Removal of Methyl Violet Dye from Synthetic Wastewater Using a Hybrid Detoxification Process

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ABSTRACT

The aim of the present study was to design a solar reactor and analyze its performance for removal of methyl violet dye (MV) from water with titanium dioxide as the photocatalyst. The solar reactor 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. Various operating parameters were studied to investigate the behavior of the designed reactor like initial dye concentration (C_{MV}=10-50 mg/L), loading of catalyst (C_{TiO2}=200-800 mg/L), suspension flow rate (Q_L=0.3-2 L/min), pH of suspension (5-10), and H_2O_2 concentration (C_{H2O2}=200-1000 mg/L). The operating parameters were optimized to give higher efficiency to the reactor performance. The designed reactor when operating at optimum conditions offered a degradation of MV up to 95.27% within one hours of operation time, while a conversion of 99.95% was obtained in three hours. The effluent from the photocatalytic reactor was fed to a LPRO separation system which produced a permeat of turbidity value of 0.09NTU. The product water was analyized using UV-spectrophotometer and FTIR. The analysis results confirmed that the water from the Hybrid-system could be safely recycled and reuse. 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.

Keywords: Solar photocatalysis, Membrane separation, Hybrid system, Titanum dioxide photocatalyst, Dye synthetic wastewater.

تنقية المياه من صبغة المثيل البنفسجية باستخدام الطريقة الهجينة لازالة السمية
الخلاصة:

يهدف البحث الى دراسة كفاءة مفاعل الطبقة الساقطة في ازالة صبغة المثيل البنفسجية من المياه باستخدام ضوء الشمس وثاني اوكسيد التيتانيوم كعامل مساعد. ثم بحث تأثير المتغيرات التشغيلية (تركيز الصبغة, تركيز العامل المساعد, معدل تدفق السائل, حامضية المحلول, تركيز بيروكسيد الهيدروجين) على

كفاءة اداء المفاعل في ازالة الصبغة. بعد ايجاد افضل الظروف التشغيلية التي تؤدي الى اعلى كفاءة للمفاعل وقد وجد ان المفاعل يحقق ازالة بمقدار 95.27% بعد ساعة من التشغيل و99.95% بعد ثلاث ساعات من التشغيل. ثم دراسة حركية التفاعل للتفاعل الضوئي ووجد ان قانون سرعة التفاعل من الدرجة الاولى بالنسبة لتركيز الصبغة وتطابق مع موديل Langmuir-Hinshelwood , كما وجدت علاقة تجريبية تربط بمعدل الازالة الصبغة مع المتغيرات التشغيلية.

INTRODUCTION:

Textile dyes and other commercial colorants have become as toxic organic compounds the focus of environmental remediation efforts because of their natural biodegradability is made increasingly difficult owing to the improved properties of dyestuffs [1, 2]. Color interferes with penetration of sunlight into the water, retards photosynthesis, inhibits the growth of aquatic biota and interferes with solubility in water bodies [3]. Various physical, chemical and biological pre-treatment and post-treatment techniques have been developed over the last two decades to remove color from dye contaminated wastewater in order to cost effectively meet environmental regulatory requirements. Chemical and biological treatments have been conventionally followed till now but these treatment methods have their own disadvantages [4].

As international environmental standards are becoming more stringent, (ISO 14001, 1996), a technological system for the removal of organic pollutants, such as dyes has to be developed. Heterogeneous photocatalysis is one of the advanced oxidation process (AOP) that has proven to be a promising method for the elimination of toxic and bio-resistant organic and inorganic compounds in wastewater by transforming them into innocuous species [5, 6]. Advanced oxidation process (AOP) is a chemical oxidative process, which can be applied to wastewater treatment to oxidize pollutants. It generates hydroxyl radicals which considered as the second strongest known oxidant (2.8V vs. standard hydrogen electrode). It is able to oxidize and mineralize almost every organic molecule, yielding CO_2 and inorganic ions [7]. AOPs not only oxidized the organic compounds, but also a complete mineralization is achievable, and the processes are not specific and therefore are capable of destroying a broad range of organic compounds. The process is very powerful, and is immune to organic toxicity. In the eighties and nineties, water reuse started to become a popular means to reduce freshwater intake and reduce treatment costs. A concept that refers to closed circuits of water, such that disposal is eliminated. Advantages and disadvantages of zero discharge facilities are currently being seriously considered and discussed. Zero liquid discharge minimizes the consumption of freshwater to that of make-up; therefore, it should help relieve freshwater availability limitations in places where it is scarce or expensive [8].

In photocatalytic degradation of dyes in wastewaters, the main operating parameters which affect the process are pH of the solution to be degraded, oxidizing agent, catalyst loading, and contaminant concentration [9].

The main objectives of this work were the evaluation and testing of photocatalytic reactor for the degradation of methyl violet (MV) dye which is selected as a model organic toxic pollutant in water using a commercial TiO_2 catalyst. And also to study the possibility to couple a membrane separation system with the reaction system, to remove

TiO_2 particles from product stream of the solar photocatalytic reactor to achieve a zero liquid discharge.

Materials and Methods
Chemicals

1. Methyl violet 6B (MV) dye (commercial grade, $C_{24}H_{28}N_3Cl$, λmax (nm) = 586, Sigma Aldrich Co., USA.),
2. Titanium dioxide powder (antase type, ≥99.5% trace metals basis, particle size ~ 21nm, specific surface area (35-65 m^2/g), particle density(4.26 g/mL (at 25 ^{o}C)), Sigma Aldrich Co.) were used as received.
3. Reagent-grade hydrogen peroxide (H_2O_2) (50% v/v solution), was used as oxidant. Technical grade hydrochloric acid (35%) and sodium hydroxide (98% flakes) were used to adjust the pH of synthetic wastewater (to around 5–10).
4. Distilled water used was obtained from the Chemical Engineering Department distillation plant (conductivity <10μS cm^{-1}, Cl^- = 0.7–0.8 mg L^{-1}, $NO3^-$ = 0.5 mg L^{-1}, organic carbon <0.5 mg L^{-1}).

Analytical determinations
Mineralization was followed by measuring,
1. The color which is a function of concentration was determined at a dominate wave length by spectrophotometric method no. 2120 Standard Method, using a Shimadzu UV -Visible spectrophotometer (UB_1201 PC).
2. COD was determined by open reflux method 5220 Standard Method (ET 108).
3. To identify the functional groups in product solutions, FTIR (Bruker Tensor 27) system was used**.
4. Turbidity of water treated by membrane system (LPRO) was measured by Turbid Direct meter (Lovibond).
5. The sunlight intensity was measured by using Davis 6152C Vantage Pro2 Weather Station radiometer**. Calibration curves of dye concentration vs. light absorbancy and TiO_2 concentration vs. turbidity were illustrated in Figures (1) and (2), respectively.

Experiment set-up
The hybrid process setup consists of two treatment systems connected together and operated in batch mode**. Figure (3) shows the schematic view of the (photocatalysis reaction/LPRO membrane) system. 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^{-1}), V= 220 volt). The solar reactor was mounted on a fixed platform tilted 37º (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 water tank. In the present work, the pH of the effluent from the photocatalytic reactor was neutralized in a 5L vessel (No.7) and then left for 4 hours. The sediment was washed with H_2O_2, dried, and weighted for further use. The neutralized solution was fed to a 5L PVC tank (No.8) which served as a feeding tank to the low pressure reverse osmosis membrane (LPRO) type (RE1812-CSM Co.) which was used to separate the TiO_2 nanoparticles from the photoreactor effluent via a diaphram pump (No.14), (type CR50-N-N-2, single phase: 50Hz, 220V). The (LPRO) was a spiral wound module made of composite polyamide with an effective area of 0.7 m^2. The separation system also contained two holding tanks, all are made of PVC, these are the concentrate tank (No.18), and the permeate tank (No.17). Each tank is supplied with suitable fittings and connections to serve the process. Laboratory portable conductivity and pH meters from Hanna-USA were used for further check and quick measurements.

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 COD removal of organic pollutant. Table (1) shows the range of operating variables that used in photocatalytic experiment. The ranges of operating variables were selected to; match the dye concentration and acidity in the wastewater effluent from the 14-Ramadhan textile mill and to investigate the effect of broad range of liquid Reynolds numbers on dye degradation.

Results and Discussion

Effect of pH

pH is an important parameter for the photocatalytic process, and it is of interest to study its influence on the degradation rate of the MV dye. Figures (4 and 5) illustrate the variation of dye degradation rate against illuminated time and the variation of COD in reactor effluent against pH after 180min, respectively. Results obtained experimentally by varying initial pH of polluted solution from 5 to 10 with keeping all other parameters unchanged, clearly indicated a neat decrease in dye degradation. It could be noticed from Figure (5) that the final degradation obtained in acidic solution at pH equal 5 was 99.95% and at pH = 6 it was 95.22% while at pH= 7, pH =9, and pH =10, the final degradation efficiency were 72.2%, 60.98%, and 48.2%, respectively. At the same condition, Figure (5) indicated that COD removal was 99.9% after two hours from start up. This could be explained from the surface charge of TiO_2 point of view. In acidic pH, the surface of TiO_2 acquires a positive charge thereby attracting the anionic MV dye, leading to a greater adsorption and hence increasing the degradation rate and COD removal in the acidic media. However, the reverse image is observed in the basic medium where the TiO_2 surface was negatively charged which repels the dye molecules away from the surface of the catalyst thereby decreasing the degradation rate. Our results have good agreement with the findings of Konstantinou and Albanis [11].

Effect of hydrogen peroxide (H_2O_2)

The addition of H_2O_2 may play an important role in the limitation rate of photogenerated hole-electron pairs which had been attributed to degradation rate and COD removal of the MV dyes. Figures (6 and 7) plot the variation of dye degradation against H_2O_2 concentration in solution keeping all other parameters unchanged and COD removal in reactor effluent after 180min at the same operating conditions, respectively. Different concentrations of H_2O_2 (300 to 1000 mg/L) were added to study the effect of H_2O_2 concentration on the decolorization rate and COD removal. As can be seen, the removal rate increased with increasing initial concentration of H_2O_2. The decolorization rate was slow at low H_2O_2 concentration, as the formation of hydroxyl radicals was insufficient, this may be explained the ability of H_2O_2 to trapping the electrons preventing the electron-hole recombination and hence increasing the chance of formation of $OH^\bullet$ radicals on the surface of the catalyst. As shown in Figure (7), the addition of H_2O_2 ($400\,mg/L$) to the dispersed solution resulted in a significant increase on the removal of COD. At the end of 180min. of irradiation, almost total removal (99.5%) was obtained. When H_2O_2 concentration was increased to 1000mg/L, COD reduction was only 87.4%. It seems that Hydrogen peroxide played a dual role in photocatalytic reaction, it is acting as an electron acceptor and could decompose to produce $OH^\bullet$ radicals. It is clear from Table 3 that the rate of degradation goes on increasing with increased concentration of H_2O_2 and approached maxima at 400 mg/L and then started to decrease with further increase in concentration of H_2O_2. The optimum hydrogen peroxide concentration for the degradation of MV dye is 400 mg/L. This amount of H_2O_2 will be employed into all experiments. The findings of [6], 12, and 13] are agreed with our results.

Effect of liquid flow rate

Falling –film reactors characterized by a high ratio of exposure (surface area to liquid volume), which positively impact the performance of such type of reactors. Flow rate of synthetic wastewater is another important parameter which must be considered. Effect of liquid flow rate on the dye degradation and COD removal was tested by taking various flow rates from (0.3 to 1.5 L/min) keeping all other parameters unchanged. Figure (8) illustrates the variation of the dye degradation against illuminated time. As can be seen from Figure (8) that liquid flow rate has negative impact on degradation rate. This may be explained from the view point of shorter contact time of aqueous suspension with illumination source as the recirculation rate increased. Figure (9) illustrates the influence of liquid flow rate on the COD of the reactor effluent. It can be concluded from the graph that effluent with 0.5 L/min has undergone almost complete degradation at 180 min of solar exposure which indicated that resulted water could be recycled in the process. When the liquid flow rate increased to 1.5 L/min, COD of the reactor effluent has dropped to 241mg/L which indicates the necessity for further light exposure. This could be firstly due to the limitation of the solar light penetration because of rise in the liquid thickness and secondly to the reduction of the residence time of substrate which lead to reduce the surface reaction efficiency.

Effect of initial dye concentration

The effect of initial concentration of dye solution on dye degradation efficiency has been investigated by varying the dye concentrations from (10 to 50 mg/L). Figure (1**0**) plots the variation of dye degradation against (MV) dye concentration in the presence of 400 mg TiO$_2$/L under solar light by keeping all other parameters unchanged. As can be seen from Figure (10) that after 180 min of irradiation time the degradation rate was 99.99%, 99.97%, 99.95%, 93.2%, and 91.52% at concentration of MV equal to (10, 20, 30, 40, and 50 mg/L), respectively. Dye degradation was observed to decrease as initial concentration increased. It could be concluded from the present experiments that as the dye concentration increases, the fraction of nonadsorbed 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 radicals, consequently the degradation rate decreased. However, the reverse image is observed at lower substrate concentration, where the light intensity and time of irradiation is 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.

Effect of catalyst loading

The amount of catalyst is one of the main parameters for the degradation studies from economical point of view. To investigate the effect of the photocatalyst, its loading in the dispersion was varied between (200 to 800 mg/L) under UV light. Figure (11) shows the variation of dye degradation (R %) against illuminated time for various photocatalyst loading by keeping all other parameters unchanged. Figure (11) demonstrates a positive impact of catalyst concentration on dye degradation; this trend was almost due the increase of active site with absorption and dye adsorption. Our results were in agreements with the findings of [10, 15]. In order to avoid the use of excess catalyst it is necessary to find out `the optimum loading for efficient removal of dye. Table (4) illustrates the optimum catalyst concentration for the degradation of MV dye after 180min of treatment process. From Table (4) it was observed that as catalyst concentration increased from (200 to 400 mg/L) the initial rate increases correspondingly, this can be explained by the fact that there was an increased in the photon adsorption with increased concentration. The results of [13] and [15] confirmed the findings of the present work.

Photocatalysis Kinetics

The photocatalytic oxidation kinetics has often been modeled with the Langmuir–Hinshelwood equation, which also covers the adsorption properties of the substrate on the photocatalyst surface. This model, developed by [16, 17], is expressed as equation (1):

$$r = -dC/dt = k_r KC/ (1+ KC) \qquad \qquad \dots (1)$$

Where r is the reaction rate (mg/L.min), k_r the reaction rate constant (mg/L.min), K the adsorption equilibrium constant (L/mg) and C the concentration of dye (mg/L). The degradation rate of dye was studied as a function of the initial dye concentration in the range (10 to 50 mg/L) , for a catalyst loading of TiO$_2$ (0.4mg/L). The results were illustrated in Figure (1**2**) which shows the initial dye concentration versus reactor operating time. Equation (2) depicts a pseudo–first order reaction with respect to the

methyl violet (MV) concentration. The relationship between the initial degradation rate (r_o) and the initial concentration of organic substrate for a heterogeneous photocatalytic degradation process has been described by Langmuir–Hinshelwood model and can be written as follows: if we consider that the kinetic of dye degradation is of pseudo-order, at t=0 and $C=C_o$, equation (1) becomes:

$$r_o = k_r KC_o / (1+ KC_o) \qquad \qquad \dots (2)$$

This Equation can be rearranged into linear form:

$$1/r_o = (1/k_r K).1/C_o \quad + \quad 1/k_r \qquad \qquad \dots (3)$$

Where $1/r_o$ and $1/C_o$ are the dependent and independent variables, respectively, $1/k_r$ is the intercept and $(1/k_r K)$ is the slope of the straight line shown in Figure (13). The L-H adsorption constant and the rate constant were obtained using initial rate method [**18**] by plotting $1/r_o$ versus $1/C_o$. The values of the adsorption equilibrium constant, K and the kinetic rate constant of surface reaction, k_r were calculated. The graphical representation of equation (3) yields a straight line as shown in Figure (13) indicating a pseudo-first order reaction. The reaction rate constants k_r for photocatalytic degradation of dye were evaluated from experimental data Figure (13) using a linear regression. The constants k_r and K in Langmuir–Hinshelwood model were obtained as 0.791 mg/L.min and 0.0209 L/mg, respectively. The correlation coefficient R^2 was equal to 0.9892 .then equation (3) will become

$$r = 0.0165C/ (1+0.0209C) \qquad \qquad \dots (4)$$

FTIR measurements
   To identify the functional groups in the reactor effluent, samples were taken after 180 min from the reactor effluent analyzed with FTIR (type: Bruker Tensor 27) and filtered with (0.25) μm flat paper to avoid disturbance during analysis.

Catalyst Recuperation
   For the purpose of catalyst reuse, a neutralization process was carried out after photocatalytic treatment for sedimentation of titanium dioxide aggregate. Table (2) presents the turbidity before and after the neutralization process, and Figure (2) was used to estimate the corresponding concentration of TiO_2.The sediment was washed with H_2O_2, dried, and weighted for further use.

Membrane Separation
   Low pressure reverse osmosis (LPRO) membrane was used to separate TiO_2 particles from product water. The experimental results indicated that separation efficiency of LPRO was feasible which suggested the use of such type of membrane for the catalyst reuse process.

As simple and quick method for estimation of suspended solids concentration in solution, turbidity method could be used to estimate the separation efficiency of the membrane using equation (5).

$$\text{Seperation efficiency} = \frac{(\text{Turbidity})_{in} - (\text{Turbidity})_{permeate}}{(\text{Turbidity})_{in}} \qquad \ldots (5)$$

Figure (14) represents the separation efficiency of the LPRO as a function of TiO_2 particles concentration into a neutralized solution of the photocatalytic reactor effluent. Despite the strong potential of membrane, one of the common problems encountered in applications is membrane fouling, which can significantly increase the energy consumption of the process over long- term operations [19]. Figure (15) plots the variation in permeate flux (L/min.m^2) with operating time for solutions of (400 mgTiO$_2$/L) and (800 mgTiO$_2$/L), respectively. The reduction in permeate flow rate was attributed to the deposition of suspended TiO_2 particles on the external surface of membrane at its pore openings or within its pores. Straight lines are observed in Figure (15) is attributed to that time period between sampling are small.

CONCLUSIONS
Photocatalysis Degradation of Dye

1.It appears that the flow rate recirculation, irradiation time catalyst load, pH, H_2O_2 concentration, and concentration of dye mainly controls the rate of degradation for which optimum conditions for achieving maximum efficiency were established.

2.The capacity of TiO_2 towards dye degradation strongly depended on pH of suspension. At basic pH, degradation was smaller than that at acidic pH where degradation of anionic dye was fast indicating that the mechanism involving complete mineralization could be achievable.

3.The impact of the liquid flow rate on dye degradation shows a positively increasing trend to a point where all the surface of the photocataytic reactor was covered with a thin falling–film of synthetic wastewater, after then the dye degradation started to decrease with further increasing of liquid flow rate.

4.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 with the following rate law. The correlation coefficient (CF) was equal to 0.9892,

$$r = 0.0165\,C/(1 + 0.0209\,C)$$

Membrane separation system

1.   The neutralization process of the reactor effluents seems to be feasible for reduction catalyst loading in the inffluent line of the membrane system.
2.   The LPRO membrane system has proved to be an efficient solution for the separation of TiO_2 suspended particles.

Nomenclature
C: concentration of dye in solution (mg/L)
C_o : initial concentration of dye in solution (mg/L)
FTIR: Fourier-transfom infrared spectroscopy.
k_r : kinetic rate constant of surface reaction (mg/L. min)
K: adsorption equilibrium constant (L/mg)
LPRO: low pressure reverse osmosis.
r: reaction rate (mg/L.min)
r_o : initial reaction rate (mg/L. min)
R%: percentage of degradation (--)
R^2 : correlation coefficient (--)
T: irradiation time (min)
UV: ultra violet
Subscriprt
MV: methyl violet
o: initial
r : reaction
TiO_2 : Titanum dioxide

REFERENCES
[1] Mohammed AO: Evaluation and Testing of a Novel Photocatalytic Reactor with Model Water Pollutants. MSc Thesis. Robert Gordon University, Environmental Engineering Department, Aberdeen; 2007.
[2] Chatterjee D, Patnam VR, Sikdar A, Joshi P, Misra R, Rao NN: Kinetics of the Decoloration of Reactive Dyes Over Visible Light-Irradiated TiO_2 Semiconductor Photocatalyst. Journal of Hazardous Materials 2008, 156:435-441.
[3] Shahryari Z, Goharrizi AS, Azadi M: Experimental Study of Methylene blue Adsorption from Aqueous Solutions onto Carbon Nano Tubes. International Journal of Water Resources and Environmental Engineering 2010, 2:16-28.
[4] Sumandeep K: Light Induced Oxidative Degradation Studies of Organic Dyes and their Intermediates. Ph.D., Thesis, School of Chemistry & Biochemistry Thapar University 2007, Patiala- India.
[5] Barhon Z, Saffaj N, Albizane A, Azzi M, Mamouni R, El Haddad M: Effect of Modification of Zirconium Phosphate by Silver on Photodegradation of Methylene Blue. J.Mater.Environ.Sci. 2012, 3:879-884.
[6] Singh C, Chaudhary R, Gandhi K: Preliminary study on optimization of pH, oxidant and catalyst dose for high COD content: solar parabolic trough collector. Iranian Journal of Environmental Health Science & Engineering 2013, 10:13
[7] Malato S, Julian B, Alfonso V, Diego A, Manuel IM,Julia C, Wolfgange G: Applied Studies in Solar Photocatalytic Detoxification: An Overview. Solar Energy 2003 75:329-336.

[8] Koppol APR, Bagajewicz MJ, Dericks BJ, Savelski MJ: On Zero Water Discharge Solutions in the Process Industry. Advances in Environmental Research 2003, 8: 151-171.

[9] Akpan UG, Hammeed BH: Parameters Affecting the Photocatalytic Dgradation of Dyes Using TiO_2-based Photocatalysts: A review. Journal of Hazardous Materials 2009, 170:520-529..

[10] Guettaï N, Amar HA: Photocatalytic Oxidation of Methyl Orange in Presence of Titanium Dioxide in Aqueous Suspension. Part I: Parametric Study. Desalination 2005, Cited in Toshinori K, 2004.

[11] Konstantinou IK, Albanis TA: TiO_2-Assisted Photocatalytic Degradation of Azo Dyes in Aqueous Solution: Kinetic and Mechanistic Investigations-A review. Appl. Catal. B: Environ. 2004, 49: 1–14.

[12] Wang Y, Hong CS: Effect of Hydrogen Peroxide, Periodate and Persulfate on Photocatalysis of 2-chlorobiphenyl in Aqueous TiO_2 Suspensions. Water Res. Cited in Mohammed A O, 2007.

[13] Dixit A, Mungray AK, Chakraborty M: Photochemical Oxidation of Phenol and Chlorophenol by $UV/H_2O_2/TiO_2$ Process: A Kinetic Study. International Journal of Chemical Engineering and Applications 2010, 1:247-250.

[14] Bird RB, Stewart WE, Lightfoot EN: Transport Phenomena, 2nd edition, John Wiley & Sons, Inc. USA (2002).

[15] Kojima T, Gad-Allah TA, Kato S, Satokawa S: Photocatalytic Activity of Magnetically Separable $TiO_2/SiO_2/Fe_3O_4$ Composite for Dye Degradation. Journal of Chemical Engineering of Japan 2011, 44:662-667.

[16] Turchi CS, Ollis DF: Photocatalytic Degradation of Organic Water Contaminants: Mechanisms Involving Hydroxyl Radical Attack. J. Catalysis 1990, Cited in Qamar M, 2009.

[17] Emeline AV, Ryabchuk V, Serpone N: Factors Affecting the Efficiency of a Photocatalysed Process in Aqueous Metal-Oxide Dispersions, Prospect of distinguishing Between Two Kinetic Models. Journal of Photochemistry and Photobiology A: Chemistry 2000, 133:89-97.

[18] Wang KH, Hisieh YH, Wu CH, Chang CY:The pH and Anion Effects on the Heterogeneous Photocatalytic Degradation of o-Methylbenzoic Acid in TiO_2 Aqueous Suspension. Chemosphere 2000, 40:389–394.

[19] Kennedy MD, Kamanyi J, Heijman BCJ, Amy G: Colloidal Organic Matter Fouling of UF Membranes: Role of NOM Composition & size. Desalination 2008, 220:200-213.

Table (1) Range of operating variables in photocatalytic experiment

Operating parameter	Range
Catalyst loading (TiO$_2$) ,mg/L	200, 300, 400, 500, 800
Hydrogen peroxide concentration , mg/L	300, 400, 500, 800, 1000
Flow rate , L/min	0.3, 0.5, 1, 1.5
pH	5, 6, 7, 9, 10
Dye concentration , mg/L	10,20, 30, 40, 50

Table (2) Variation of turbidity against C$_{TiO2}$ before and after neutralization process

Exp. No.	C$_{TiO_2}$ (mg/L)	Turbidity input (NTU)	Residual Turbidity (NTU)
1	200	1710	285.133
2	300	3300	351.845
3	400	5320	416.405
4	500	5820	459.445
5	800	8690	663.885

Table (3) Effect of hyderogen peroxide concentration on photocatalytic degradation efficiency at (C_{MV}= 30 mg/L , C_{TiO_2}= 400 mg/L, pH =5, and liquid flow rate = 0.5 L/min).

$C_{H_2O_2}$ (mg/L)	C_{MV} input (mg/L)	C_{MV} output (mg/L)	Dye degradation %
300	30	0.054	99.82
400	30	0.015	99.95
500	30	0.15	99.5
800	30	3.564	88.12
1000	30	5.01	83.3

Table (4) Effect of catalyst concentration on photocatalytic degradation efficiency at (C_{MV}= 30 mg/L , $C_{H_2O_2}$= 500 mg/L, pH =5, and liquid flow rate = 0.5 L/min).

C_{TiO_2} (mg/L)	C_{MV} input (mg/L)	C_{MV} output (mg/L)	Dye degradation %
200	30	0.339	98.87
300	30	0.24	99.2
400	30	0.15	99.5
500	30	1.065	96.45
800	30	3.48	88.4
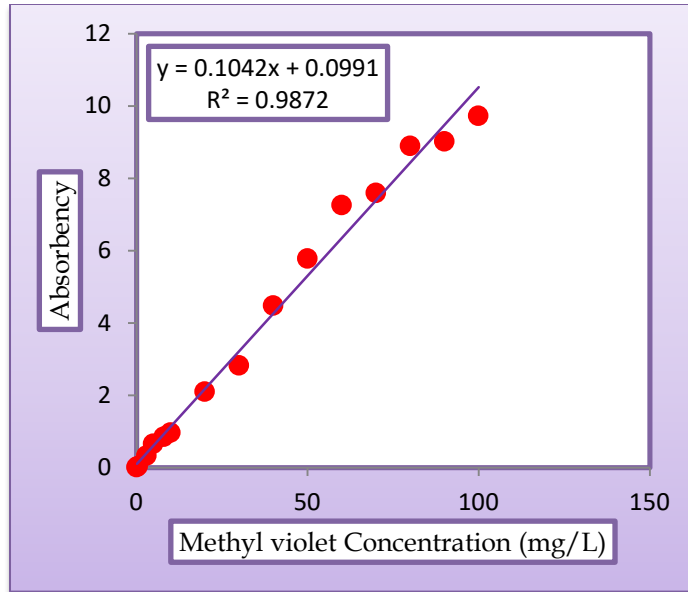
Figure (1) Calibration curve of methyl violet dye.
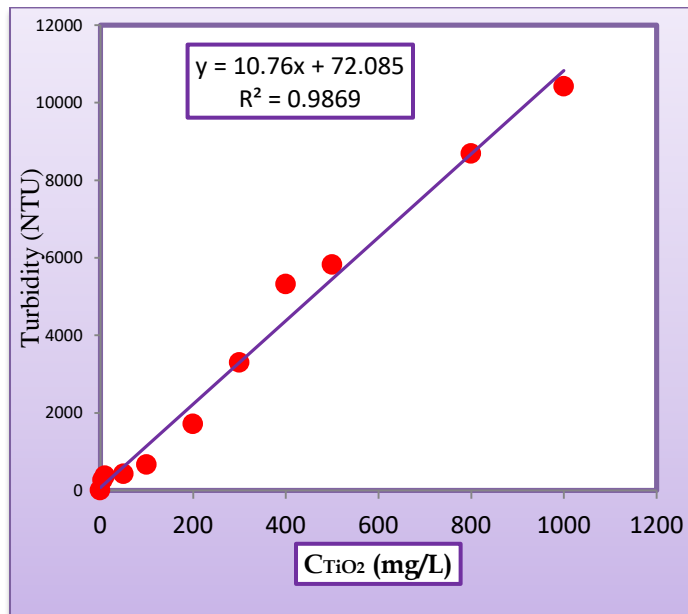
Figure (2) Calibration curve of Turbidity for various TiO$_2$ loadings in water.
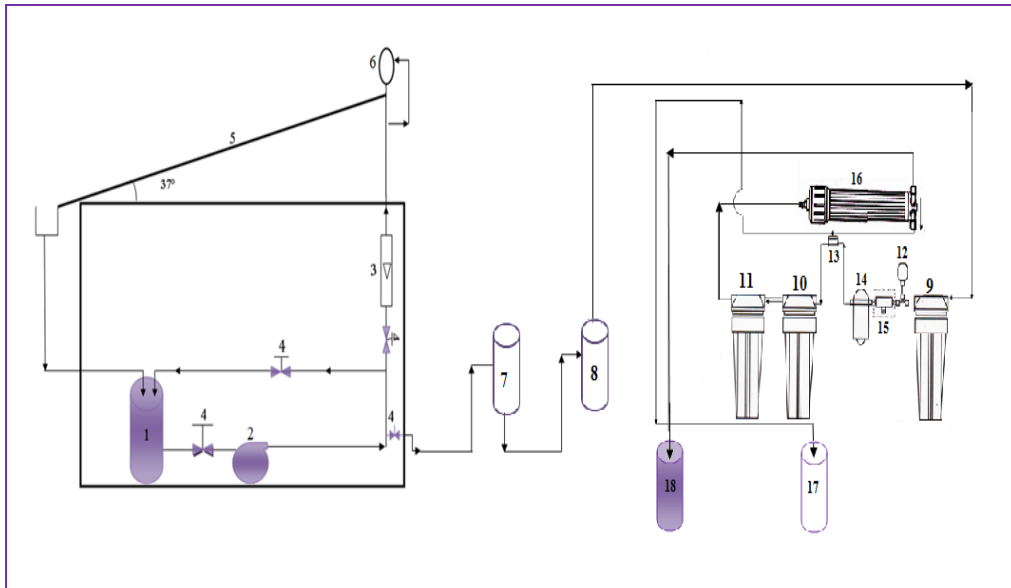
Figure (3): Experiment Setup (Feed tank to reactor; 2- Feeding pump; 3- Rotameter; 4- Valve; 5- Flate plate reactor; 6- Liquid distributo; r 7- Neutralization tank; 8- Feed tank to membrane; 9- 5micron PP filter; 10&11- Buffer vessels; 12- Low pressure switch 13- Auto shut off 14- Booster pump; 15- Inlet solenoid valve; 16- LPRO membrane; 17- Permeate tank; 18- Concentrate tank).
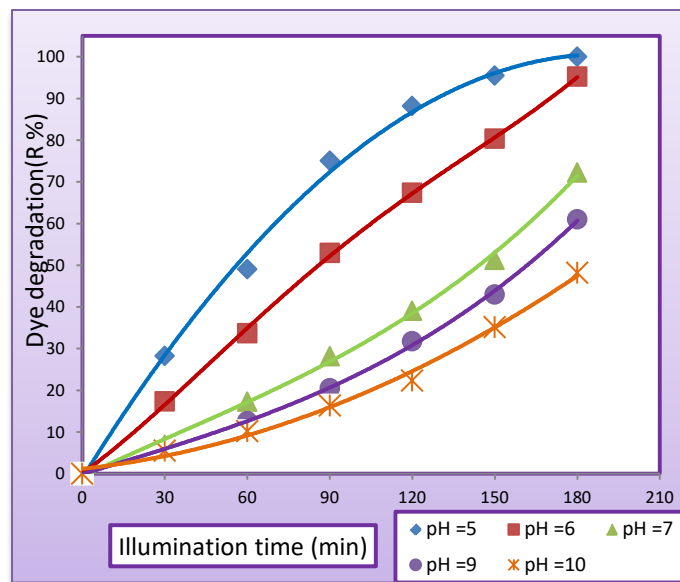
Figure (4) Variation of dye degradation against illuminated time at different pH (C_{MV}=30mg/L, C_{TiO2}=400mg/L, C_{H2O2} =400mg/L, and Q_L =0.5L/min).
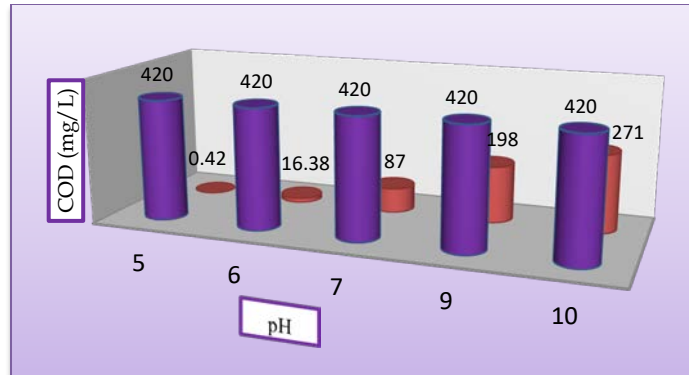
**Figure (5) Effect pH on COD removal (C_{MV}=30mg/L, C_{TiO2}=400mg/L, C_{H2O2}
=400mg/L, and Q_L =0.5L/min) after180 min.**
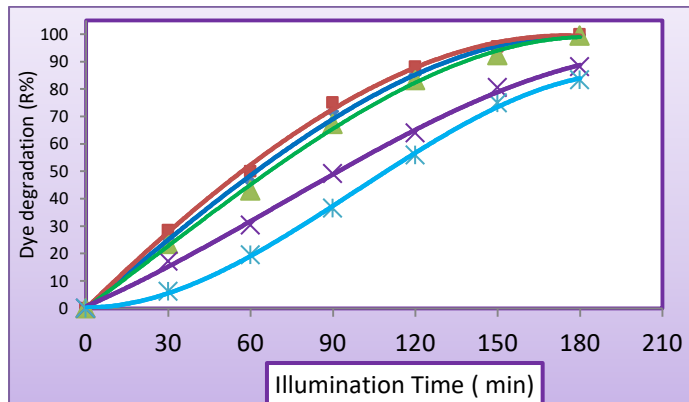
**Figure (6) Variation of dye degradation with illuminated time at different
concentration of H_2O_2 (C_{MV}=30mg/L, C_{TiO2}=400mg/L, pH=5, and Q_L =0.5L/min)**
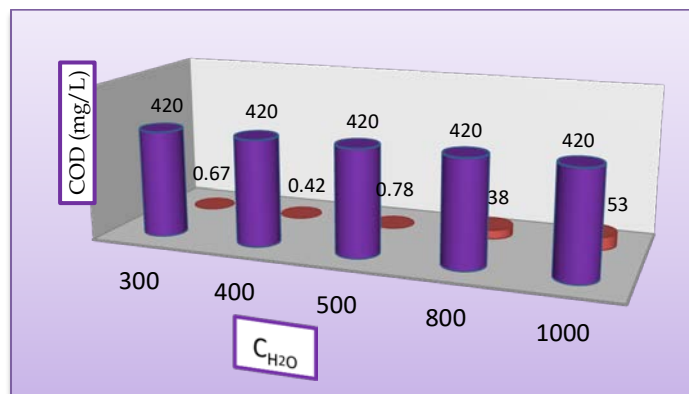
**Figure (7) Variation of COD removal in reactor effluent at different concentration
of H_2O_2 (C_{MV}=30mg/L, C_{TiO2}=400mg/L, pH=5, and Q_L =0.5L/min) after 180min.**
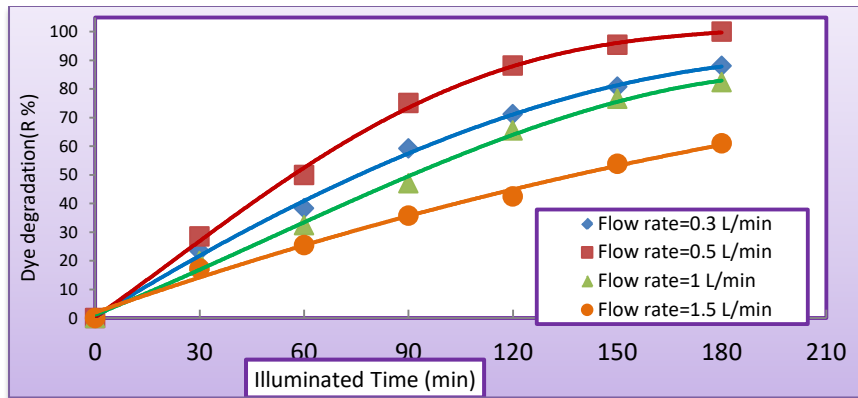
Figure (8) Variation of dye degradation with illuminated time at different liquid flow rate (C_{MV}=30mg/L, C_{TiO2}=400mg/L, pH=5, and C_{H2O2} =400mg/L)
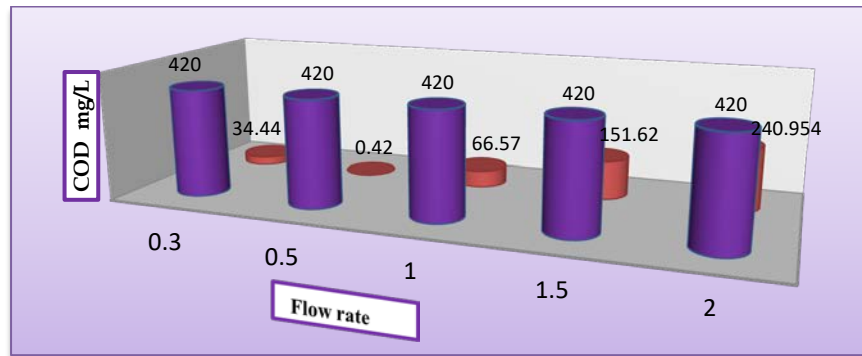
Figure (9) Effect of liquid flow rate on COD removal in reactor effluent (C_{MV}=30mg/L, C_{TiO2}=400mg/L, pH=5, and C_{H2O2} =400mg/L) after180 min
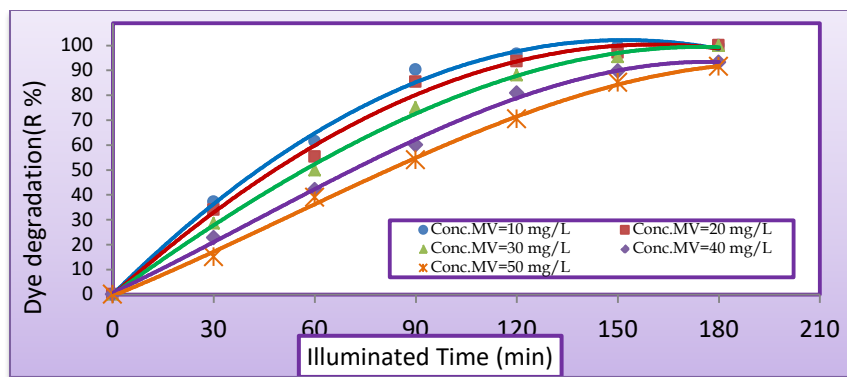
Figure (10) Variation of dye degradation with illuminated time at different concentrations of MV dye (C_{H2O2}=400mg/L, C_{TiO2}=400mg/L, and pH=5, Q_L=0.5L/min and pH=5).
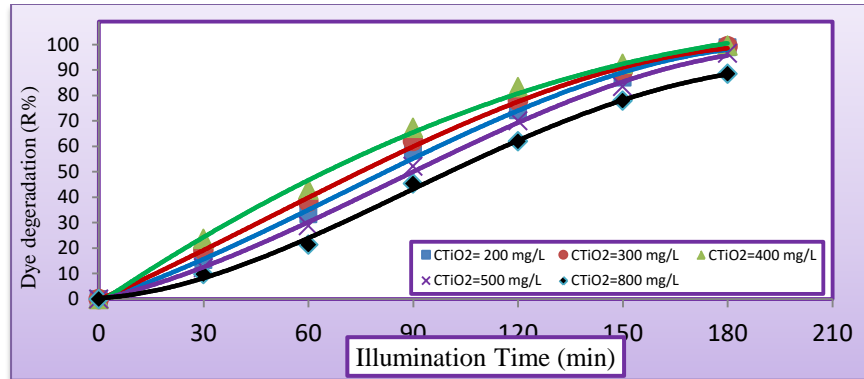
Figure (11) Variation of dye degradation against time at different concentration of TiO$_2$ (C$_{MV}$=30mg/L, C$_{H2O2}$=500mg/L, pH =5, and Q$_L$ =0.5L/min)
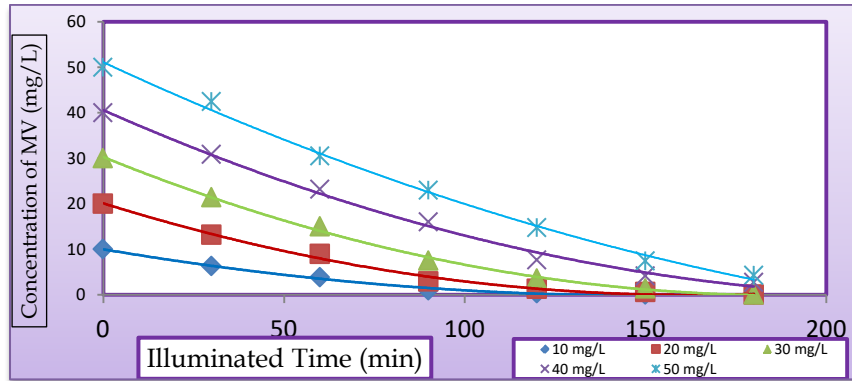

Figure (12) Effect of initial concentration of MV on the Photocatalytic degradation at optimum operating conditions.
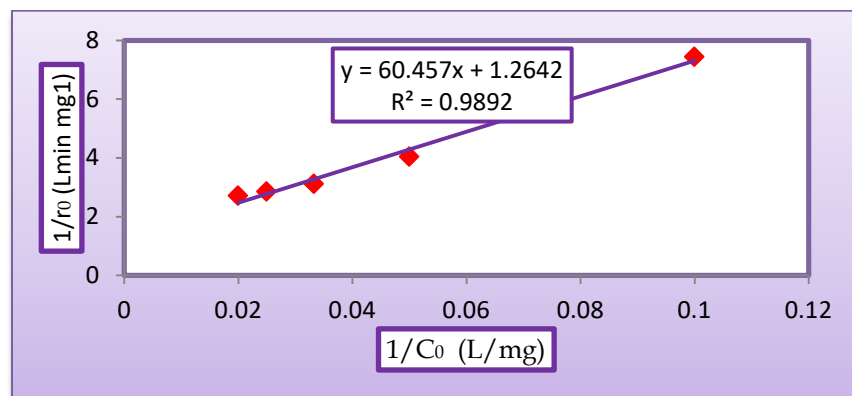

Figure (13) Linearization of Langmuir–Hinshelwood's equation of MV dye (C$_{TiO2}$=400mg/L, C$_{H2O2}$=500mg/L, pH =5, and Q$_L$ =0.5L/min).
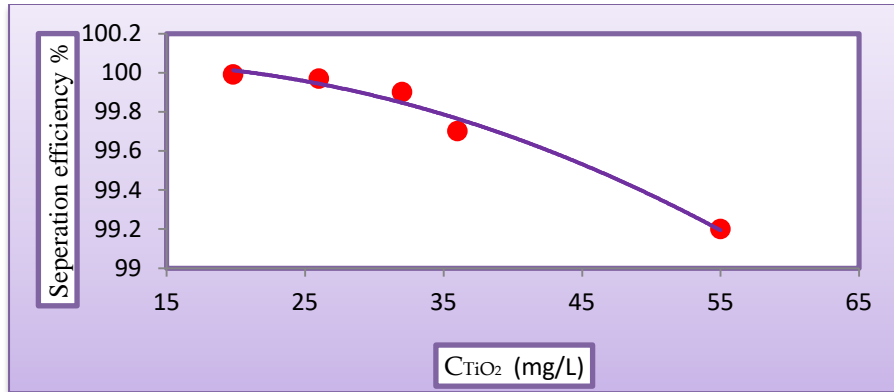
Figure (14) Variation of membrane separation efficiency against TiO$_2$ concentration in neutralized solution of the reactor effluent
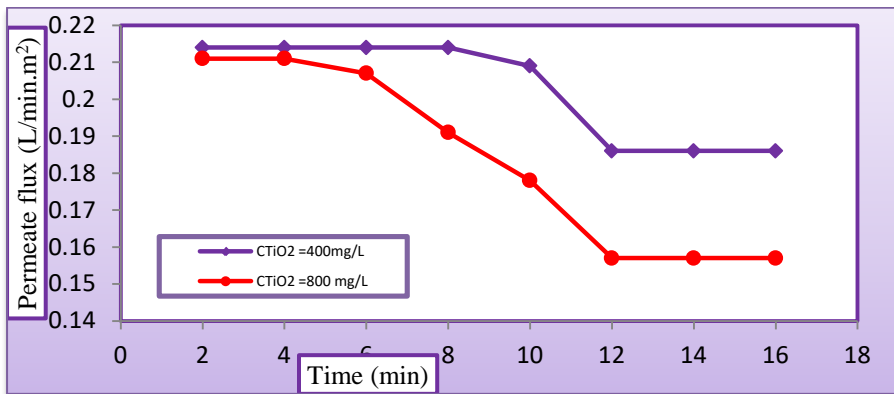

Figure (15) Variation of permeate flux of LPRO membrane against operating time at different catalyst loadings.