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Photocatalytic degradation of malachite green in aqueous solution using TiO₂ nanocatalyst

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Abstract

The main objective of this work was to study the degradation of the Malachite Green (MG) in aqueous solution by using titanium dioxide as a photocatalyst in a Multi-tube photoreactor. The effects of operating conditions such as initial substrate concentration, catalyst loading, pH value, inorganic salts and light intensity on the removal efficiency were evaluated. The apparent first-order rate constants (k_{ap}) were used to evaluate the degradation efficiency of MG. The optimum conditions were evaluated with initial concentration ranging from 5-50 mg/L, and TiO₂ dosing ranging from 0.05-1.0 g/L in the presence of three UV-C lamps. The optimum condition was found to be 0.1 g/L of TiO₂ and 10 mg/L of MG at pH=5. However, the presence of HCO_3^- anion leads to an increase in the effectiveness of the photocatalytic degradation. Results showed considerable reductions of MG concentration using UV/TiO₂ process. Finally, this process compared with UV/H₂O₂ process. The results of this work proof that photocatalysis is a promising technology to reduce dyestuff (MG) from aqueous solutions.

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Introduction

One of the major problems concerning textile wastewaters is dye effluent (Hammed *et al.*, 2006). Dyes are chemicals, which is binding with material and give color to the material. Dyes are ionic, aromatic organic compounds with structures including aryl rings which delocalized electron systems. The color of a dye is provided by the presence of chromosphere group. Most dyes are non-biodegradable in nature and the dye will be affected the photosynthetic activity in aquatic systems by reducing light penetration (Guibal *et al.*, 2002). Dyes also impede the solubility of gases in water as well as producing tri-halomethanes during chlorination. Due to their chemical structure, dyeare resistant to fading when exposed to light, water and many chemicals. It also damages the quality of the receiving streams and is toxic to food chain organisms (Padmesh *et al.*, 2006).

Malachite green dye (MG) is a cationic dye and widely used for the dyeing of leather, wool and silk, distilleries, jute, paper, as a food coloring agent, food additive. Discharge of MG into the hydrosphere can cause environmental degradation as it gives undesirable color to water and reduces sunlight penetration. It is also extensively used as a bactericide, fungicide and parasiticide in aquaculture industries worldwide. The most important physicochemical properties of MG are presented in Table 1. MG is highly toxic to mammalian cells and causes kidney tumors in mice and reproductive problems in rabbit and fish (Anbia *et al.*, 2011; Gupta *et al.*, 2004). Moreover, malachite green has detrimental effects on liver, gill, kidney, intestine and gonads of aquatic organisms (Srivastava *et al.*, 2004).When it was inhaled or ingested by human, it may cause irritation to the gastrointestinal tract and even cancer (Garg *et al.*, 2004). Contact of malachite green with skin causes irritation with redness and pain. Intermediate products after degradation of MG are also reported to be carcinogenic (Srivastava *et al.*, 2004).
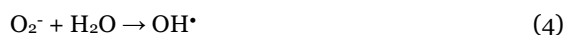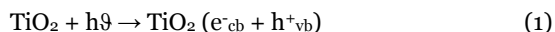
Table 1. Some physicochemical properties of Malachite Green (MG).

Properties	value
Common Synonyms	Aniline green; Basic green 4; Diamond green B;
Commercial name	Malachite Green
Molecular formula	$C_{23}H_{25}ClN_2$
Molecular Weight	364.92
Absorption maxima	617 nm
Solubility in water	$4 \times 10^{+4}$ mg/L
Log K_{ow}	0.62
Colour	Green crystals with metallic luster

Advanced Oxidation Processes (AOPs) has been developed and employed to treat dye contaminated wastewater effluents (Rauf *et al.*, 2009). Heterogeneous photocatalysis is an emerging technique for environmental remediation, where semiconductor materials are used as photocatalysts (Guo *et al.*, 2013; Zhang *et al.*, 2011). When organic pollutants are decomposed by heterogeneous catalytic reactions, the pollutant molecules are adsorbed on the surface of the catalysts, where chemical bonds are broken and formed, and eventually small organic molecules are released as decomposed products. The semiconductor TiO_2nanoparticle has been widely utilized as a photocatalyst for inducing a series of reductive and oxidative reactions on its surface. Titania appears to be the most promising and important one due to its stable physical and chemical characteristics, unique electronic properties, strong oxidizing power, non-toxicity and low price (Zeng *et al.*, 2013; Zhang *et al.*, 2011). Photocatalysis using TiO_2 degrade toxic organic compounds (Hoffmann *et al.*, 1995), reduce metal-ions (Litter *et al.*, 1999), improve the biodegradability in cellulose effluents (Yeber *et al.*, 1999) and decolorization a great variety of dyes in solution (Wang *et al.*, 2000).

When titania suspensions are irradiated, electrons and holes are produced by irradiating UV light on TiO_2 catalyst. By absorbing light, the electron present in the valence band of TiO_2 is energized and promoted to conduction band thereby creating an electron hole pair. This is known as photo excitation state of semiconductor. The generated electrons react with oxygen molecule to form superoxide radical

anions (O_2^-) and the holes react with the water molecule or hydroxyl ion (OH^-) to form hydroxyl radicals ($OH\cdot$). The hydroxyl radical is the second strongest known oxidant having an oxidation potential of 2.8 eV. It has an ability to oxidize the organic pollutant and yielding H_2O, CO_2 molecules. The reaction steps are shown below;

$$TiO_2 + h\vartheta \rightarrow TiO_2\ (e^-_{cb} + h^+_{vb}) \qquad (1)$$

$$TiO_2\ (e^-_{cb} + h^+_{vb}) + H_2O\ (ads) \rightarrow TiO_2 + OH^- + H^+ \quad (2)$$

$$e^-_{cb} + O_2(ads) \rightarrow O_2^- \qquad (3)$$

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

$$h^+_{vb} + OH^- \rightarrow OH^\bullet \qquad (5)$$

$$OH^\bullet + Organics \rightarrow H_2O, CO_2, etc \qquad (6)$$

Nonetheless, Liu *et al.*, (2013) studied the influence of native defects on the adsorption and photocatalytic degradation of anionic and cationic dyes for different ZnO nanoparticles. It was found that there was no relationship between the dye adsorption onto ZnO nanoparticles and their photocatalytic activity. While the absorption of cationic dyes was not significantly affected by ZnO nanoparticle properties, dye adsorption of several anionic dyes was strongly affected by native defects in ZnO.

Saha *et al.*, (2001) used commercial TiO_2 impregnated with silver nanoparticles with a simple liquid impregnation method followed by heat treatment. The UV induced photodegradation of malachite green in aqueous medium using these modified TiO_2 catalysts was studied to evaluate the effect of silver impregnation. It was observed that the presence of silver in TiO_2 enhances the photon induce dmineralization of malachite green but reduces its decolorization efficiency.

Oturan *et al.*, (2008) an elegant indirect electrochemical study by electro-Fenton method on MG mineralization has been reported for oxidation pathways of malachite green by Fe^{3+} catalyzed electro-Fenton process. Despite this, No work has been reportedin the literature on the removal of Malachite Green from aqueoussolutions using TiO_2 nanocatalyst.

In this work, a representative MG was used as a model; photocatalytic degradation was investigated in the TiO_2/UV system. The effect of initial concentration, amount of photocatalyst, initial pH value, and inorganic salts on the photodegradation of MG was evaluated and kinetics analysis was conducted.

Materials and methods
Materials
Dye, Malachite green (MG, 99.5% purity) also called 4-[(4-dimethylaminophenyl)   phenyl-methyl]-*N,N*-dimethylaniline was purchased from Sigma-Aldrich. Its formula is shown in Fig. 1. Titanium dioxide P-25 (Degussa) was used as a catalyst. This product contains 80% anatase and 20% rutile, and has a specific surface area of 50 $m^2\ g^{-1}$ and a particle size of 21 nm. Other chemicals were purchased from Merck (Darmstadt, Germany) with a purity of >99% and deionized laboratory water was used for making aqueous mixtures. Initial pH of the solution was adjusted by using 0.1N NaOH and 0.1N HCL. Other chemicals like Na_2SO_4, NaCl, $NaNO_3$, Na_2CO_3 and $NaHCO_3$ were purchased from Merck.
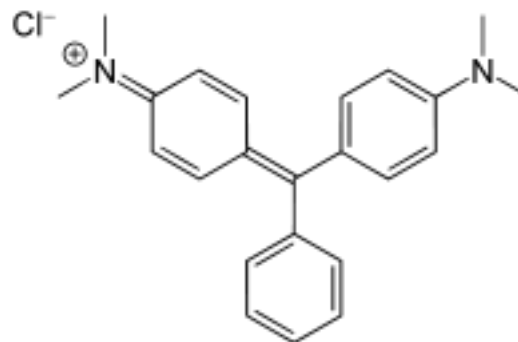

Fig. 1. Molecular structure of MG.

Photocatalytic degradation experiment
Irradiation experiments were carried out in stainless steel batch cylindrical photoreactor (9 cm ID×25 cm H). The reactor was equipped with three UV-C (F6T5/GL 6W, low pressure Hg lamp close to monochromatic output at 254 nm, Philips, Poland) lamps, and UVA (Black Light Blue, Haichao F6T5 6W at 365 nm, China),The UV light sources were

surrounded by a Quartz glass tube to preventing direct contact with solution(Fig. 2). Suspensions of the photocatalyst and aqueous contaminant solutions were kept aerated and stirred by a steady stream of air in the dark (for the adsorption–desorption equilibrium of the MG on the TiO₂ surfaces) and exposed to UV light. The conditions of 0.1 g/L photocatalyst, 10 ppm MG, were used throughout the course of the investigation.
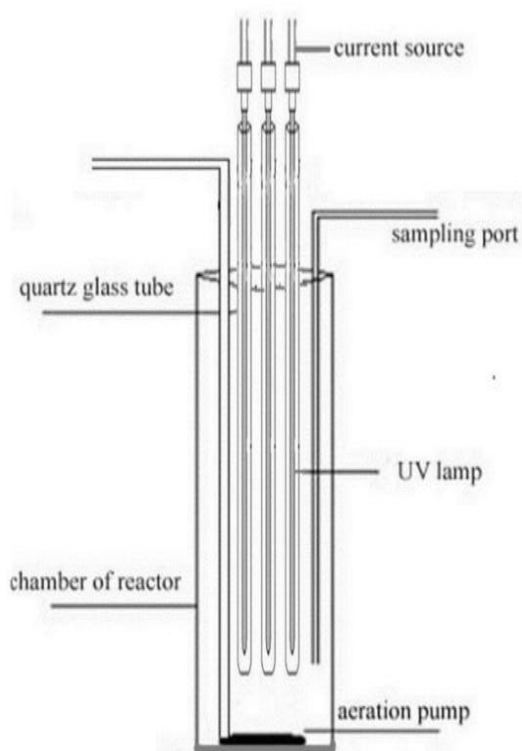

Fig. 2. Schematic diagram of slurry cylindrical batch reactor.

Analysis

The photocatalytic experiments were conducted to investigate the photodegradation of the MG in aqueous suspension system. After the UV light irradiation for a certain time interval, each sample was centrifuged at 4,000 rpm for 20 min in B3.11 (Jouan), to separate the suspensions of the TiO₂ nanoparticles. The residual MG concentration in the solution was analyzed by a UV-Vis Spectrophotometer (JENWAY 6305 UV/Vis model) at 617 nm. A 5 mL aliquot was collected after 0, 5, 15, 30, 60, 90 and 120 min of reaction time.

Results and discussion

Kinetics of Malachite Green disappearance

Aqueous solution of MG in the presence or absence of TiO₂ was irradiated by three UV-lamps. The role of photocatalytic degradation and the effect of direct photolysis on the decomposition of MG were studied. In Fig. 3, the removal efficiency of MG is plotted as a function of reaction time. A control experiment was performed by an identical aqueous solution without catalyst. Pseudo-first-order reaction has been widely and successfully used for the description of photocatalytic degradation of organic pollutants. The removal rates of MG in UV/TiO₂ process is therefore expressed as:

$$-Ln\frac{C}{C_0} = K_{ap}t \qquad (7)$$

Where, C_0 is the initial concentration of MG, C the concentration at time t and K_{ap} (min⁻¹) is the pseudo-first-order photocatalytic removal rate constant.
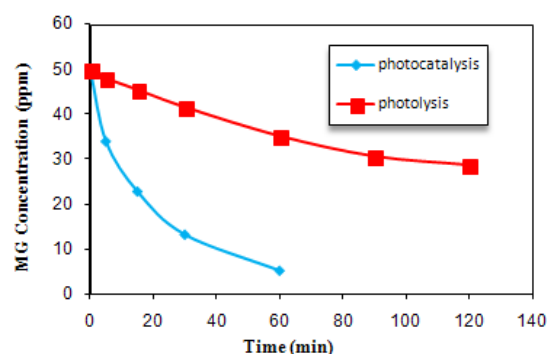

Fig. 3. Variation of MG concentrations versus irradiation time without and with the photocatalysis.

Effect of the amount of TiO₂ on photodegradation of MG

To evaluate the photocatalytic activity of TiO₂ catalysts, a set of MG photocatalytic degradation tests was carried out in an aqueous suspension with an initial concentration of 10 ppm. The effect of catalyst loading on degradation of MG was investigated using TiO₂ (0.05 to 1.0 g/l). Fig. 4 shows that the MG photodegradation decreased when the amount of catalyst in the reactor increased up 0.1 g/l. It should be pointed out that, the catalyst loading affect the

number of active sites on photocatalyst and the penetration of UV light through the suspension. As the catalyst loading increases, the number of active sites increases but the penetration of UV light decreases due to shielding effect (Kartal *et al.*, 2001).
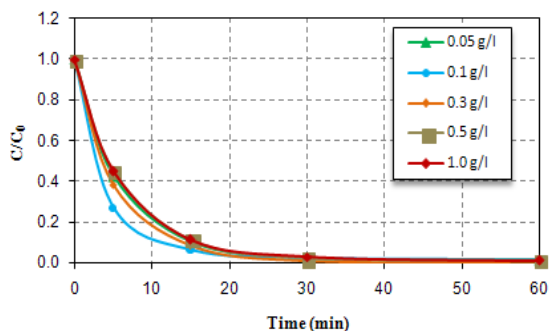

Fig. 4. Effect of TiO_2 loading on the photocatalytic degradation of MG (T = 25 °C, $[MG]_o$=10mg/L).

It should also be noted that the optimum value of catalyst loading will strongly be dependent on the type, initial concentration of the pollutant and the operating conditions of the photoreactor (Gogate *et al.*, 2004). A similar phenomenon has also been reported, for example the optimum value of catalyst loading has been reported to be 0.5g/l TiO_2 for photocatalytic removal of Phenol Red (Sagharigar *et al.*, 2014).for azo dyes acid red 18 and Reactive Orange 4, optimum value of TiO_2 is 4 g/L for photocatalytic degradation (Sobana *et al.*, 2007).

Generally, in any given photocatalytic application, the optimum catalyst concentration must be determined, in order to avoid the excess catalyst and ensure the total absorption of the efficient photons (Krysa *et al.*, 2004). This is because the scattering of an unfavorable light and reduction of lightpenetration into the solution is observed with excess photocatalyst loading (Saquib *et al.*, 2003). So the optimum catalyst loading is 0.1g/l.

Effect of initial MG concentration
Fig. 5 shows the effect of the initial MG concentration on the photocatalytic degradation efficiency. The initial MG concentration in this study was 5, 10, 20

and 50ppm. MG degradation efficiency decreased as initial MG concentration increased. A possible reason is that the generation of hydroxyl a radical on the catalyst surface is reduced when the initial MG concentration is increased (Daneshvar *et al.*, 2005). More MG molecules are adsorbed on the surface of TiO_2 photocatalyst will make fewer active sites available for the hydroxyl radicals' adsorption. Hence, large amounts of adsorbed MG would have an inhibitory influence on the reaction between MG molecules and hydroxyl radicals due to the lack of any direct contact between them. Once the MG concentration is increased, most of UV light is absorbed by the MG molecules. Abdul Rahman *et al.*,(2010),indicate similar results, and photons do not reach the surface of photocatalyst to activate it to generate hydroxyl radicals. As presented in Fig.5, it is concluded that 10 ppm is the optimum concentration for efficient degradation of MG.
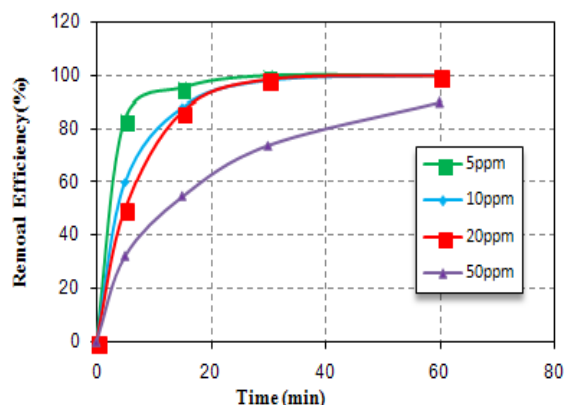

Fig. 5. The effect of initial MG concentration on the photodegradation rate (T = 25 °C, and C_{cat}= 0.1 g L^{-1}).

Effect of pH
Many of the literature revealed that pH played an important role in photo catalytic degradation process. The effect of pH values (3-5-7) on photodegradation of MG using initial concentration of 10 ppm and optimum value of catalyst loading (0.1 g/l) (was obtained in preliminary experiments) is illustrated in Fig. 6. The highest degradation efficiency occurred at pH 5 in a UV/TiO_2 system (Table 2).

Table 2. Effect of pH on the photodegradation rate of MG.

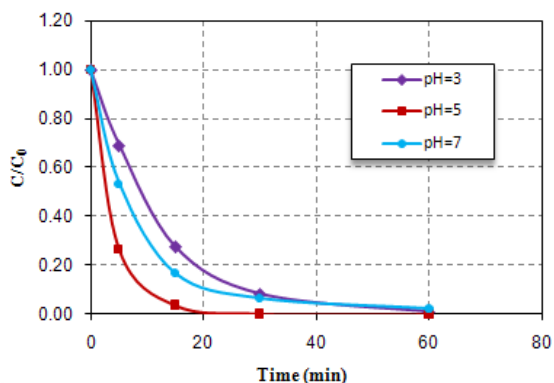| pH	k(min⁻¹)	R²
3	0.075	0.995
5	0.221	0.998
7	0.062	0.930

Fig. 6. Effect of pH on the photocatalytic degradation of MG; (T = 25°C, Under UV-C light [MG]$_o$=10mg/L,and C$_{cat}$= 0.1 g L⁻¹).

After a certain pH value i.e. above pH>7 the rate of photo bleaching of MG decreases due to columbic repulsion between the negatively charged surface of photocatalyst and hydroxide anions. This fact could prevent the formation of hydroxyl radicals.

Under acidic conditions (pH<5), the phenomenon of electron-hole pairs recombination prevents the formation of a large number of hydroxyl radicals, the latter being essentially formed from the holes of the semiconductor band valence (Fernandez *et al.*, 2000). Furthermore, it is worthy to note that, under acidic conditions, TiO₂ particles may tend to agglomerate, and the surface area available for adsorption of contaminants and photon would be reduced what eventually affects the MG degradation rate.This could explain the low percentage of degradation of MG in this pH.

Effect of inorganic salts

The importance of anions effect on the photodegradation of pollutants has been remarkably recognized due to the occurrence of the competitive adsorption, resulting in the inhibitive effect on the photoreaction of organic pollutants. Evolution of the inorganic ions (SO_4^{2-}, Cl^-, CO_3^{2-},NO_3^- and HCO_3^-) as a function of irradiation time from 0 to 60 min is shown in Fig. 7.

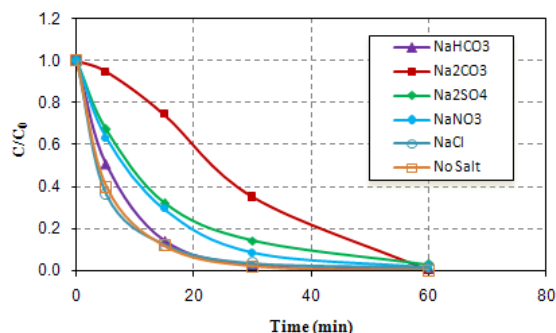**Fig. 7.** Effect of inorganic anions additions on the photocatalytic degradation of MG; (T = 25 °C, [MG]$_o$=10mg/L, and C$_{cat}$= 0.1 g L⁻¹).

These anions can also compete with the target pollutant for the active sites. The adsorption of these anions to catalyst surface reduces ·OH formation. Although hydroxyl radical scavenging by the anions resulted in corresponding anion radicals. Consequently all these reactions can influence the overall rate of photocatalytic oxidation (Giri *et al.*, 2010).

All the experiments were carried out using 0.5mM solutions of the anions with initial MG concentration of 10 ppm and 0.1 g/l catalyst loading. The effect of presence of these anions on photocatalytic degradation of MG showed the following trend:
CO_3^{2-}<NO_3^-< SO_4^{2-}<Cl^-< HCO_3^-

The pseudo-first-order reaction rate constants obtained for the photocatalytic degradation of MG in the presence of various anions are presented in Table 3.

Table 3. Pseudo-first order rate constant for the degradation of MG.

Anion	k(min⁻¹)	R²
No anion	0.125	0.993
NO_3^-	0.081	0.999
SO_4^{2-}	0.064	0.992
Cl^-	0.106	0.970
CO_3^{2-}	0.035	0.948
HCO_3^-	0.120	0.998

Effect of different light sources

The rate of initiation for photocatalysis electron-hole formation in the photochemical reaction is strongly dependent on the light intensity (Cassano *et al.*, 2000). Malachite Green has a characteristic absorption band at 617 nm; however, the rate of photodegradation is followed using the decay of this band. The degradation of MG was carried out under their radiation of light from two different sources, UV-C light and UV-A lamp which emits light around 254, 365nm respectively. It has been reported that the photodegradation rate increases as increasing the light intensity during photocatalytic degradation reaction (Ascari *et al.*, 2003; Wang *et al.*, 2006). Our results clearly indicate that UV-C irradiation causes higher rate of degradation for MG than with UV-A light, due to high intensity of light which is suitable for the excitation of many electrons from the valence band of the metal oxide semiconductor as illustrated in Fig. 8 and Table 4. Consequently the dependency of pollutant degradation rate on the light intensity has been studied in numerous investigations for various organic pollutants (Savitri *et al.*, 2008).

Table 4. Effect of different light sources on the photodegradation efficiency of MG.

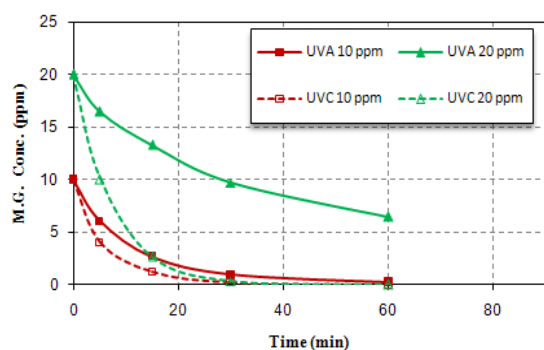| Parameters	k (min^{-1})	R^2
UVC lamps 10ppm	0.103	0.985
UVClamp 20ppm	0.101	0.967
Black LightBlue(UVA) lamps 10ppm	0.061	0.980
Black Light Blue(UVA) lamps 20ppm	0.018	0.974

Fig. 8. The effect of light sources on the photocatalytic degradation of MG (T = 25 °C, [MG]$_o$=10mg/L, and C_{cat}= 0.1 g L^{-1}).

Effect of the initial H$_2$O$_2$ concentration

UV irradiation of MG dye at optimum conditions (dye concentration= 10 mg/L and catalyst dose = 0.1 g/L) was carried out for 60 minutes using different concentrations (0.1-0.5-1.0 mM) of H$_2$O$_2$. The maximum removal was obtained at 1.0mM ofH$_2$O$_2$ concentration. The results are shown in Fig. 9 and Table 5. As it can be seen, the removal efficiency increases with increasing H$_2$O$_2$ concentration. The occurrence can be explained by the two opposing effects. With increasing H$_2$O$_2$ concentration: (1) More hydroxyl radicals are available to attack aromatic rings and the rate of the removal increases. (2) Above 1.0 mM hydroxyl radical efficiently reacts with H$_2$O$_2$ and produces HO$_2$· Similar result was observed about acid brown dye (Aravindhan *et al.*, 2006) and Acide orange 7 (Behnajady *et al.*, 2004) their concentration slightly decreased more than optimum value because highly reactive hydroxyl radicals reacted with excess amount of H$_2$O$_2$ and produced hydroperoxyl radicals (HO$_2$·), which were less reactive and ultimately inhibited the degradation. The reaction

Table 5. Effect of initial concentration of hydrogen peroxide on the photodegradation efficiency of MG.

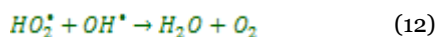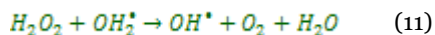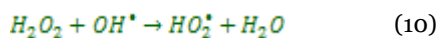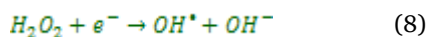| [H$_2$O$_2$](mM)	k(min^{-1})	R^2
0.1	0.054	0.915
0.5	0.071	0.860
1.0	0.145	0.954
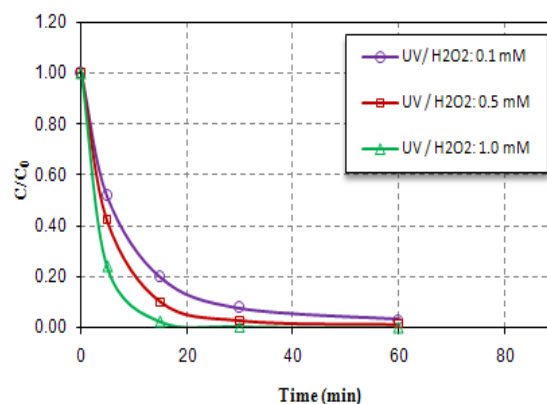
Fig. 9. Effect of initial concentration of hydrogen peroxide in oxidative decolorization of MG. [MG]$_o$=10mg/L,C_{cat}= 0.1 g L^{-1}and [H$_2$O$_2$=0.5mM].

mechanism is explained below:

$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^- \qquad (8)$$

$$OH^- + h^+ \rightarrow OH^\bullet \qquad (9)$$

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O \qquad (10)$$

$$H_2O_2 + OH_2^\bullet \rightarrow OH^\bullet + O_2 + H_2O \qquad (11)$$

$$HO_2^\bullet + OH^\bullet \rightarrow H_2O + O_2 \qquad (12)$$

Conclusions

In this study, we investigated the degradation of Malachite Green as the model pollutant of water by TiO_2 dispersion under irradiation with UV light. Treatment of dyes has been carried out by varying the parameters like MG initial concentration, catalyst loading, pH, inorganic salt and light intensity. The degradation process follows pseudo first-order degradation behavior. Experimental results indicate that the decolorization of dye is effective in the presence of catalyst. Increasing TiO_2 concentration beyond 0.1 g/L showed a reduction on the photodegradation of MG due to light shielding effect. The removal efficiency and the constant rate of degradation decreased with increasing initial concentration of MG. The optimum range of MG concentration was 10ppm. The color removal of MG is very effective by maintaining pH at 5. The inhibition effect of anions on degradation of MG was related to CO_3^{2-}. The order of degradation rate using different light sources was shown to be UV-C > UV-A. Experimental results indicate that the decolorisation of dye is effective in the presence of catalyst.

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