

## **Optimum Conditions of Photocatalysis Process in a Wastewater Treatment**

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### **ABSTRACT**

The aim of the present study was to investigate the optimum operating conditions which yield the best performance of the photocatalysis process for the degradation of the synthetic dye in wastewater. The solar reactor was made up of a flat-plate colorless glass of dimensions of (1000 x 750 x 4 mm). The base of the reactor was made of aluminum. This geometry enables the light entering the liquid film from almost any direction to be reflected and can also be employed for the photocatalytic reaction. Various operating parameters were studied to investigate the behavior of the designed reactor like initial dye concentration ( $C=10-50$  mg/L), loading of catalyst ( $C_{TiO_2}=300-800$  mg/L), suspension flow rate ( $Q_L=0.3-2.0$  L/min), pH of solution (5-9), and  $H_2O_2$  concentration ( $C_{H_2O_2}=200-1000$  mg/L). The operating parameters were optimized to give higher efficiency to the reactor performance. Optimum parameters of the photocatalysis process were loading of catalyst (400mg/L), suspension flow rate (0.5L/min),  $H_2O_2$  concentration (400mg/L), and pH=5. The designed reactor when operating at optimum conditions offered a degradation of MV up to 0.9527 within one hours of operation time, while a conversion of 0.9995 was obtained in three hours. The product water was analyzed using UV-spectrophotometer and FTIR. Analysis of the results confirmed that produced water from the solar reactor system could be safely recycled and reuse.

**Keywords:** Solar photocatalysis, wastewater reuse, synthetic dye, Optimum conditions, Falling-film slurry reactor.

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## افضل الظروف التشغيلية في معالجة المياه الملوثة باستخدام المفاعل الشمسي

### الخلاصة :

يهدف البحث لدراسة افضل الظروف التشغيلية التي تؤدي الى اعلى كفاءة للمفاعل في تكسير وازالة المواد العضوية السامة (صبغة المثل البنفسجية) في المياه الملوثة. المفاعل الشمسي يتكون من لوحة مسطحة من زجاج شفافة عديمة اللون بابعاد (1000x750 x 4 mm). قاعدة المفاعل مصنعة من الالمنيوم . هذا التصميم يسمح لضوء الدخول الى طبقة السائل من اي اتجاه تقريبا ومن ثم الانعكاس من على طبقة الالمنيوم . تم دراسة تأثير المتغيرات التشغيلية المختلفة على سلوك المفاعل في ازالة الصبغة مثل تركيز المادة العضوية من 10 الى 50 ملغم/لتر, تركيز العامل المساعد النانوي (TiO<sub>2</sub>) من 200 الى 800 ملغم/لتر, تركيز (H<sub>2</sub>O<sub>2</sub>) من 200 الى 1000 ملغم/لتر, حامضية المحلول (pH) من 5 الى 9, تدفق جريان المحلول من 0.3 الى 2 لتر/دقيقة . وجد ان افضل الظروف التشغيلية التي تؤدي الى اعلى كفاءة للمفاعل هي عندما يكون تركيز العامل المساعد 400 ملغم/لتر, تدفق جريان المحلول 0.5 لتر/دقيقة, تركيز العامل المؤكسد 400 ملغم/لتر وحامضية المحلول (pH) هي 5. تم الحصول على نسبة ازالة 95.27% بعد ساعة واحدة من التشغيل ونسبة ازالة 99.95% بعد ثلاث ساعات من التشغيل عند افضل الظروف التشغيلية . ثم تم تحليل المياه الناتجة باستخدام FTIR, UV- spectrophotometer. حيث ان تحليل النتائج أكدت أن المياه المنتجة من نظام مفاعل الشمسي يمكن إعادة تدويرها وإعادة استخدامه بأمان.

### INTRODUCTION

Everyday human activities introduce contaminant substances and wastes into rivers, lakes, groundwater aquifers and oceans. Many of the contaminants are so toxic that they can cause health problems in humans at trace levels. Water pollution also reduces the available amount of freshwater resources for both people, and ecosystems. Freshwater scarcity is already a reality in many developing countries. The United Nations, for instance, predicts that two-thirds of the world's population will live in water-scarce regions by 2025 (Ganoulis, 2009).

Dyes are widely used in the textile, leather, paper, printing inks, plastics, cosmetics, paints, pharmaceutical, and food industries. The total world colorant production in 2008 alone was estimated to be about 1.5 million tons. It is estimated that 15% of these dyes is lost in the synthesis, processing of colorants, dyeing, printing and finishing (Aye et al., 2003). This invariably corresponds to a release of about 615 tons per day into the environment and ecological system. Due to their toxicity and recalcitrance, these dyes are hazardous to the environment and even when they are present in very low concentrations, can present serious carcinogenic effects (Brown and DeVito, 2003). Degradation of dye molecules sometimes results in the formation of non-colored dye fragments which, although satisfying the requirement of decolorization, leads to the formation of environmentally unfriendly degradation products, such as aromatic amines, which are sometimes much more toxic than the parent dyes. Because of the high levels of aromatics present in these molecules and the stability of modern dyes, conventional biological treatment methods are ineffective for decolorization and degradation (Gonçalves et al., 2005; Abbas and Robab, 2010). Physico-chemical methods such as coagulation/flocculation, activated carbon adsorption and reverse osmosis techniques have been developed in order to remove the color (Neamtu et al., 2000). However, the latter methods can only transfer the contaminants (dyes) from one phase to the other

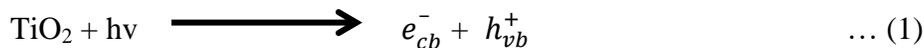
leaving the problem essentially unsolved (Philippe *et al.*, 1998). In general, each technique has its limitations. The use of one individual process may often not be sufficient to achieve complete decolorization. Dye removal strategies consist therefore mostly of a combination of different techniques. Therefore, attention has to be focused on techniques that can lead to the complete destruction of the dye molecules. This had led to the study of other methods.

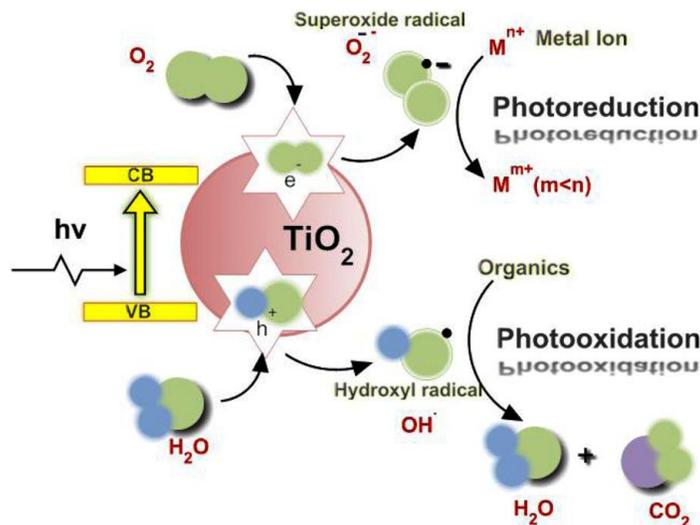
In this respect, Advanced Oxidation Processes (AOPs) have emerged as promising water treatment technologies for the complete destruction of organic contaminants in water (Bahnmann, 2004). AOPs for the removal of bio-recalcitrant compounds in wastewater are universally recognized today, and many researchers around the world are devoting their efforts to the development and improvement of these processes (Franch *et al.*, 2004). Photocatalysis, which is one of the Advanced Oxidation Processes, is a new method used to mineralize dye compounds (Dai *et al.*, 1996; Perez *et al.*, 2006). The utilization of photocatalysis has been attracting increasing attention. It may be developed to a useful process for the reduction of water pollution caused by dyeing compounds because of their mild conditions required and their efficiency in the mineralization. It also has the potential ability to oxidize most of the organic contaminants to CO<sub>2</sub> and H<sub>2</sub>O (Sahel *et al.*, 2007; Skorb *et al.*, 2008).

The aim of the present study was to investigate the optimum operating conditions which give the best performance of the photocatalysis process for the degradation of the synthetic dye in wastewater.

### Mechanism of UV photocatalysis

The heterogeneous photocatalysis is based on a semiconductor used as catalyst which is activated by UV light. The anatase form of Titanium dioxide is mainly used as the catalyst, because of its high activity. The photocatalytic process consists of the excitation of the titanium dioxide by a UV light wavelength of  $\lambda \leq 400$  nm, electron-hole pairs ( $e_{cb}^-$ ,  $h_{vb}^+$ ) are generated (Figure 1), the hydroxyl radicals are generated by the hole which can degrade organic pollutants present in the wastewater. Oxygen, provided from the air (when the system is stirred), dissolved in the solution scavenges the electron generated, preventing the recombination of electrons and holes. UV illumination of TiO<sub>2</sub> yields conduction band electrons and valence band holes (Eq.1), which interact with surface adsorbed molecular oxygen to yield superoxide radical anions, O<sub>2</sub><sup>-•</sup> (Eq.2), and with water to produce the highly reactive HO<sup>•</sup> radicals (Eq.3), respectively. The latter radical species are well known to oxidize a large number of organic substrates (Eq.4), (Horikoshi *et al.*, 2001; Emeline *et al.*, 2001).





**Figure (1): Mechanism of photocatalytic degradation in presence of UV radiation**

## Materials and Methods

### Materials

Chemicals used in the present work are: The hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution obtained from Henan, China was in a stable form (50% (w/w)). To control pH of solution, H<sub>2</sub>SO<sub>4</sub> (98%), and NaOH from Merk Co., Germany were used. The nano catalyst (TiO<sub>2</sub>, 80% anatasa) of Size (5-30nm) (specific surface area 60±15 m<sup>2</sup>/g (BET), was obtained from Sigma Aldrich Company, USA. Synthetic methyl violet 6B (C<sub>24</sub>H<sub>28</sub>N<sub>3</sub>Cl) was supplied from Sigma Aldrich Company, USA.

### Methods

#### Experimental setup

Figure 2 (a & b) shows the schematic and photographic views of the photocatalysis reaction system, respectively. The photocatalytic reactor was operated as a batch process. The system consists of a solar reactor (No.5), wastewater preparation tank (No.1) made of 5L-PVC, a circulation pump (No.2), Type: In-line centrifugal pump (Wtg204), Head (H) = (25-40) m, variable impeller speed (750, 1200, 1850 min<sup>-1</sup>), V= 220 volt). The solar reactor was mounted on a fixed platform tilted 37° (local latitude) and directed south-east. It was made up of a flat-plate colorless glass of dimensions 1000 x 750 x 4 mm. The base of the reactor was made of aluminum. This geometry enables the light entering the liquid film from almost any direction to be reflected and can also be employed for the photocatalytic reaction. The circulating pump was used to feed the water from the tank to the reactor via a calibrated flow meter (No.3). The aqueous solution was allowed to trickle down freely from a pipe (No. 6) pierced by several openings placed at the top of the reactor. The water and reagents added to the tank from openings in the lid. A thermocouple type (pt-100) was placed into the water preparation

tank to measure the mixture temperature. A mechanical mixer was used to obtain homogeneous conditions in the feed tank. In the present work.

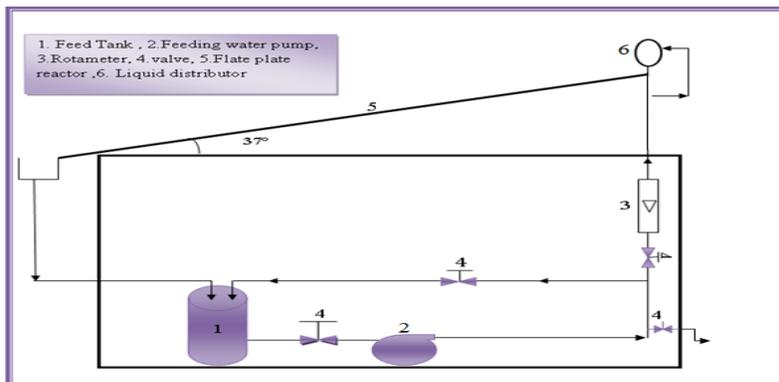


Figure (2A): schematic diagram of photocatalytic slurry reactor

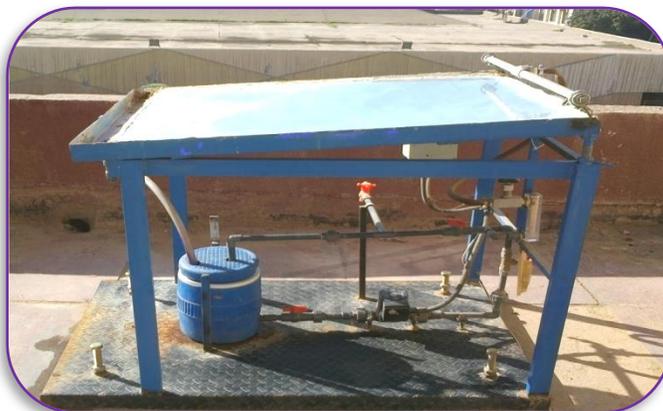


Figure (2b): photographic view of the photocatalytic reactor

### Analytical determinations

Mineralization was followed by measuring, the color which is a function of concentration was determined at a dominate wavelength by spectrophotometric method no. 2120 Standard Method, using a Shimadzu UV –Visible spectrophotometer (UB\_1201 PC). TOC was determined by TOC analyzer type (E6811). To identify the functional groups in product solutions, FTIR (Bruker Tensor 27) system was used. To estimate the concentration of dissolved oxygen, on-line DO-Model 862A was used. On-line pH meter Model Excel 25PH/mV/ISL was used to measure pH of suspension. Laboratory portable conductivity and pH meters from Hanna-USA were used for further check and quick measurements. Calibration curve of dye concentration vs. light absorbance was illustrated in Figures (3).

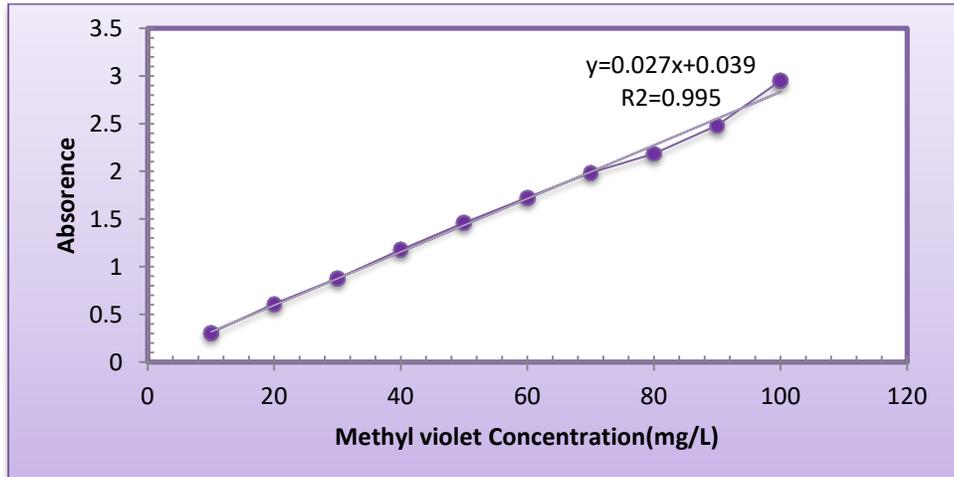


Figure (3): Calibration curve of light absorbance against methyl violet concentration.

**Evaluation of solar UV radiation**

The sunlight intensity was measured by using Davis 6152C Vantage Pro2 Weather Station radiometer which provides also data in terms of incident W UV/ m<sup>2</sup>. This gives an idea of the energy reaching any surface in the same position with regard to the sun. With Eq. (5), combination of the data from several days’ experiments and their comparison with other experiments is possible.

$$Q_{UV/n} = Q_{UV,n-1} + \Delta t_n * UV_{gN} * \frac{A}{V} \quad \dots (5)$$

Where t<sub>n</sub> is the experimental time for each sample, UV<sub>gN</sub> the average ultra-violet energy during Δt<sub>n</sub>, A<sub>CPC</sub> the collector surface, V the total plant volume and Q<sub>UV, n</sub> is the accumulated energy (per unit of volume, kJ/l) incident on the reactor for each sample taken during the experiment. Where, A= area of reactor (750\*100) cm<sup>2</sup> = 0.75m<sup>2</sup>, V= 5L, n= number of samples. This result is shown in Figure (7), which plots the variation in dye concentration against accumulative energy.

**Experimental Design**

Photocatalytic reactor experiments were aimed to study the effect of operating parameters (catalyst loading, hydrogen peroxide concentration, flow rate, pH, and dye concentration) on the degradation efficiency and TOC removal of organic pollutant. Table 1 shows the range of operating variables that used in photocatalytic experiment.

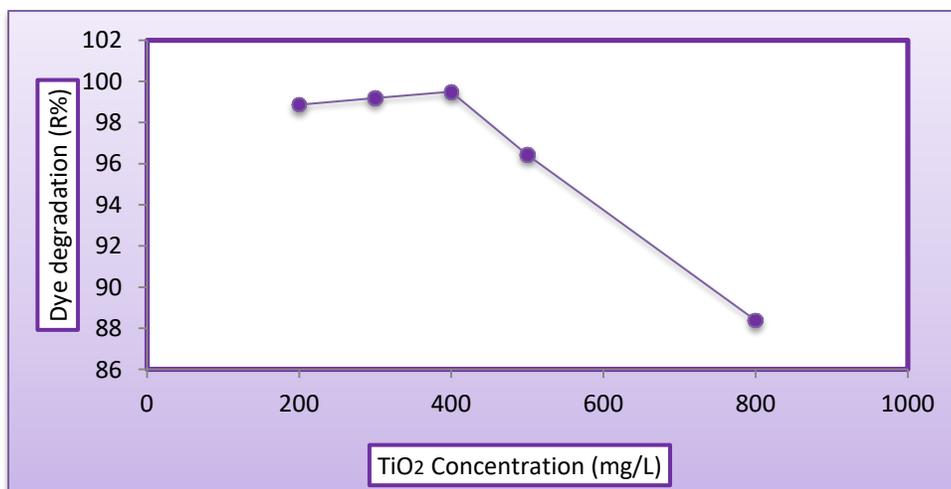
Table (1): Ranges of operating variables of photocatalytic experiments.

Operating parameter	Range
Catalyst loading (TiO <sub>2</sub> ) ,mg/L	200, 300, 400, 500, 800
Hydrogen peroxide concentration , mg/L	300, 400,500, 800,1000
pH of solution	5, , 7, 9
Dye concentration ,mg/L	10, 20,30, 40,50

## Results and Discussion

### Optimum Catalyst Loading

In recent years, titanium dioxide ( $\text{TiO}_2$ ) has been an important photoactive material with existing and potential uses in a wide variety of environmental and energy applications, and has attracted great attention due to its promising applications in many areas such as photocatalysis, transparent conducting electrodes, self-cleaning windows, photo-degradations and sensor applications.  $\text{TiO}_2$  a catalyst is largely available, inexpensive, non-toxic and shows relatively high chemical stability (Akira *et al.*, 2000; Guettai, and Amer, 2005; Jinsong *et al.*, 2011). Degussa P25, is commercially available. It consists of two forms of  $\text{TiO}_2$  (closely approximating 20% rutile, 80% anatase). Figure (4) illustrates the optimum catalyst concentration for the degradation of MV dye after 180min of treatment process.



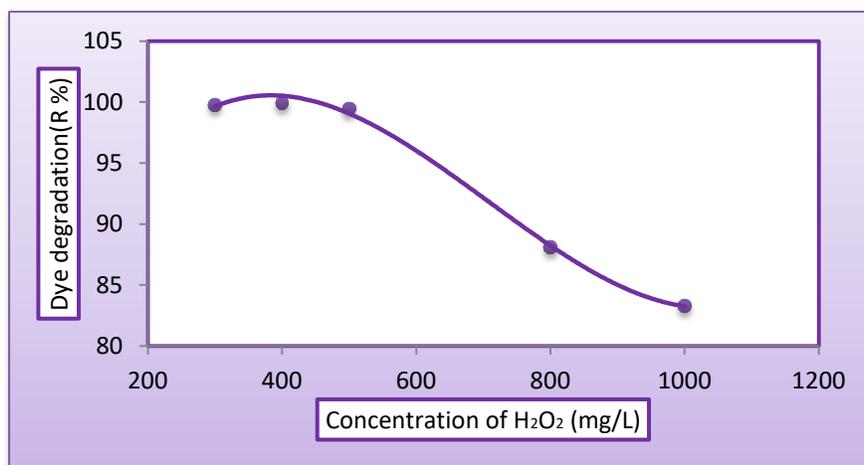
Figure(4): Variation in dye degradation(R%) with concentration of  $\text{TiO}_2$  ( $C_{\text{H}_2\text{O}_2} = 500 \text{ mg/L}$ ,  $C_{\text{MV}} = 30 \text{ mg/L}$ ,  $Q_L = 0.5\text{L/min}$ , and  $\text{pH}=5$ ) after 180min

In Figure (4) it is observed that the initial rate increases with the increase in catalyst concentration which increased from 200 mg/L to 400 mg/L. This could be explained by the fact that there was an increase in the photon adsorption with increased catalyst concentration. Further increase from 400 mg/L to 800 mg/L resulted in decreased degradation rate, this phenomena may be explained by the light scattering, caused by the lightproof suspended catalyst (Guettai and Amar, 2005; Zanjanchi *et al.*, 2010; Dixit *et al.*, 2010). This amount of catalyst (i.e., 400 mg/L) will be employed in the other experiment.

### Optimum Hydrogen Peroxide

Hydrogen peroxide plays a dual role in photocatalytic reaction acting as electron acceptor and could decompose to produce  $\text{OH}^{\cdot}$  radicals (Jun and Chaoxia, 2010). It is clear from Figure (5) that the rate of degradation goes on increasing with the increase in

concentration of  $H_2O_2$  and becomes maximum at 400 mg/L and then starts decreasing with further increase in concentration of  $H_2O_2$ . The decolorization rate is slow at low  $H_2O_2$  concentration, as the formation of hydroxyl radicals is insufficient, this may explain the ability of  $H_2O_2$  to trapping the electrons preventing the electron-hole recombination hence increasing the chance for formation of  $OH^\bullet$  radicals on the surface of the catalyst (Wang and Hong, 1999). However, as the initial concentration of  $H_2O_2$  increases beyond a certain value (400mg/L), the increase in decomposition rate becomes less. This is because at higher  $H_2O_2$  concentration, more  $OH^\bullet$  is produced leading to a faster oxidation rate. However, these free radicals prefer to react with the excess of  $H_2O_2$  rather than with the dye (Legrini et al., 1993; Dixit et al., 2010). The optimum hydrogen peroxide concentration for the degradation of MV dye is 400 mg/L. This amount of  $H_2O_2$  will to employ in the other experiment.

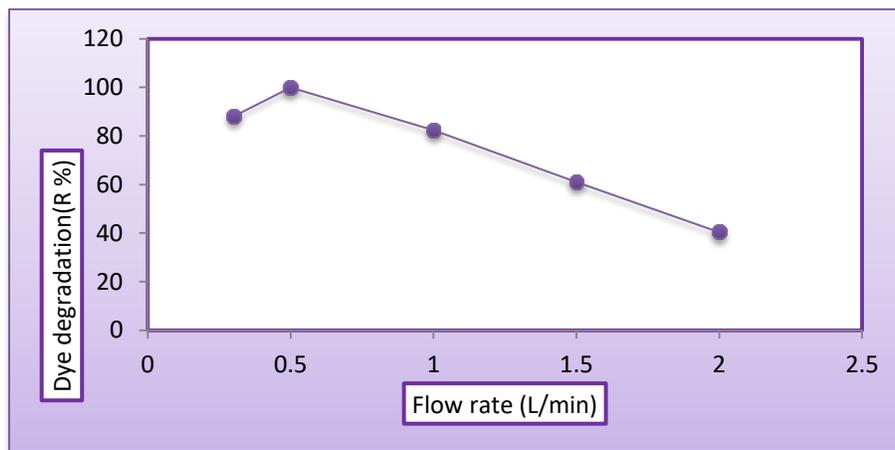


**Figure (5): Variation in dye degradation (R%) y with concentration of  $H_2O_2$  ( $C_{TiO_2} = 400$  mg/L,  $C_{MV} = 30$  mg/L,  $Q_L = 0.5$  L/min, and  $pH = 5$ ) after 180min**

#### Optimum Liquid Flow Rate

In heterogeneous catalysis, the factors for the rate controlling step are mass transfer and surface reaction control. The photocatalytic degradation of the MV dye was carried out, and the degradation efficiencies of the MV dye under different flow rates from 0.3 to 2 L/min are shown in Figure (6), it was found that the photocatalytic degradation increases with increasing the flow rate from 88% to 99.95% for flow rate (0.3 and 0.5) mg/L, respectively. It can be concluded from the graph that effluent with 0.5 L/min flow rate has undergone almost complete degradation on only 180 min of solar exposure which shows that resulting water can be recycled in the process, when the liquid flow rate increased further to 2 L/min, dye removal of the reactor effluent has dropped to 40.32% which indicates the necessity for further light exposure. This is firstly due to the limitation of the solar light penetration on account of the rise of the liquid thickness and secondly to the reduction of the residence time which leads to reduce the surface

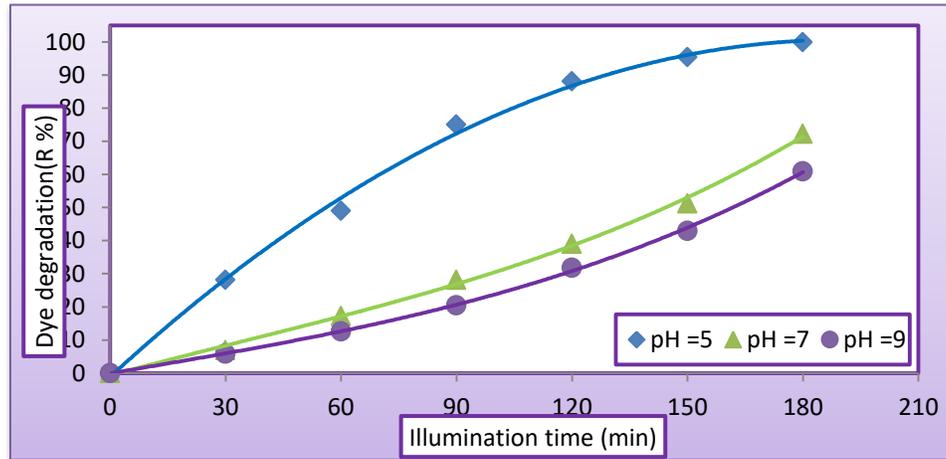
reactions efficiencies. . The experimental results showed that the photocatalytic reaction efficiencies of MV dye over the  $\text{TiO}_2$  all exhibit maximum values at certain flow rate. So the optimum flow rate for the degradation of MV dye is  $0.5\text{L}/\text{min}$ . This amount of flow rate will be employed in the other experiments.



**Figure (6):** Variation in dye degradation(R %) with flow rate ( $C_{\text{TiO}_2}=400\text{mg}/\text{L}$ ,  $C_{\text{H}_2\text{O}_2}=400\text{mg}/\text{L}$ ,  $C_{\text{MV}}=30\text{mg}/\text{L}$ ,  $\text{pH}=5$ ) after 180 min

### Optimum pH of the Solution

pH is an important parameter in the photocatalytic process, and it is of interest to study its influence on the degradation rate of the MV dye. Figure (7) illustrates the variation of dye degradation rate against illuminated time. Results obtained experimentally by varying initial pH of polluted solution from 5 to 10 with keeping all other parameters unchanged. Figure (7) clearly indicated a neat decrease in dye degradation. It could be noticed that the final degradation obtained in acidic solution at  $\text{pH}=5$  was 99.95% and at  $\text{pH}=7$  it was 72.2% while at  $\text{pH}=9$ , the final degradation efficiency was 48.2%. This could be explained from the surface charge of  $\text{TiO}_2$  point of view. In acidic pH, the surface of  $\text{TiO}_2$  acquires a positive charge thereby attracting the anionic MV dye, leading to a greater adsorption and hence increasing the degradation rate in the acidic media. However, the reverse image is observed in the basic medium where the  $\text{TiO}_2$  surface was negatively charged which repels the dye molecules away from the surface of the catalyst thereby decreasing the degradation rate.



**Figure (7): Variation in dye degradation(R %) with illumination time at different pH ( $C_{MV}=30\text{mg/L}$ ,  $C_{TiO_2}=400\text{mg/L}$ ,  $C_{H_2O_2}=400\text{mg/L}$ , and  $Q_L=0.5\text{L/min}$ )**

### Dye and TOC removal

The effect of initial concentration of dye solution on the dye degradation efficiency and TOC removal of methyl violet (MV) dye has been investigated by varying the dye concentrations from 10  $\text{mg/L}$  to 50 $\text{mg/L}$ . Figure (9) plots the variation in dye degradation against methyl violet (MV) dye concentration in solution in the presence of 400  $\text{mg/L}$   $TiO_2$  under solar light with keeping all other parameters unchanged. It could be noticed from Figure (9) that after 180  $\text{min}$  of irradiation time: the degradation rate is 99.99%, 99.97%, 99.95%, 93.2%, and 91.52% at concentration of MV equal to (10, 20, 30, 40, and 50)  $\text{mg/L}$ , respectively; and is observed to decrease with increasing initial concentration. It could be concluded from the present experiments, as the dye concentration increases, the fraction of unadsorbed dye in the solution increases, leading to lesser penetration of light through the solution onto the surface of  $TiO_2$ , thereby decreasing the rate of formation of OH radical which is the most reactive species formed on the surface and hence, decreasing the rate of degradation. Since the relative number of the OH radicals attacking the substrate decreases, the photo-efficiency of the reaction also decreases. However, the reverse image is observed at lower substrate concentration, where the light intensity and time of irradiation are the same but interception of the photons to the catalyst surface is increased leading to the formation of more numbers of OH radicals, thereby increasing the rate of reaction. The explanation of this behavior, as the initial concentrations of the dye increase, the probability of reaction between dye molecules and oxidizing species also increases, leading to an enhancement in the decolourization rate. Figure (10) shows the effect of MV concentration on the TOC removal of the reactor effluent after 180 $\text{min}$  of treatment keeping other parameters unchanged. As shown in Figure (10), the TOC decreases by increasing the dye concentration. The reason is the photogeneration of holes or OH' a radical on the catalyst

surface is reduced since the active sites are covered with dye ions. This leads to the conclusion that as the initial concentration of the dye increases, the requirement for catalyst surface needed for the degradation also increases. Our results are confirmed by the findings of many researchers (Epling and Lin, 2002; Guettaï and Amar, 2005).

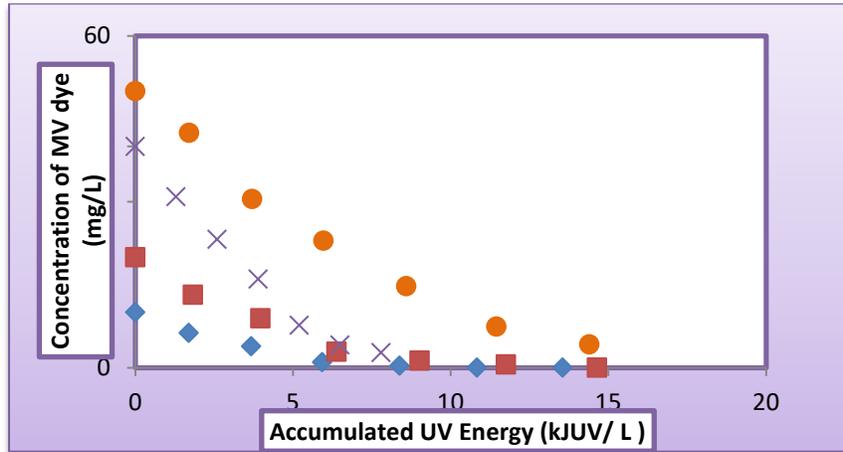


Figure 8: Variation of concentration of dye vs. Accumulated UV energy with different initial concentration at ( $C_{H_2O_2}=400\text{mg/L}$ ,  $C_{TiO_2}= 400\text{mg/L}$ ,  $Q_L =0.4\text{L/s}$  and  $\text{pH}=5$ ).

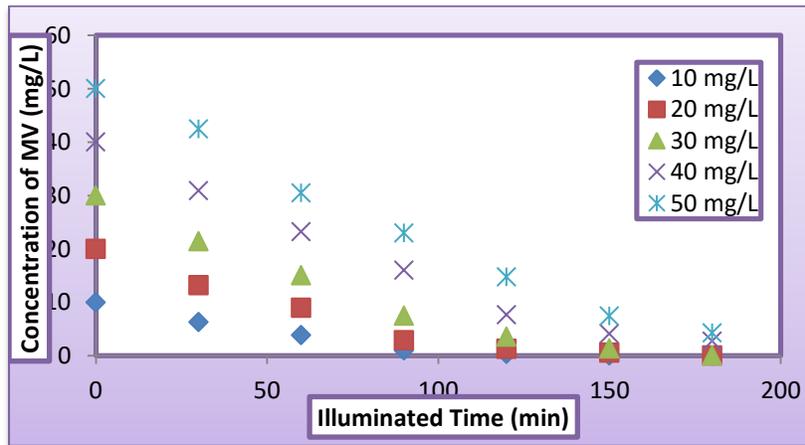


Figure (9) Effect of initial concentration of MV on the photocatalytic degradation at optimum operating conditions.

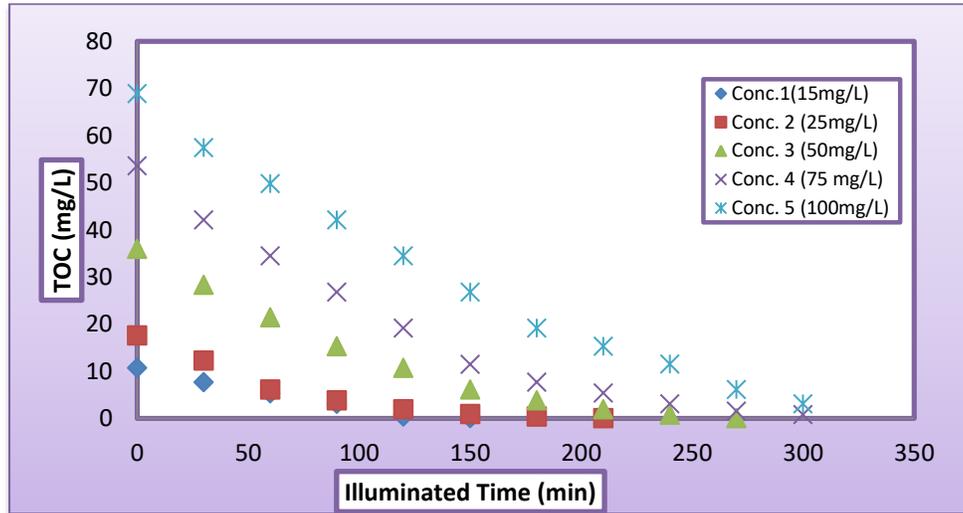


Figure 10: Variation of TOC with illuminated time at optimum conditions.

Figure (11) shows a photographic view for a sample of (a) synthetic wastewater at feed conditions (30 mg MV/L); b) after treatment by photoreactor at optimum operating conditions. The whit color in (b) represents the TiO<sub>2</sub> particles which removed by simple filtration to obtain the sample in (c).

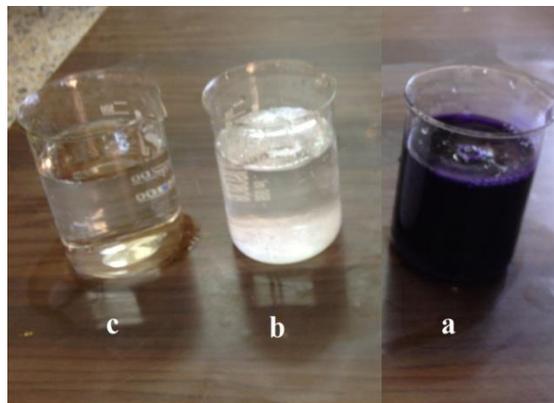
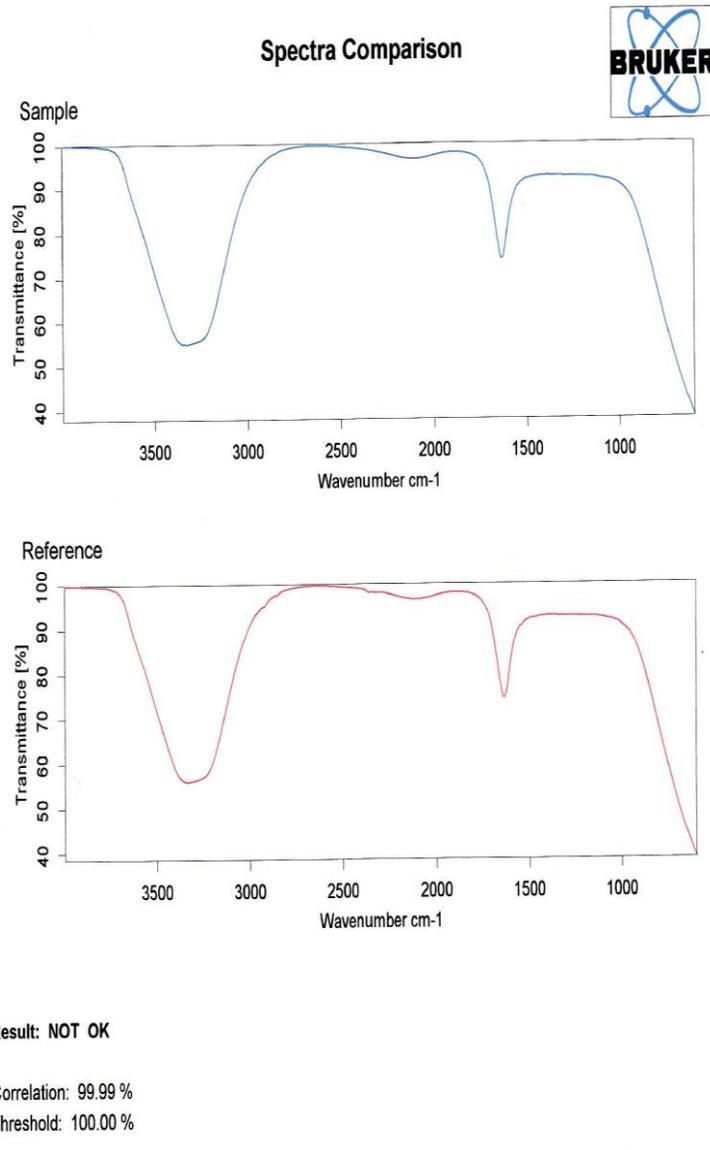


Figure (11): Samples of wastewater before and after treatment.

Figure (12) shows a printout of the FTIR instrument for a sample taken from the effluent of the solar reactor operating at the optimum conditions. The Figure at the top illustrates the functional groups in the sample taken while the Figure at the bottom shows an analysis of drinking water. Obviously the plots confirm that the degradation almost complete.



**Figure (12): Contrast of FTIR of MV dye Compared with tap Water After 180 min at Optimum Operating Conditions**

### CONCLUSIONS

Results of degradation rate and TOC removal of substrate (i.e., synthetic dye and phenol) by solar photocatalytic reactor indicated the followings:

*a-* It appears that the irradiation time, catalyst load, pH, H<sub>2</sub>O<sub>2</sub> concentration, and concentration of substrate mainly controls the rate of degradation and TOC removal for which optimum conditions of achieving maximum efficiency were established.

**b** -At the optimal conditions (i.e.,  $C_{\text{TiO}_2} = 400\text{mg/L}$ ,  $C_{\text{H}_2\text{O}_2} = 400\text{mg/L}$ ,  $\text{pH} = 5$ ) 99.95 % and 99% of dye (at concentration = 30 mg/L) was degraded after approximately 3 hours of operation.

**c** - Regarding catalyst load, the degradation increased with the mass of catalyst up to an amount of 400mg/L. It decreased as the mass continued to increase attributed to the UV light penetration depth which is considerably smaller than in suspension containing catalyst of 400 mg/L.

**d** - The capacity of  $\text{TiO}_2$  towards substrate degradation strongly depended on the solution pH. At basic pH, degradation was slow, and at acidic pH, degradation of substrate was fast indicating that the mechanism involving complete mineralization could be achievable under prolonged exposures.

**e** - The addition of  $\text{H}_2\text{O}_2$  to  $\text{TiO}_2$  suspension resulted in an increase in the degradation rate. The  $\text{H}_2\text{O}_2$  increased the concentration of  $\cdot\text{OH}$  radicals and acted as electron acceptors to make electron/hole recombination avoided.

**f**- It was found that the kinetics of dye degradation was first order with respect to dye concentration and could be well described by Langmuir-Hinshelwood model.

**g** - The designed setup proved to be efficient for degradation of toxic organic compounds using solar photocatalysis process.

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