



Titanium dioxide as a Catalyst for Photodegradation of Various Concentrations of Methyl Orange and Methyl Red dyes using Hg Vapour Lamp with Constant pH

A. KISTAN^{1,2*}, V. KANCHANA³, L. SAKAYASHEELA², J. SUMATHI²,
A.PREMKUMAR², A.SELVAM² and THAMINUM ANSARI A⁴

¹Research and Development Centre, Bharathiar University at Coimbatore, India.

²Panimalar Institute of Technology, Chennai-123, India.

³Sree Sastha Institute of Engineering & Technology, Chennai, India.

⁴P.G. Research Department Muthurangam Government Arts College, Vellore, India.

*Corresponding author E-mail: vishmikrish@gmail.com

<http://dx.doi.org/10.13005/ojc/340250>


(Received: January 01, 2017; Accepted: February 10, 2018)

ABSTRACT

The photo-catalytic activity of TiO₂ catalyst is very much useful to removal of color from dye industry effluent from tanneries, textile industry, and Ink factory. The Novelty of this study, we have found on a very simple method to compare the photocatalytic activity of titanium dioxide for the different concentration of two different Organic dyes (Methyl Orange and Methyl Red) which were not compared in the past studies. This method can be carried out in a normal chemical laboratory. and easy way with limited use of chemicals and simple lab equipment's. Dye solutions having pigments with high photocatalytic activity lose their color within several minutes of UV-Visible radiation exposure (optical windows 160W (Hg lamp medium pressure)) whereas, dye solutions having UV-stable TiO₂ would not degrade within several hours of radiation exposure. For both dyes the color started fading quickly when the light radiation was passed continuously for a long time (15 to 120 minutes).It was also found that concentration of both dyes decreased, with time or the degradation increased. The effect of varying the dye concentration increases with degradation rate decreases. The rate constant value undergoes a marginal decreases at pH = 4.2 when the Methyl Orange dye concentration was increased. The degradation measurements were carried out using Shimadzu UV-Visible 1601 spectrometer in the photon energy range of wave length 200 to 700 nm aid of glass cell (made of Quartz) with 10mm optical path length.

Keywords: Organic dyes, Hg lamp, pH, Methyl Orange (MO), Methyl Red (MR), Degradation.



This is an  Open Access article licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License (<https://creativecommons.org/licenses/by-nc-sa/4.0/>), which permits unrestricted NonCommercial use, distribution and reproduction in any medium, provided the original work is properly cited.

INTRODUCTION

Water pollution by tanneries, Textile and dye industries

More than thirty thousand trading dyes founded. According to more than eighty thousands various chemical structures are utilized in industries such as textile, tanneries, food pharmaceutical, paper and ink industries and used dyes are normally discharged in waste water³. The effluent containing these dyes are normally removed by physical, oxidative or common method called as sludge process. Above mentioned process has a various draw backs and its produce secondary pollution due to utilizations of chemicals and its accumulated in species creates bio-resistant in the environment. Both textile and tanneries are very highest (more 50%) user of dyes. Utilizing dyes in wide range of supporting reagents for different coloring skins, dyeing, cleaning leathers, printing and finishing procedure. Mill effluents, Fiber class or irrespective of dyes are extremely colored by unabsorbed dyes were varied due to the dye-fiber system.

In textile industry Azo-dyes are normally used and create the various environmental issues. In general waste water produced from various industrials includes tanneries, food and pharmaceuticals, and ink industries are utilizing dyes for various purposes, which requires proper treatments afore it is released to the surrounding. In addition, effluent streams released from tanneries and textile industry consists of toxic or carcinogenic substances along with their by-products. Recently, treatments are more concentrated not only to elucidate the environment impact but also suggest that dyes can be reused.

Treatment of polluted water

From the environmental perspective, the elimination of synthetic dyes is one of the great concerns, because degradation of dye and dye by-products are also may be carcinogenic so treatment cannot fully depends upon the biodegradation alone. Henceforth, decolonization of dye house effluent by elimination of dyes has become a very essential need in waste water treatments, tanneries and textile industry². The environment concerns about use of dye in effluent ongoing problem for dye stuff productions, dyers and water industries.

The problem of color in waste water is common in many Tanneries and dyes houses. Hence, significant increase in standards of stringent color is enforced by common bodies to decrease the amount of effluent and water courses. Many methods are employed to treat waste water containing organic dyes and pigment such as adsorption, sedimentation, flocculation, floatation, reverse osmosis, fractionation etc., but the treatment of dye containing waste water containing dye by the above conventional methods has various limitation due to the significant increase in the refractory materials originated in waste water effluents, complications in the elimination of color and expensiveness. Elimination of organic non-biodegradable chemicals is an essential ecological problem. Dyes are main class of synthetic organic compounds utilized in the textile industry as well as its also common industrial pollutants, due to modern dyes stability, management of biological treatments techniques for industrial waste water are ineffective resulting often in an intensively colored release from the treatment facilities⁵⁻⁸. The above problems could be overcome by the 'photocatalytic method' which is widely employed in complete degradation process. The direct photocatalytic reaction by using semiconductor powders has been shown to effectively degrade many kinds of pollutants.

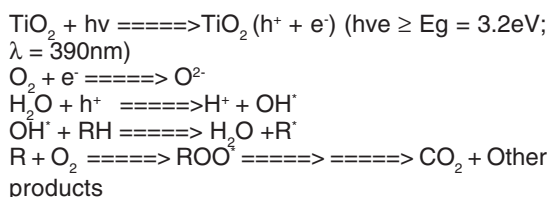
Photodegradation

Photodegradation is degradation of molecules caused by the absorption of UV-Visible radiation i.e., the dissociation of molecules into smaller pieces. There are also irreversible structural changes such as the denaturing of proteins, and the addition of other atoms or molecules. A common Photodegradation reaction is photo-oxidation¹⁰. This type of Photodegradation is used by some drinking water facilities to destroy pollutants. Photodegradation in the environment is part of the process by which ambergris evolves from its fatty precursor. Photosensitized degradation of colored contamination in waste water on semiconductor surface is of current importance¹⁰⁻¹⁴. Although semiconducting TiO₂ in presence of UV radiation has become the bench mark photo-catalyst for degradation of myriad or a water bound¹⁵⁻¹⁸ pollutants as documental in the literature, the vital drawback of TiO₂ semiconductor is that it absorbs a small portion of solar spectrum in the UV region

(band gap energy of TiO_2 is 3.0 to 3.2eV). hence the photo-catalytic process has the disadvantage that it cannot harvests maximum solar energy by utilizing visible light. A large number of dyes stuff material so with intense color and toxicity introduced into the aquatic systems, are resistant to degradation. More recently the degradation of colored ones in environmental protection studies has gained importance. Azo dyes are typical class of organic pigments and they are represented as toxic compounds. Method of decolorizing dye effluents has been gaining attention. An inherent advantage of heterogeneous or homogenous photo catalysis emerges when solar irradiation is used as a photon source¹⁹.

Titanium dioxide as photocatalyst

TiO_2 semiconductor is a very good Photocatalyst for the elimination of pollutants from air and water due to its low cost, chemical stability, no toxicity, high photocatalytic reactivity and insolubility. A further important advantage is the fact that the process can be powered by solar energy^{20, 21}, thus reducing significantly the electrical power requirements and operational costs. It should be noted that with visible light, the Photodegradation processes by different routes, involving for example electron transfer from the excited state of the dye molecules adsorbed on the TiO_2 surface into the conduction band of TiO_2 are possible but such process are less efficient than those occurring with UV light⁴. For the photocatalytic oxidation (TiO_2/UV), the semiconductor absorbs UV light and hydroxide Radicals are generated mainly from the absorbed water and hydroxide ions. The mechanism of the TiO_2/UV degradation has been described using the band-gap model²². It is well established that by irradiation of an aqueous TiO_2 suspension with light energy greater than the band gap energy of the semiconductor, conduction band electrons and valence band holes are generated²³. These will act as strong oxidizing agents that can easily attack any organic molecules and adsorbed on, or located close to the surface catalyst, thus leading to their complete degradation into small inorganic species.



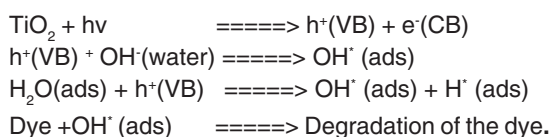
Earlier work of photodegradation

The photo-assisted degradation of erythrosine and Rhodamine B has been investigated in an aqueous TiO_2 dispersion under irradiation by visible light²⁴. Wang investigated²⁵ the photocatalytic degradation of eight commercial dyes including MO using TiO_2 suspension under solar light. The possibility of using solar irradiation for detoxification of MO as a model compound was also explored by other workers²⁶. Wang²⁷ prepared and investigated the photocatalytic activity of $\text{ZnO}/\text{TiO}_2/\text{SnO}_2$ mixture for decolonization of MO under UV light and found that this mixture was photocatalytically more active than TiO_2 and SnO_2 but slightly less active ZnO ²⁸⁻³⁰. In recent years, the Photo catalyzed oxidation kinetics of acid blue-40 at different pH Values by TiO_2/UV were studied³². It is found that pH =3, photocatalytic Oxidation kinetics of Acid blue40 follows the Longmuir Hinshelwood Model with reaction rate constant (k) of 0.0074m/min. It is found that ferrous ion does not have significant influence on the reaction while H_2O_2 could retard the reaction when its concentration is higher than 0.01nm. Photodegradation of series of dyes (Rhodamine B, Orange II, Alizarin red and Eosin) in the presence of TiO_2 particles under visible light irradiation led to formation of H_2O_2 . H_2O_2 was detected because its formation rate was greater than decomposition rate³³. Photocatalytic decolorization and degradation of an Azo dye Reactive orange4 with TiO_2 / P-25(Degussa) as Photocatalyst is examined. The effect of various parameters such as catalyst loading, pH and initial concentration of the dye has been examined³⁵.

The degradation was strongly enhanced in the presence of electron acceptors such as H_2O_2 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and KBrO_3 ³⁵. The photocatalytic decolorization of reactive Blue19 (RB-19)³⁴⁻³⁸. In aqueous solutions containing TiO_2 or ZnO as catalyst and concluded that ZnO is more efficient catalyst that TiO_2 in the color removal of RB of RB-19³⁹. The degradation rates were compared with disappearance and elimination rates. In this photo catalytically Degradation of Azo dye, the disappearance proceeds through both Oxidation and reduction⁴¹. Photo catalytically degradation of Methylene blue a cationic dye and procion red, an anionic dye has been examined under TiO_2 pH dependent because of its amphoteric nature. It has been found that

pH -9.5 and pH -3.5 are suitable for Methylene blue and procion red respectively⁴². The degradation of biological dyes such as Methylene blue and Malachite green 7 was carried out with Nano TiO₂ which have a particle size of 16-17nm. The absorption peak of Methylene blue decreases Photocatalyst time⁴³.

Desensitization, a method according for degradation of colorants in actinic radiation well-lighted dye changed TiO₂ dispersion, might even be possible for degradation of colorless lake water pollutants^{44,45}. Recently a number and researchers have restricted heterogeneous photocatalytic decomposition of dye within the presence of ultraviolet illumination or visible light⁴⁶.



Desensitization, a method according for degradation of colorants in actinic radiation well-lighted dye changed TiO₂ dispersion, might even be possible for degradation of colorless lake water pollutants^{44,45}. Recently a number and researchers have restricted heterogeneous photocatalytic decomposition of dye within the presence of ultraviolet illumination or visible light 46. Aerophilous method has been additionally accustomed decolorize and mineralize several styles of group dyes in a very bench scale by exploitation each artificial irradiation^{47,48} and star technology, industrial dyes in TiO₂ suspension underneath star lightweight however the set of equipment employed by wang⁴⁸⁻⁵⁰ were regardful and concentration of the dye resolution was totally different in comparison to the current work.

Novelty of in this present studies: we have found on a very simple method to compare the photocatalytic activity of TiO₂ for different Concentration of two different Organic dyes (Methyl Orange and Methyl Red) which were not compared in the past studies. This experiment was done in a normal chemical lab and easy way with limited use of chemicals and simple lab equipment's. For both dyes, Methyl Orange and Methyl Red dyes the color started fading quickly when the light radiation was passed continuously for a long time (120 minutes).

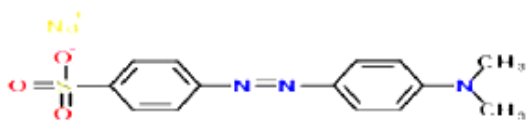
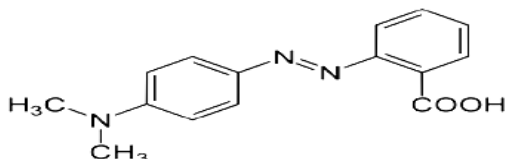
It has been observed that concentration of both dyes decreased, with time or the degradation increased. The effect of varying the dye concentration increases with degradation rate decreases. The rate constant value undergoes marginal decreases at pH = 4.2 when the methyl orange dye concentration was increased. The rate constant value undergoes a marginal decreases at pH= 4.5 when the methyl orange dye concentration was increased. From these researches it has been observed that degradation of methyl red organic dye (MR) dye slightly faster than degradation of methyl orange dye (MO) which was not studied in the previous similar works.

The present work deals with photocatalytic (TiO₂/hv) degradation for color removal from solution containing acid-base indicator, Methyl Orange and alkyl Red, Methyl Red dyes. Mercury (Hg) vapour lamps were used as irradiation sources. Utilization of daylight because the ultraviolet radiation energy supply is useful from ecological purpose of read. The dependence of dye icon oxidation rate on the subsequent parameters: Initial dye concentration, irradiation time, irradiation intensity were additionally investigated.

Scope of the investigation

The removal of artificial dyes in effluent water from workplace industries, dye industries, textile industries etc., is of nice concern since a number of the dyes and its degradation products are harmful to human life. Therefore degradation of dyes becomes a crucial facet within the treatment of waste water. Several strategies are used for the dye degradation method however the photocatalytic degradation method' as wide used for the entire degradation method chiefly thanks to economic practicability and also the easier nature of the technique concerned. Much attention has been centered within the past two decade on the photocatalytic degradation of organic pollutants mediate by TiO₂ particles in liquid dispersion irradiated by ultraviolet radiation and visual light³².

The big body of proof that has been collected suggests that this technique is beyond any doubt a possible and effective approach towards the degradation of big variety harmful organic pollutants in waste water and towards the purification of beverage. Therefore TiO₂ is one the normally used environmental icon catalyst for the reaction of liquid organic pollutants and TiO₂ catalyst exhibits smart activity for the icon reaction or chemical group dyes³¹.

Structure of Methyl Orange (MO)**Structure of Methyl Red (MR)****Visible light pathway**

The mechanism of photocatalytic degradation of dye by visible light has been shown to be different from that of UV irradiation. In this process, the dye is excited by the visible light and not by semiconductor TiO_2 is mixed with methyl orange and Methyl Red solution and magnetically stirred under visible light irradiation ($\lambda_{\text{max}} = 365\text{nm}$). The TiO_2 particles are isolated from the solution and the change in the absorbance of organic methyl orange and organic methyl red dyes are monitored spectrometrically. The rate constant for the degradation kinetics is determined for

- (i) Effect of dye concentration
- (ii) % of degradation is evaluated.

EXPERIMENTAL METHOD**(a). Preparation of methyl orange solution**

A stock solution ($1 \times 10^{-3}\text{M}$) of methyl orange was prepared by dissolving 0.032g of methyl orange powder (A.R. Qualigens) in 100ml of demineralised water.

(b). Preparation of methyl red solution

A stock solution ($1 \times 10^{-3}\text{M}$) of methyl red prepared by dissolving 0.28g of methyl red powder (A.R. Qualigens) in 5ml and 95ml of demineralised water.

Photo- reactor and light source

The Photo-reactor used for the degradation method could be a cylindrical cell with optical windows 160w (Hg lamp medium pressure). The sunshine supply is Hg lamp medium pressure actinic ray culminated by lens. The setup was lined employing a cardboard box to make sure darkness throughout the passage of sunshine from the sunshine supply.

Degradation experiments

The aqueous TiO_2 suspension was prepared by the addition of 30mg of Titanium dioxide (A.R. Qualigens) to a 50 ml of aqueous dye solution, whose concentration is changed between $1 \times 10^{-5}\text{N}$ to $1 \times 10^{-4}\text{N}$. The suspension was magnetically stirred with irradiation within the dark for 1hr to confirm the institution of associate degree adsorption/desorption equilibrium. The dispersions were unbroken underneath constant air equilibrated condition before and through the passage irradiation. At regular time intervals, 5ml of aliquots were collected and centrifuged to get rid of the TiO_2 particulate. The unvaried solutions were collected and their sorption measured victimization Shimadzu UV-Visible 1601 spectroscope.

Degradation kinetics

The decrease in the absorbance of the Methyl Orange and Methyl red dye solutions are monitored by UV-Visible spectrometer at 460nm and 550nm respectively. The decrease in absorbance is noted as function of time in minutes. The visible spectrum is recorded in the region of 300nm to 700nm both prior and after irradiation.

Absorbance measurement

The absorbance of dye goes to scientific method. Solutions before and when degradation were measured at completely different completely different) degradation time and different irradiation sources. Measurements were meted out victimization Shimadzu UV-Visible 1601 spectroscope within the gauge boson energy vary of wave length three hundred to 700nm aid of glass cell(made of Quartz) with 10mm optical path length. The percentage of degradation was calculated from the following equation:

$$\text{Degradation \%} = 1 - \frac{A_t}{A_0}$$

Where A_t is that the absorbance once time t and A_0 is that the absorbance of initial concentration of dye before degradation.

RESULT AND DISCUSSION**Study of photo degradation**

The degradation of the dye in aqueous solution occurs when it is irradiated with visible light (Fig. 1.c and 2.c) The photocatalytic degradation of

Organic dyes of Methyl Orange and Methyl Red with Titanium dioxide catalyst obeys the first order reaction kinetics at all dye concentration and the rate expression is given by the equation.

$$\frac{-dC}{dt} = k^1[C]$$

Where k^1 is the first order rate constant. The dye is adsorbed on to TiO_2 surface and the adsorption-desorption equilibrium is reached within

30 minutes. The equilibrium constant of the dye solution is determined after this period and it is taken as the initial dye concentration for the kinetic analysis. Integrating the above equation (with the limit) $C = C_0$ and $t = 0$ with C_0 being the equilibrium concentration of the bulk solution $\frac{\ln\left(\frac{C_0}{C}\right)}{[C]} = k^1 t$, where C_0 is the equilibrium concentration of dye and C is the concentration at time t and k^1 . The plot of $\log(a-x)$ against Time follows the first order kinetics, and from this plot the rate constant is calculated.

Table.1(a): Kinetic plot of Visible/Titanium dioxide-Photocatalyzed degradation of Methyl Orange dye

Kinetic plot of Visible/ Titanium dioxide Photocatalyzed degradation of Methyl Orange dye				
	Time(min.)	% of Degradation (No unit)	$\log \frac{a}{(a-x)}$ (No unit)	$\frac{C}{C_0}$ (No unit)
[Dye] = $1 \times 10^{-5}N$				
pH= 4.2	30	4.16	0.0182	0.9581
[TiO_2] = 30mg / 50ml	60	9.16	0.0417	0.9084
Rate Constant = $2.4152 \times 10^{-4} N$	90	14.58	0.0681	0.8512
	120	17.51	0.0835	0.8252

Table1(b): Kinetic plot of Visible/Titanium dioxide -Photocatalyzed degradation of Methyl Orange dye

Kinetic plot of Visible / Titanium dioxide Photocatalyzed degradation of Methyl Orange dye				
	Time(min.)	% of Degradation (No unit)	$\log \frac{a}{(a-x)}$ (No unit)	$\frac{C}{C_0}$ (No unit)
[Dye] = $4 \times 10^{-5} N$				
pH = 4.2	15	14.59	0.0678	0.8548
[TiO_2] = 30mg / 50ml	30	24.86	0.1235	0.7521
Rate Constant = $2.4152 \times 10^{-4} N$	45	35.35	0.1889	0.6571
	60	48.11	0.2853	0.5183

Table1(c): Kinetic plot of Visible/Titanium dioxide Photo catalyzed degradation of Methyl Orange dye

Kinetic plot of Visible / Titanium dioxide Photocatalysed degradation of Methyl Orange				
	Time(min.)	% of Degradation (No unit)	$\log \frac{a}{(a-x)}$ (No unit)	$\frac{C}{C_0}$ (No unit)
[Dye] = $5 \times 10^{-5}M$				
pH = 4.2	15	20.08	0.0951	0.8017
[TiO_2] = 30mg / 50ml	30	37.58	0.2033	0.6262
Rate Constant = $2.4152 \times 10^{-4} M$	45	45.37	0.2611	0.5481
	60	63.12	0.4322	0.3697

Table1(d): Kinetic plot of Visible/TiO₂ Photocatalyzed degradation of Methyl Orange dye

Kinetic plot of Visible/ TiO₂ Photocatalyzed degradation of Methyl Orange

	Time(min.)	% of Degradation (No unit)	$\frac{a}{\log(a-x)}$ (No unit)	$\frac{C}{C_0}$ (No unit)
[Dye] = 6 X 10 ⁻⁵ N				
pH = 4.2	15	20.76	0.1282	0.7071
[TiO ₂] = 30mg / 50ml	30	38.31	0.2471	0.6004
Rate Constant = 2.4152 X 10 ⁻⁴ N	45	46.19	0.3667	0.5211
	60	63.74	0.4881	0.2446

Table2(a): Kinetic plot of Visible/Titanium-dioxide Photocatalyzed degradation of Methyl Red dye

Kinetic plot of Visible/ Titanium dioxide Photocatalyzed degradation of Methyl Red dye

	Time(min.)	% of Degradation (No unit)	$\frac{a}{\log(a-x)}$ (No unit)	$\frac{C}{C_0}$ (No unit)
[Dye] = 4 X 10 ⁻⁵ M				
pH = 4.2	15	5.26	0.0354	0.9215
[TiO ₂] = 30mg / 50ml	30	10.52	0.0795	0.8325
Rate Constant = 2.4152 X 10 ⁻⁴ M	45	15.78	0.1136	0.7697
	60	23.69	0.1622	0.5448

Table 2(b): Kinetic plot of Visible/Titanium dioxide Photocatalyzed degradation of Organic Methyl dye

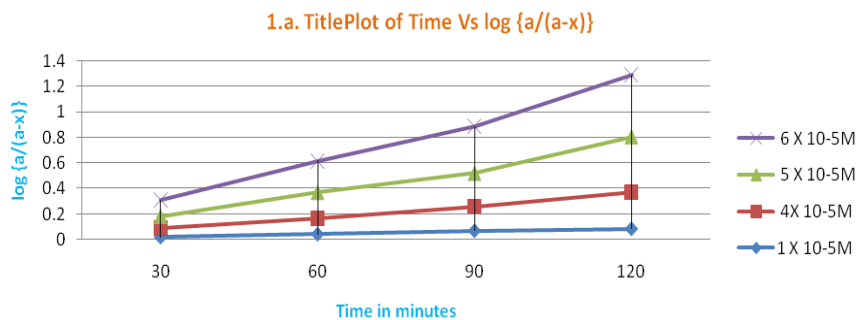
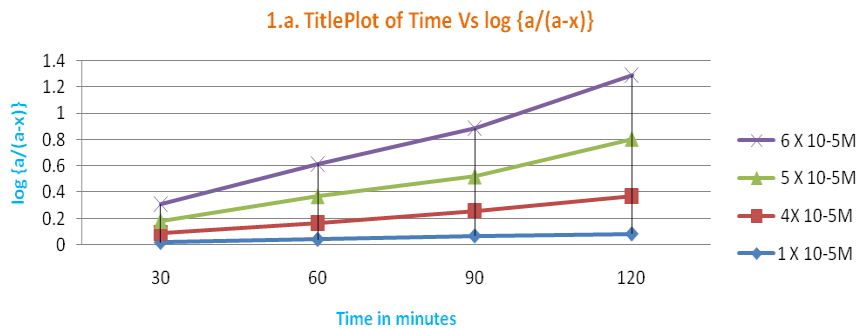
Kinetic plot of Visible/ Titanium dioxide Photocatalyzed degradation of Methyl Red dye

	Time(min.)	% of Degradation (No unit)	$\frac{a}{\log(a-x)}$ (No unit)	$\frac{C}{C_0}$ (No unit)
[Dye] = 5 X 10 ⁻⁵ M				
pH = 4.2	15	7.88	0.0569	0.8761
[TiO ₂] = 30mg / 50ml	30	16.77	0.1082	0.7792
Rate Constant = 2.4152 X 10 ⁻⁴ M	45	23.05	0.1661	0.6801
	60	28.99	0.2332	0.5844

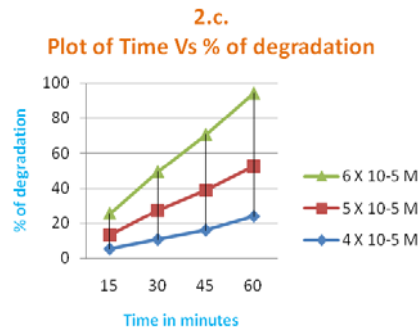
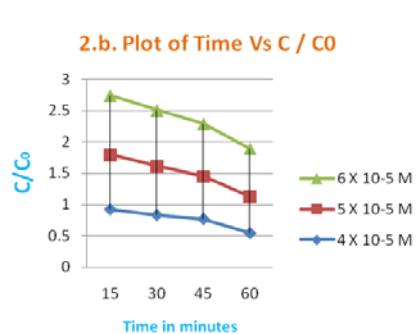
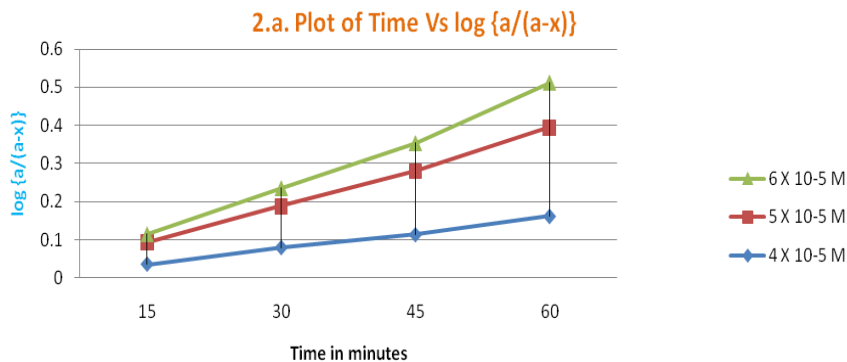
Table 2(c): Kinetic plot of Visible/Titanium dioxide Photocatalyzed degradation of Methyl Red dye

Kinetic plot of Visible/ Titanium dioxide Photocatalyzed degradation of Methyl Red dye

	Time(min.)	% of Degradation (No unit)	$\frac{a}{\log(a-x)}$ (No unit)	$\frac{C}{C_0}$ (No unit)
[Dye] = 6 X 10 ⁻⁵ M				
pH = 4.2	15	12.33	0.0232	0.9478
[TiO ₂] = 30mg / 50ml	30	22.07	0.0482	0.8951
Rate Constant = 2.4152 X 10 ⁻⁴ M	45	31.81	0.074	0.8416
	60	41.55	0.1169	0.7635



Graph. 1. Kinetic graphs of Visible / Titanium dioxide Photocatalysed degradation of Methyl Orange dye



Graph. 2. Kinetic graphs of Visible / Titanium dioxide Photocatalysed degradation of Methyl Red dye (MR)

Effect of dye concentration

The pollutant concentration is a variable parameter in wastewater treatment. The effect of various initial dye concentrations on the photocatalytic decolorization and degradation has been investigated with dye solution. The

degradation rate constant for the Methyl Orange dye and Methyl Red dye under same pH and concentration values are shown in the table.3 with respect to pH = 4.2, Temperature = 27 °C and $\lambda_{max} = 460\text{nm}$ and pH = 4.5, Temperature = 27 °C and $\lambda_{max} = 520\text{ nm}$.

Table 3: The rate of color degradation of Methyl Orange and Methyl Red dyes

S.NO	[Dye] (M)	[CATALYST] (mg)/50ml	Degradation of Methyl Orange dye Rate constant X 10 ⁻⁴ Sec ⁻¹ (pH at 4.2)	Degradation of Methyl Red dye Rate constant X 10 ⁻⁴ Sec ⁻¹ (pH at 4.5)
1	1 X 10 ⁻⁵	30	2.4152	-
2	4 X 10 ⁻⁵	30	1.2748	9.6282
3	5 X 10 ⁻⁵	30	1.2507	8.0551
4	6 X 10 ⁻⁵	30	0.8418	7.6653

It determined that from higher than the Table.1, Table 2, Table 3, Graph1 and Graph 2 pair of shown the degradation rate constant decreases perpetually with [dye] concentration, degradation of different dyes^{39,40,41}. Thus, the time taken for the entire degradation of the dye is most for the dye of upper concentration and it's minimum for the dye of lower concentration. Once the dye concentration will increase, the number of dye absorbed on the chemical process surface will increase. This affects the chemical process activity of TiO₂. The rise in dye concentration conjointly decreases the trail length of gauge boson getting in the dye solutions. At high dye concentration, a big quantity of lightweight ultraviolet illumination [UVI actinic radiation actinic ray} light is also absorbed by the dye molecule instead of the catalyst and this might cut back the chemical process potency.

Visible light pathway

The mechanism of photocatalytic degradation of dye by visible light has been shown to be different from that of UV irradiation. In this process, the dye is excited by the visible light and not by semiconductor TiO₂.

Mechanism

Initial of photocatalytic reaction

1. Dye + hv → Dye* (initiation)
2. Dye + TiO₂ → Dye* + TiO₂(e)
3. TiO₂(e) + O₂ → TiO₂ + O₂⁻. TiO₂(e) + O₂⁻ + 2H⁺ → H₂O₂

5. H₂O₂ + TiO₂(e) → OH* + OH⁻
6. Dye* + O₂⁻ (or O₂⁻ or OH⁻) → Peroxylated or hydroxylated intermediates

Subsequently, TiO₂ plays the pivotal role of an electron and dye cation radicals. The processes described by equations from 1 to 5, example electron transfer, generation of peroxide radical anion, H₂O₂ and OH* radical formation have been demonstrated earlier. In the present investigation the degradation of Methyl Orange and Methyl red with TiO₂ catalyst is irradiated with visible light ($\lambda_{max} = 365\text{nm}$).

Photo degradation of dyes by visible light

The photolysis of the dye in aqueous solution is carried out by varying the following parameters;

Concentration of the dyes, 2. pH, and the catalyst concentration is kept constant in all experiments.

The solution were irradiated with visible light ($\lambda_{max} = 365\text{nm}$) near UV light. The absorption peak (λ_{max} for MO is 460nm, and λ_{max} for MR is 520nm) corresponding to the dye diminished and finally disappeared during photolysis, indicating the complete degradation of Methyl Orange. No new bands appeared in the visible region, corresponding to aromatic moieties and other similar intermediates. In the absence of UV light no significant degradation occurred prior to irradiation. Since the photo

degradation of dye occurs predominantly on TiO₂ surface the absorption of dyes molecule from aqueous solution on to TiO₂ surface is very important. The extent of adsorption of dye at various concentrations in blank solution after the adsorption desorption equilibrium had been reached i.e. prior to UV irradiation. The absorbance of the solution prior to irradiation provides the initial concentration (C⁰).

Photocatalytic degradation mechanisms

The complete assumption of dye catalyzed abasement advance that blind bandage holes (h⁺) and advice bandage electron(electrons-CB) are produced if aqueous TiO₂ abeyance is apparent with ablaze activity > than (E_g = 3.2eV) its bandage gap energy. The photon produced electrons can abatement the dye or acknowledge with electron can be abatement the dye or accompany with electron acceptors includes O₂ captivated on the Ti(II) – apparent or attenuated in baptize abbreviating it to superoxide abolitionist anion O₂⁻. The photo produced holes can burn the amoebic atom to anatomy R*, or added awful oxidant breed (Peroxide radicals) they are appear to be amenable for the heterogeneous. TiO₂ photo atomization of amoebic substrate as dyes. Based on this adapted action in the semiconductor exoteric creates the abasement of dyes can be represented as follows.

1. $TiO_2 + hv (UV) \rightarrow TiO_2 (electron (CB) + h^+(VB))$
2. $TiO_2 (h^+(VB)) + H_2O \rightarrow TiO_2 + H^+ + OH^-$
3. $TiO_2 (h^+(VB)) + OH^- \rightarrow TiO_2 + OH^{\cdot}$
4. $TiO_2 (electron (CB)) + O_2 \rightarrow TiO_2 + O_2^{\cdot-}$
5. $O_2^{\cdot-} + H^+ \rightarrow HO_2^{\cdot}$
6. $Dye + HO_2^{\cdot} \rightarrow Degradation\ products$

The resultant OH* radical, getting a actual able acerbic abettor (standard redox abeyant +2.8V)

can burn a lot of the dye. Substrate not acknowledging against hydroxyl radicals are base employing TiO₂ photochemical reaction catalysis with ante of adulteration awful afflicted by the semiconductor blind bandage bend position.

CONCLUSION

1. For both the Organic dyes (MO and MR) the blush started crumbling bound while the ablaze radiation was anesthetized continuously for a continued time (2 hours).
2. It was as well beginning that absorption of both dyes decreased, with time or the abasement increased.
3. The aftereffect of capricious the dye absorption increases with abasement amount decreases.
4. The amount connected amount undergoes a bordering abatement (from 2.4152 X 10⁻⁴ Sec⁻¹ to 0.8418 X 10⁻⁴ Sec⁻¹) at pH = 4.2 if the Methyl Orange dye absorption was adapted from 1 X 10⁻⁵ to 6 X 10⁻⁵ N.
5. The amount connected amount undergoes a bordering abatement (from 4.6181 X 10⁻⁴ Sec⁻¹ to 2.7046 X 10⁻⁵ Sec⁻¹) at pH = 4.5 if the Methyl Orange dye absorption was adapted from 1 X 10⁻⁵ to 6 X 10⁻⁴ N.
6. From this analysis it has been empiric that abasement of Organic Methyl Red dye (MR) hardly faster than a basement of Methyl Orange dye (MO).
7. It has been acclaimed that the abasement of all amoebic dyes blush could be removed by this method.
8. It was clear that this method applicable for removal color from effluent coming from tanneries, dye industries, Ink industries.

REFERENCES

1. Fu, G.; and. Allen, H.E. ; *Water Res.*, **1992**, *26*, 225.
2. Kannan, N; and Meenakshi Sundram, M.; *dyes pigments.*, **2001**, *25*, 51.
3. Chen. L.; *Water Res.*, **2000**, *34*, 974-982.
4. Gonculves. M.; Pinto. E.; Nikeonye P.; and Oliveria- Campus. *Dyes and Pigments.*, **2005**, *64*, 135-139.
5. Daton. J.S.; Janes N.G.; Nicholso J. A.; Halman K. R.; Allen. G.C.; *Envir. Pollut.*, **2001**, *32*, 415-422.
6. Malato S.; Marc. G.; Palmisano L.; Pazzi M.; Pramauro. E.; **2009**, *49*(10), 1223-1230.
7. Tanaka. K.; Reddy. KSN.; *Appl. Catal. B: Environ.*, **2002**, *39*, 305-310.
8. Konstantinou. I.; Albanis. TA.; *Appl. Catal. B: Environ.*, **2004**, *49*, 1-14.
9. International Union of Pure and applied

- chemistry(*IPUAC*), **1996**, *12*, 2223-2286.
10. Hoffmann, M.R.; Martin, S.C.; Choi, W.; Bahnemann, D.W.; *Chem. Rev.*, **1995**, *95*, 69.
 11. Stafford, U.; Gray, K.A.; Kamat, P.V.; *Chem. Rev.*, **1996**, *3*, 77.
 12. Peral, J.; Domenech, X.; Ollis, D.F.; *J. Chem. Tech. Biotech.*, **1997**, *70*, 177.
 13. Fujishima, A.; Rao, T.N.; Trya, D.A.; *J. Photochem. Photobiol. c; Photochem Rev.*, **2000**, *1*, 1.
 14. Hidaka, H.; Zhao, J.; Pellizzetti, E.; Serpone, N.; *J. Phychem.*, **1992**, *96*, 2226.
 15. Sahate, J.; Anderson, M.A.; Kikkawa, H.; Edwards, M.; Hill, C.G., Jr. *J. Catal.*, **1991**, *127*, 167.
 16. Fox, M.A.; Dulay, M.T.; *Chem. Rev.*, **1993**, *93*, 341.
 17. Muszkat, L.; Bir, L.; Feigelson, L.; *J. Photochem. A: chem.*, **1995**, *87*, 85.
 18. Stafford, U.; Gray, K.A.; Kamat, P.V.; *Res. Chem. Intermed.*, **1997**, *23*, 355.
 19. Martin, S.C.; Choi, W.; Bahnemann, D.W.; *Chem. Rev.*, **1995**, *95*, 69.
 20. Saquib, M.; and Munner, M.; *Dys and pigments.*, **2002**, *53*, 237-249.
 21. Augugliaro, V.; Baiocchi, C.; *Chemosphere.*, **2002**, *49*, 1223-1230.
 22. Bukelmann, D.; and Shugui, D.; *Springer-Verlag*, Berlin., **1992**, *16*, 253-256
 23. Haffman, M.R.; *chem Rev.*, **1995**, *95*, 69-96.
 24. Zhang, F.; Zhao, J.; Zang, L.; Shen, T.; *Catal. A: chem.*, **1997**, *120*, 134-138.
 25. Wang, Y.; *Wat. Res.*, **2000**, *34*, 990.
 26. Al-Qaradawi, S.; Salman, S.R.; *J. Photochem. Photobiol. A: Chem.*, **2002**, *148*, 161.
 27. Wang, C.; Xu, B.; Wang, J.; Zhao, *Chemi.*, **2005**, *178*, 3500.
 28. Chen, J.; Liu, M.; Zhang, J.; Ying, X.; Jin, L.; *J. Environ. Manage.*, **2004**, *70*, 43.
 29. Hoffman, M.R.; Martin, S.T.; *Chem. Rev.*, **1995**, *95*, 69-96.
 30. Hung, C.H.; *Water Sci. Tech.*, **2001**, *43*(2), 313-320.
 31. Tanaka, K.; Padempole, K.; and Hisanaga, T.; **2000**, *34*(1), 327-333.
 33. Tang, W.Z.; and An, H.; *Chemosphere.*, **1995**, *31*, 4171. We, J.; Liu, G.; and Zhao, J.; *J. Phys. Chem. B.* **1999**, *103*, 4862.
 34. VinodGopal, K.; Kamat, *Environ. P.V.; Sci. Technol.*, **1995**, *29*, 841
 35. Veppolian, B.; Choi, H. C.; Sakthivel, S.; Arabindo, B.; Murugesan, V.; *J. Hazzard. Mater.*, **2002**, *89*, 303.
 36. Lathashree, S.; Nageswara, R.; Shivasankar, B.; Sadassivaam, V.; Rengarai, K.; *J. Mole. Catal. A: Chem.*, **2004**, *223*, 101.
 37. Lizama, C.; Freer, J.; Baeza, J.; Mansilla, H.D.; *Catal. Today.*, **2002**, *76*, 235.
 38. Akyol, A.; Yatmaz, H.C.; Bayaramoglu, M.; *Environ.*, **2004**, *54*, 19.
 39. Daneswar, N.; Salari, D.; Khataee, A.R.; *Chem.*, **2003**, *157*, 111.
 40. Sakthivel, S.; Neppolian, B.; Shankar, B.V.; Arabindoo, B.; Palanichamy, M.; Murugesan, V.; *Sol. Ener. Mater. Sol. Cells.*, **2003**, *77*, 68.
 41. Vindgopal, K.; Kamat, P.V.; *J. Phys. Chem.*, **1992**, *96*, 5053.
 42. Hasnat, M.A.; Siddiquey, J.A.; and Nuruddin, A.; *Dyes and pigments.*, **2005**, *66*, 185.
 43. Jifan, H.; Zhengai, S.; and Hingliang, L.; *Gongneng Cailiao.*, **2002**, *34*, 336.
 45. Chatterjee, D.; *Bull. Catal. Soc. India.*, **2004**, *32*, 56-58.
 46. Olivira-Campos, A.; Peter, O.N.; Poullos, L.; Situation and Perspectives for the European Union 6-10 May, Porto, Portugal, P., **2003** 1-6.
 47. Goncalve, M. S.; Oliverira, T.; Campus, A.M.F.; *Chemosphere.*, **1999**, *39*, 781-786.
 48. Kiriakidou, F.; Kondarides, D.I.; Verykios, XE.; *Catal. Today.*, **1999**, *54*, 119-130.
 49. Wang, G.; Liao, C.; Wa, F.; *Chemosphere.*, **2000**, *42*, 379-387.
 50. Tanaka, K.; Perdempole, K.; and Hisanaga, T.; *Water. Res.*, **2000**, *34*, 327.