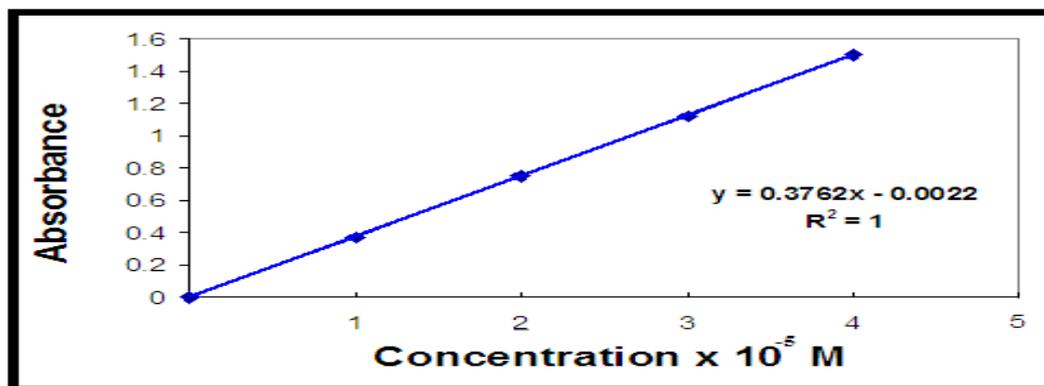


Figure 4: Calibration curve for methylene blue at T=298K

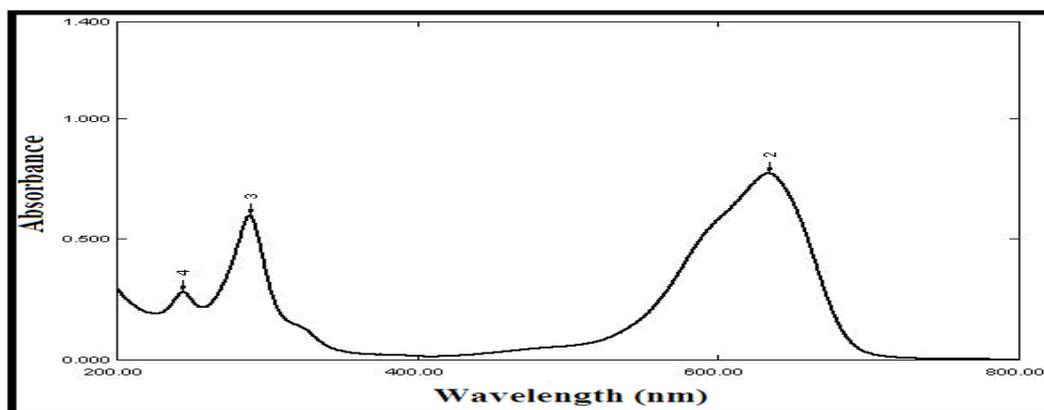


Figure 5 . UV-Visible spectrum of aqueous solution of methylene blue  $1 \times 10^{-5}$  M, T=298K

## RESULTS AND DISCUSSION

### 3.1.Effect of initial dye concentration

Various initial dye concentration in the range  $1 \times 10^{-5}$ - $5 \times 10^{-5}$  M were exposed to UV/ $\text{ClO}_2$ . It has been found that increase in the initial concentration of dye leads to decrease the color removal and COD, because the decrease of penetration of photons enter into the solution and lower the formation of hydroxyl free radicals[14-16]. The behavior of concentration impact may be sometimes depends on the structure of dye[17]. The results are shown in Figure 6.

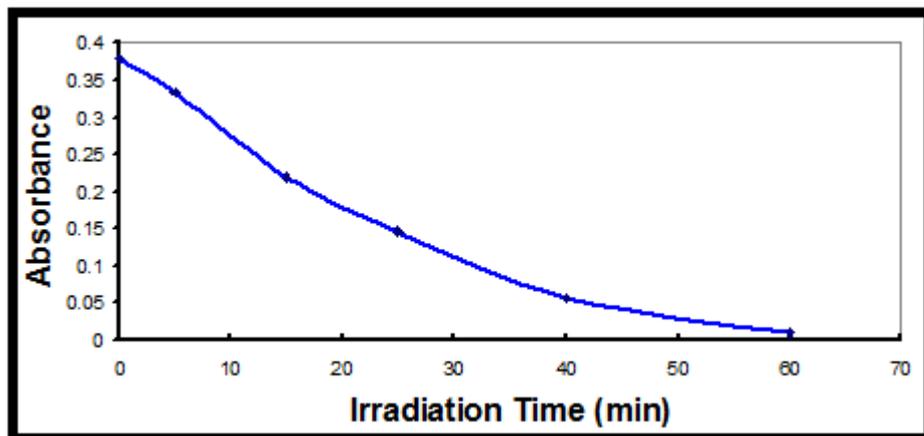


Figure 6 . Absorbance of methylene blue as a function of irradiation time at T=298k ,Io=173.711mW/cm2 and f=160 L/h

Also the overall spectrum of dye decreases as the irradiation time increases show as figure 7.

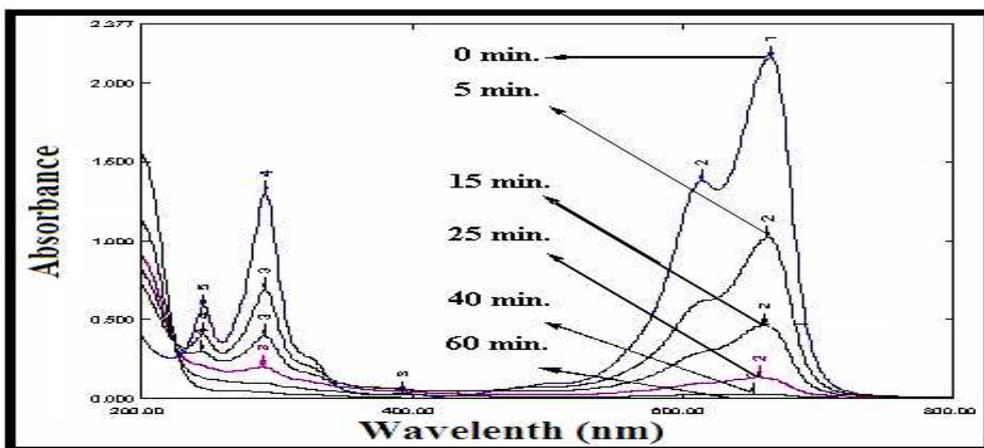


Figure 7. UV-visible spectra of dye solution  $1 \times 10^{-5} M$  as a function of irradiation time at T=298 k , Io=173.711mW/cm2 and f=160 L/h

The results proved that the highest percentage with COD at the concentration  $1 \times 10^{-5} M$  while, the lowest percentage with COD at the concentration  $5 \times 10^{-5} M$ . The results are shown in Figure 8.

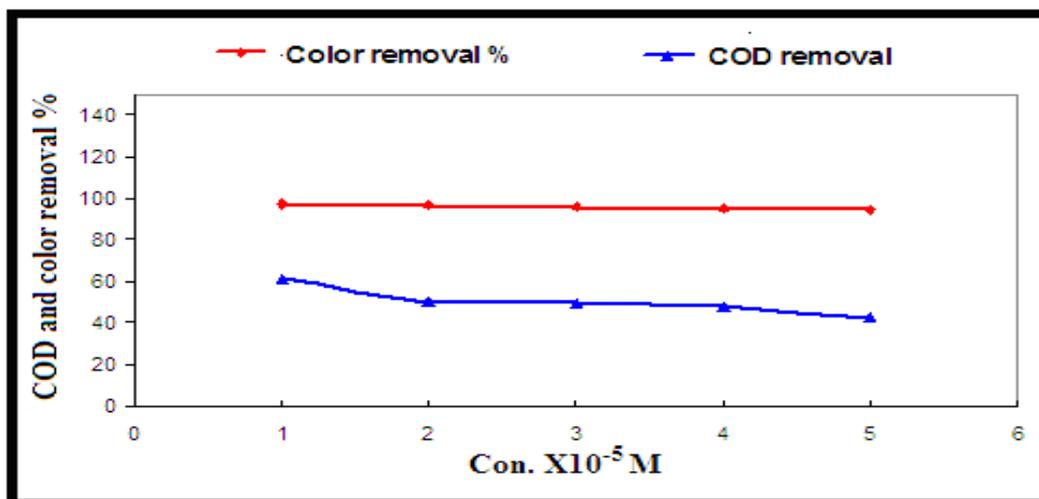


Figure 8. Effect of dye concentration on color and COD removal at T=298bk, Io=173.711mW/cm<sup>2</sup> and f=160 L/h

The relationships between  $C_t/C_0$  and irradiation time are shown in Figure 9. It is clear the higher dye concentration increased the absorption of UV radiation, led to decrease the availability of UV and lower the formation of hydroxyl radicals in the solution.

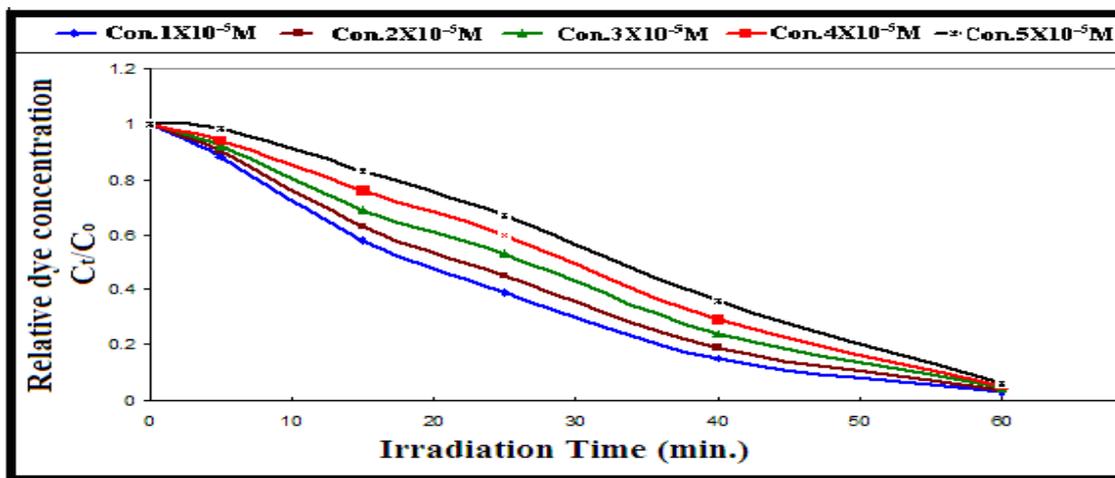


Figure 9 . Relative dye concentration versus irradiation time at different initial dye concentration ,  $T=298k$ ,  $I=173.711mW/cm^2$  and  $f=160$  L/h

The obtained results proved that the decolorization reaction of the methylene blue e follows the pseudo first order kinetics. Figure 10 shows the relationship between  $\log R$  and  $\log C$  according to following relationship:

$$\log k = \log R - n \log C \tag{1}$$

Where: C: concentration of dye n: order reaction, R: reaction rate, k: reaction rate constant.

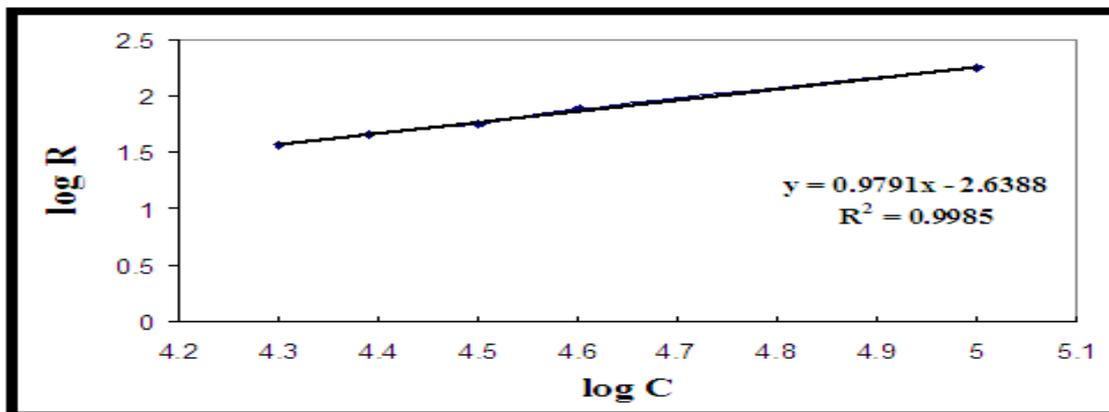


Figure 10. Relationship between  $\log R$  and  $\log C$  of oxidation of methylene blue  $1 \times 10^{-5}$  M,  $T=298k$ ,  $I=173.711mW/cm^2$  and  $f=160$  L/h

### 3.2.Effect of temperature

It is found that the reaction rate increases with gradual increase of temperature from 298-318 K. Therefore the color removal efficiency increases with increasing of temperature as shown in figure 11.This indicates the importance of temperature factor to study the stability and degradation of compounds[18-20].

This study has proven that the rate of COD removal increases with the increase of temperature because of less amount of oxygen need for oxidation of dye .The results are illustrated in Figure 12.

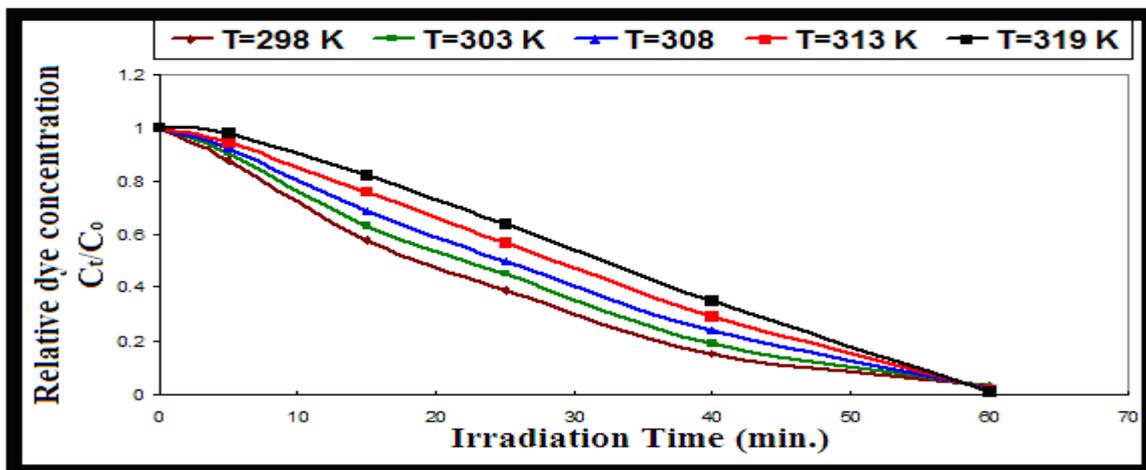


Figure 11. Effect of different temperatures on the relative dye concentration, [MB]= $1 \times 10^{-5}$  M,  $I_0=173.711 \text{ mW/cm}^2$  and  $f=160 \text{ L/h}$

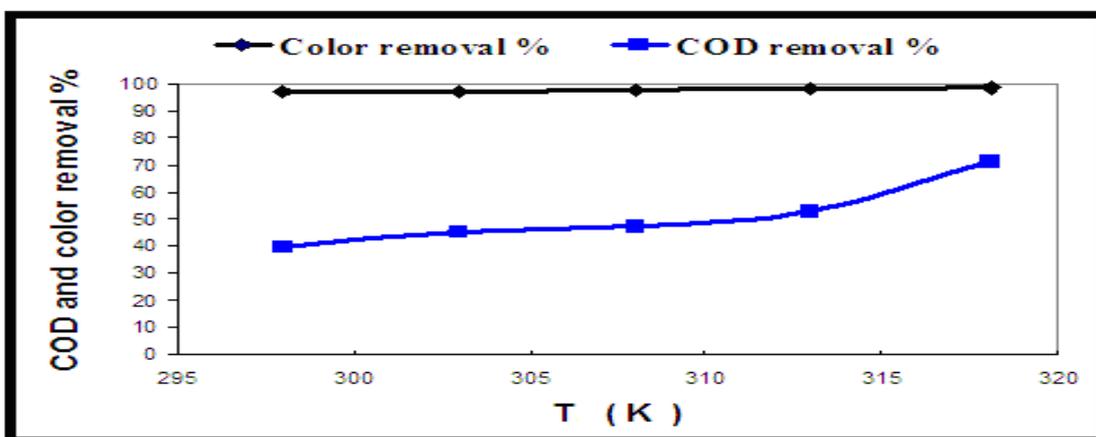


Figure 12. Effect of different temperatures on the color and COD removal of methylene blue using UV/ClO<sub>2</sub> [M.B.]= $1 \times 10^{-5}$  M,  $I_0=173.711 \text{ mW/cm}^2$  and  $f=160 \text{ L/h}$

The Arrhenius equation is used to describe the relationship between rate constants and temperature and draw this relationship as show in Figure 13.

$$k = A e^{(-E_a/RT)} \tag{2}$$

Where: k: rate constant, A: frequency factor,  $E_a$ : activation energy, R: ideal gas constant. Calculated activation energy is equal of 16.577 KJ/mole.

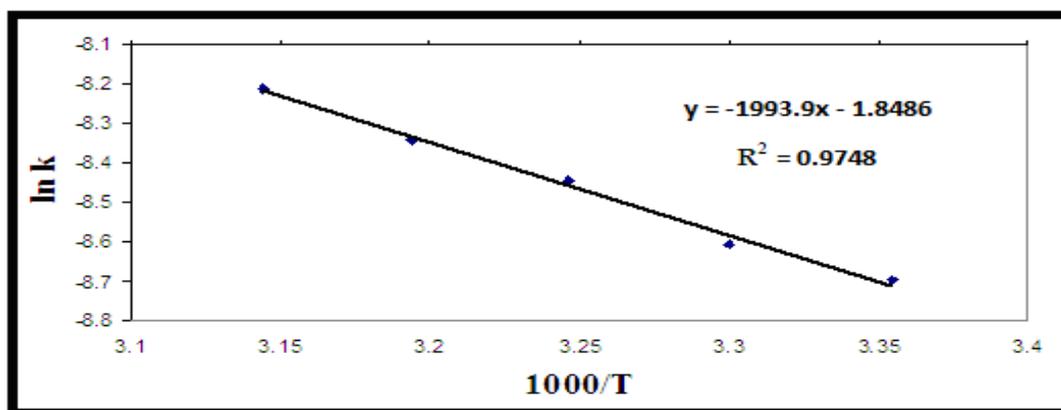


Figure 13: Arrhenius plot of color removal of dye, [M.B.] =  $1 \times 10^{-5}$  M,  $I_0=173.711 \text{ mW/cm}^2$  and  $f=160 \text{ L/h}$

3.3- Effect of gas flow rate

Figure 14 shows the relationship between  $C_t/C_0$  and irradiation time. The effect of gas flow rate was evaluated at ( $f=40, 80, 120$  and  $160$  L/h), the results proved that high color removal was 93.8% at high gas flow rate and low value 90.2% was obtained in low gas flow rate as Figure 15 shows. The effect of different gas flow rate on the COD removal was studied as shown in Figure 15. It clear the importance of oxygen flow rate (oxygen dose) to enhancing the degradation and decolonization of organic compounds [21,22]

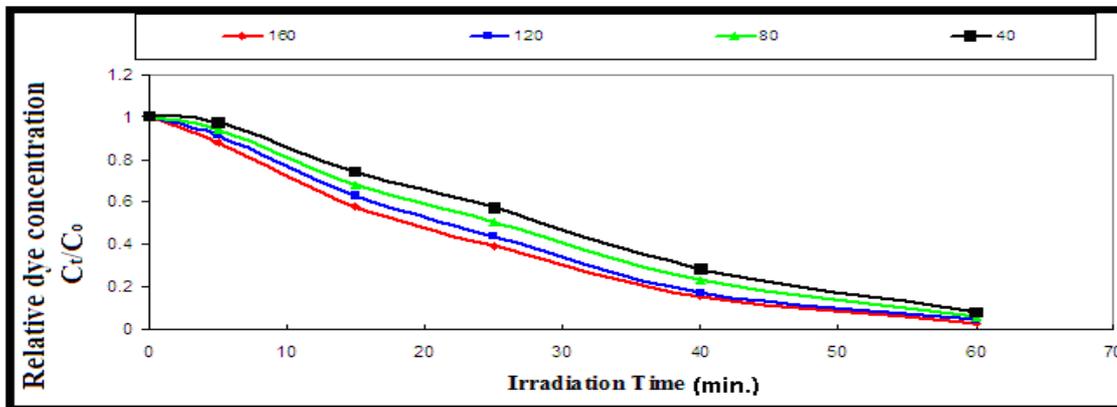


Figure 14. Effect of gas flow rate value on color removal from methylene blue dye as function of irradiation time, [M.B.]= $1 \times 10^{-5}$  M,  $T=298$  K and  $I_0=173.711$  mW/cm<sup>2</sup>

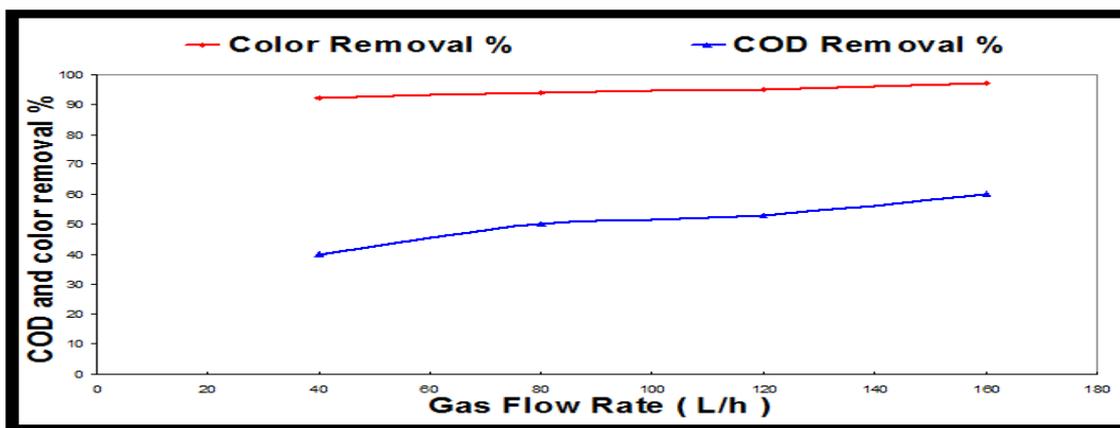


Figure 15: Effect of gas flow rate on the COD and color removal of methylene blue dye. [MB]= $1 \times 10^{-5}$  M,  $T=298$  K and  $I_0=173.711$  mW/cm<sup>2</sup>

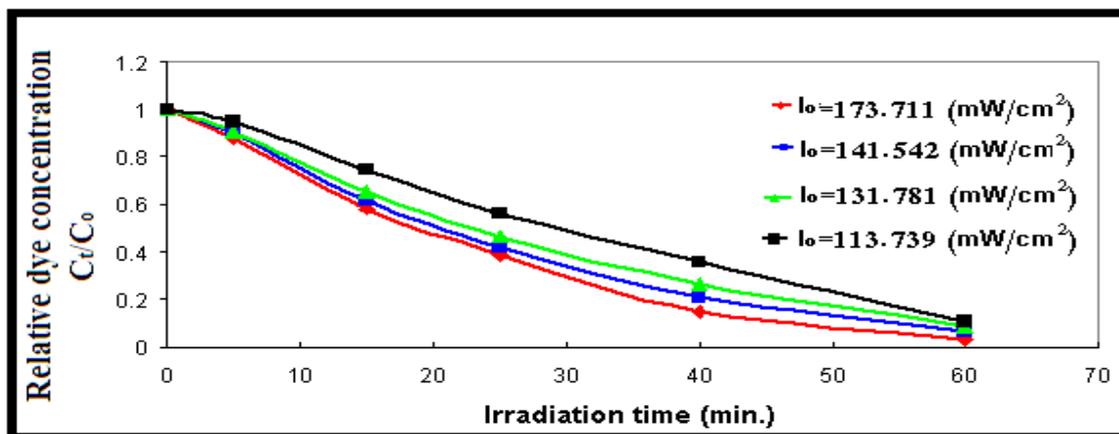


Figure 16. Effect of different light intensity value on relative dye concentration as function of irradiation time, [MB]= $1 \times 10^{-5}$  M,  $T=298$  K and  $f=160$  L/h

### 3.4. Effect of light intensity

Many works proved that the rate of removal of organic pollutants increases gradually with increase of light intensity, because the number of photons entering the dye solution increases and hence increasing the rate of degradation[23-26]. So the speed of the color removal depends on the number of photons collide with dye molecules and its ability to break down the chromospheres bonds in the dye molecules. The effect of light intensity was evaluated at ( $I_0 = 113.739, 131.781, 141.711, \text{ and } 173.711 \text{ mW/cm}^2$ ). Figure 16 shows the relationship between  $C_t/C_0$  and irradiation time. Figure 17 clarify that higher color removal 97% was obtained at high light intensity ( $173.711 \text{ mW/cm}^2$ ) and low value (89%) was obtained in low light intensity ( $113.739 \text{ mW/cm}^2$ ).

The effect of above light intensities were also studied on COD removal as shown in Figure 17

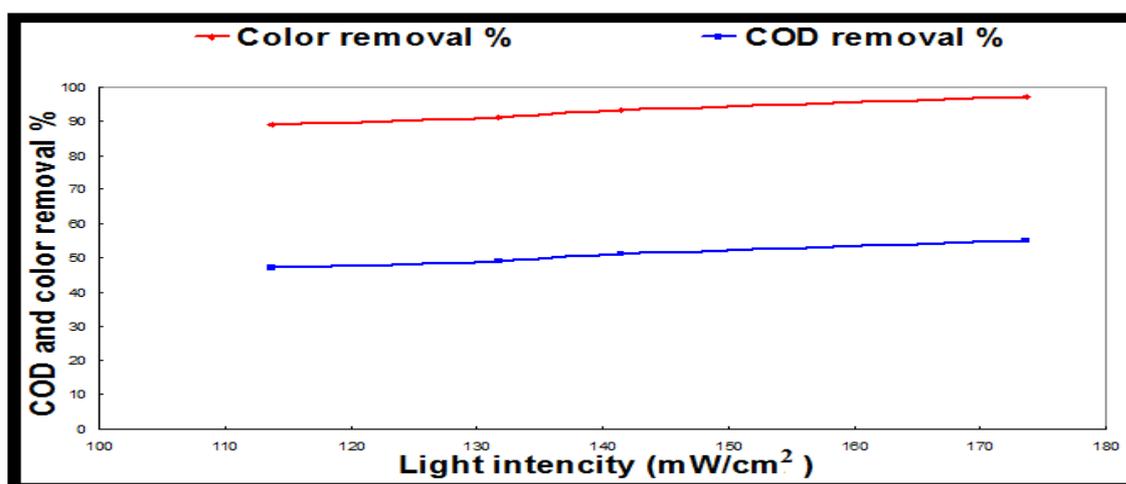


Figure 17. Effect of the light intensity on the COD and color removal of methylene blue, [MB] =  $1 \times 10^{-5}$  M, T = 298 K and f = 160 L/h

### CONCLUSION

1. The degradation was strongly influenced by various parameters, particularly the temperature, dye concentration, gas flow rate, light intensity as well as irradiation time.
2. Faster degradation kinetics, higher color removal and COD removal efficiency was observed at higher temperature 318K.

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