

Full Length Research Paper

Photocatalytic degradation of methyl orange in aqueous TiO₂ under different solar irradiation sources

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Accepted 8 March, 2007

The main causes of surface water and groundwater contamination are industrial discharges. Updating the field of polluted water treatment by photochemical technique has led to an important in oxidative degradation processes applying solar photochemical methods using crystal TiO₂ as a catalyst. Photocatalytic oxidation of methyl orange dye under different irradiation sources (Halogen lamp 1000 W, fluorescent lamp and natural sun light) have been studied over TiO₂ catalyst. The effect of initial dye concentrations, irradiation time and light intensity were also studied. The results revealed that dyes under go fast degradation with the natural sun light than the halogen and fluorescent lamp sources. On other hand, fast degradation was obtained with increasing time of the Halogen and fluorescent lamps as a light source. The rate of decolorization was estimated from residual concentration spectro- photometrically. At the used experimental conditions the substrate photo-oxidation rate follows pseudo-first order kinetics.

Keywords: Photodegradation, solar irradiation, dyes, pollution, treatment, catalyst.

INTRODUCTION

The removal of the non-biodegradable organic chemicals is a crucial ecological problem. Dyes are an important class of synthetic organic compounds used in the textile industry and are therefore common industrial pollutants. Due to the stability of modern dyes, conventional biological treatment methods for industrial wastewater are ineffective resulting often in an intensively colored discharge from the treatment facilities. Heterogeneous photocatalysis by semiconductor particles are a promising technology for the reduction of global environmental pollutants. Inorganic photocatalysts, such as TiO₂, have shown to be a relatively cheap and effective way of removing organic compounds and pollutant gases (Dalton et al., 2001). Oxidation processes with TiO₂ photocatalyst have been shown to be an effective alternative regard (Malato et al., 2000; Marinas et al., 2001; Tanaka et al., 2002; Konstantinou and Albanis, 2004), the vital snag of TiO₂ semicon-

ductor is that it absorbs a small portion of solar spectrum in the UV region (band gap energy of TiO₂ is 3.2 eV). Hence in order to harvest maximum solar energy it is necessary to shift the absorption threshold towards visible region. Light excitation of TiO₂ semiconductor, under a wavelength between 360 - 380 nm, generates electrons and holes in the conduction and valence bands respectively.

Dye sensitization, a technique reported for degradation of colorants in visible light illuminated dye modified TiO₂ dispersion, could also be workable for degradation of colorless water pound pollutants (Chatterjee and Mahata, 2001; Chatterjee, 2004) Recently a number of researches have dealt with the heterogeneous photocatalytic decomposition of dye in the presence of UV-A or visible light (Oliveira-Campos, 2003; Konstantinou and Albanis, 2004; Gomes et al., 2000; Peralta-Zamora et al., 1998; Alaton et al., 2002). Also, oxidative process has been also used to decolorate and mineralizes many kinds of azo-dyes in a bench scale by using both artificial irradiation (Goncl-

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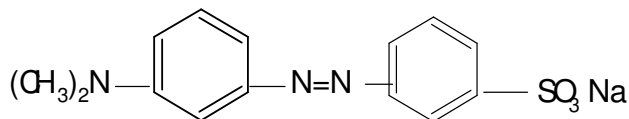


Figure 1. Structure of Methyl-Orange (MeO).

aves et al., 1999; Kiriakidou et al., 1999; Chun and Yizhong, 1999) and also solar technology (Wang, 2000). Wang investigated the photocatalytic degradation of eight commercial dyes including MeO in TiO_2 suspension under solar light.

The present work deals with photocatalytic ($\text{TiO}_2/h\nu$) degradation for color removal from aqueous solution containing methyl orange dye (MeO). Tungsten halogen, fluorescent light and sunlight were used as irradiation sources. Utilization of sunlight as the UV energy source is beneficial from ecological point of view. The dependence of dye photo-oxidation rate on the following parameters: initial dye concentrations; irradiation time; irradiation intensity were also investigated.

MATERIALS AND METHODS

Material and reagents

Methyl orange was obtained from Sigma Chemie GmbH (Germany) and used without further purification. The photocatalyst used in this work was the nonionized TiO_2 , which was supplied via Degussa "P25, ca. 80% anatase, 20% rutile; BET surface area $\sim 50 \text{ m}^2/\text{g}$, mean diameter ca. 30 nm". This photocatalyst was used without further treatment. Methyl orange (MeO) ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{SO}_3\text{Na}$) structures is reported in Figure 1, and characterized by sulphonic groups, which are responsible for the high solubility of these dyes in water. Different concentrations of MeO dye (10^{-4} , 10^{-5} , 10^{-6} , 10^{-7} and 10^{-8} M) were prepared using deionized water with the solid dye.

Photocatalytic reactors and degradation experiments

Schematic diagram is illustrated in (Figure 2).

Photocatalytic reactor with tungsten halogen source: This reactor was laboratory-built system consisting of Tungsten Halogen light source (1000 W). The light source emitted light just above the sample. The intensity level of light is controlled by fixing the distance between the source of light and the specimen. The sample was added in the thermostated quartz measurement cell under constant stirring. 50 ml of dye sample solution and 55 mg of TiO_2 were used in this method. The suspension was constantly stirred for 30 min in the dark before irradiation to reach equilibrium absorption of the TiO_2 in the organic substance solution. During the irradiation the photoreactor was maintained under magnetic stirring for having always a homogeneous suspension, to promote the adsorption on the surface of TiO_2 . The degraded solution was taken for spectra measurement at various times intervals after centrifuga-

tion and filtration.

Photocatalytic reactor with fluorescent light source: In this reactor, which is laboratory-built system, three fluorescent lamps were fixed at a fixed distance from the sample cell. 50 ml of dye sample solution and 55 mg of TiO_2 were used in this method. The suspension was constantly stirred for 30 min in the dark before irradiation to reach equilibrium absorption of the TiO_2 in the organic substance solution. During the irradiation the photoreactor was maintained under magnetic stirring for maintaining a homogeneous suspension. The degraded solution was taken for spectra measurement at various time intervals after centrifugation and filtration.

Photocatalytic reactor with sunlight source: Outdoor experiment was carried out with 1000 ml Pyrex glass reservoir placed outside the laboratory building. Pyrex glass beaker containing methyl orange dye sample (50 ml) and 55 mg of TiO_2 catalyst was placed in the reaction reservoir. Incident solar radiation was measured with a radiometer (W/m^2) in the wavelength range of 285 – 2800 nm. The mean sunlight intensity at the beginning, middle and end of the day was estimated as 350, 745 and 450 W/m^2 respectively. The average total daily short wave radiation for this period was 734 W/m^2 , with a 10 h mean sunshine duration from sunrise to sunset. The mean daily temperature was 25°C. The suspension was constantly stirred for 30 min in the dark before irradiation reached equilibrium absorption of the TiO_2 in the organic substance solution. During the irradiation the photoreactor under magnetic stirring was maintained having a homogeneous suspension, to promote the adsorption on the surface of TiO_2 and sun light absorption. The degraded solution was taken for spectra measurement at various time intervals after centrifugation and filtration.

Conditions for irradiation experiments

These simple photochemical designs (Figure 2) depend on using Archimedes Principle in order to move the specimen under the light source. For this movement water droplet from left flask was controlled by using weight equilibrium of Archimedes principle in the right hand. The temperature was varied by controlling the current passing through the Peltier device (the deionized water was cited between the radiation source and the specimen). The aqueous suspension was magnetically stirred throughout the experiment. Five concentrations of the Methyl Orange (10^{-4} , 10^{-5} , 10^{-6} , 10^{-7} and 10^{-8} M) were used to find the effect of initial dye concentration on color removal. Also all of these experiments were performed in different time intervals (0 "absence of illumination", 4, 5, 6, 9 and 13 h). Temporal changes in the concentration of Methyl Orange were monitored by examining the variation in the maximal absorption. At different time intervals aliquot was taken out with the help of a syringe and then filtered through Millipore syringe filter of 0.45 μ . Then absorption spectra were recorded and the rate of decolorization was observed in terms of change in intensity at λ_{max} of the dyes.

Absorbance measurement: The absorbances of dye solutions before and after degradation were measured at different degradation times and different irradiation sources. Measurements were carried out using Perkin-Elmer 1900 spectrophotometer in the photon energy range of wavelength from 350 to 600 nm and with aid of glass cells (10 mm optical path length). The percentage of degradation was calculated from the following equation:

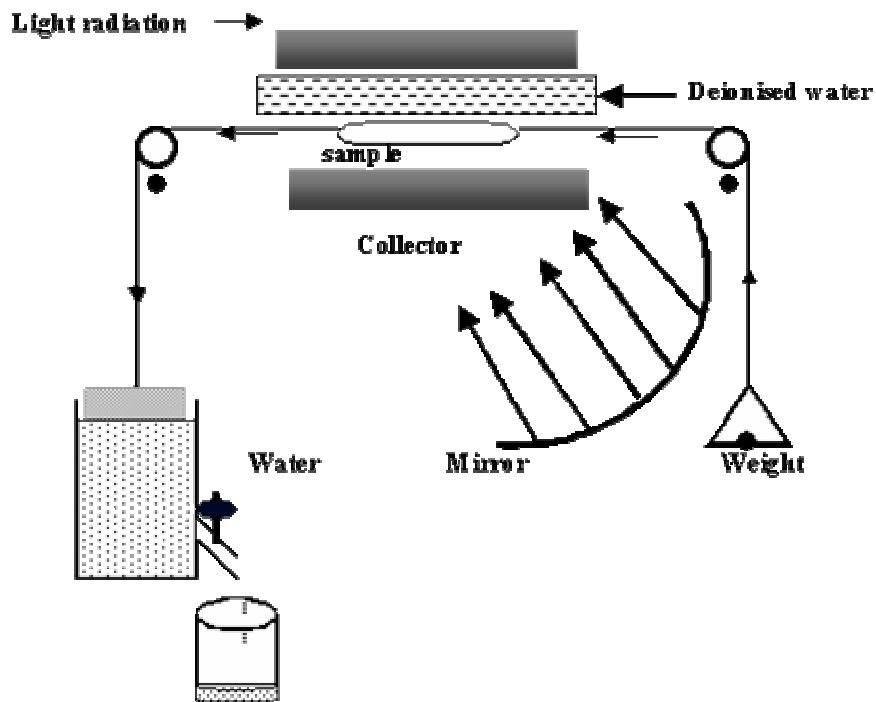


Figure 2. Schematic diagram of photocatalytic reactor

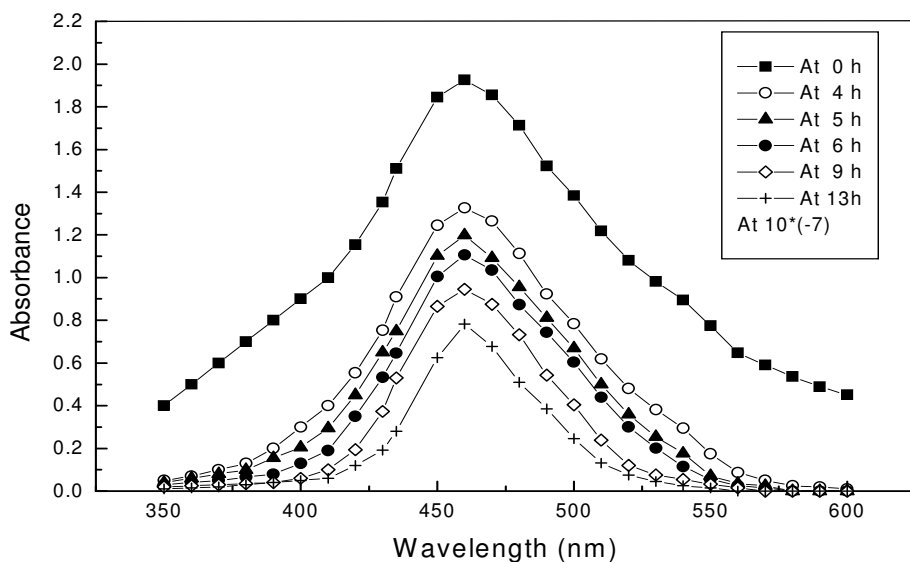


Figure 3. Time effluence on photocatalytic degradation of Methyl Orange dye using halogen irradiation.

$$\text{Degradation \%} = \left[1 - \frac{A_t}{A_o} \right] \times 100$$

Where A_t is the absorbance after time t and A_o is the dye initial concentration before degradation.

RESULTS

The results reveal that:

- i) For all the time intervals applied, the maxima of the absorption spectra undergo a vertical shift toward the low

Table 1. Photodegradation of different concentrations of methyl orange using florescent irradiation (using 1 lamp)

% degradation		Absorbance	Absorbance	Absorbance	Concentration
1h	3h	After 3h	After 1h	before	
63.15	51.67	0.077	0.101	0.209	10^{-7} M
62.93	73.70	0.086	0.061	0.232	10^{-6} M
61.57	34.36	0.161	0.275	0.419	10^{-5} M
37.02	10.83	1.342	1.900	2.131	10^{-4} M

Table 2. Photodegradation of different concentrations of methyl orange using florescent irradiation (using 3 lamps)

% degradation	Absorbance	Absorbance	Concentration
	After 3h	before	
92.82	0.015	0.209	10^{-7} M
87.93	0.028	0.232	10^{-6} M
79.74	0.086	0.419	10^{-5} M
59.97	0.853	2.131	10^{-4} M

Table 3. Rate constants for catalytic photodegradation of MeO dye using halogen irradiation

R ²	Slop (k)	MeO concentrations (M)
0.992	0.057	10^{-5}
0.913	0.084	10^{-6}
0.962	0.094	10^{-7}
0.822	0.135	10^{-8}

k is the rate constant

values of the absorbance with decreasing the concentration of the Methyl Orange in which degradation percentage for MeO 10^{-8} M (47.02%) using Halogen irradiation was twice higher than that for 10^{-5} M (23.57%) The concentration effect on the photodegradation of methyl orange is illustrated in Figure 4.

ii) In all experiments, increasing in the duration time of illumination allows the absorption spectra to be shifted toward the low absorbance values (Figure 3). The loss in the spectral features of the Methyl Orange dye as described above may be associated with the reduction reaction of the photoexcited dyes (Figures 4 and 5). The degradation efficiency passes through a maximum at dye concentration 10^{-8} M.

With fluorescent lamp source, photocatalyzed degradation of methyl orange in TiO₂ suspensions was carried out for one concentration 10^{-4} M, and this experiment was performed in dark and in irradiation with time interval of 9 h (Figure 6). The rate of dye removal increases as the

dye initial concentration decreases and this is illustrated by the high degradation rate for 10^{-7} M MeO (63.15%) compared to those for 10^{-4} M MeO (37.02 %) (Table 1). As the source intensity increases, using 3 fluorescent lamps, the dye degradation increases to rich 92.82% (for 10^{-7} M MeO) compared to using one lamp (63.15%) (Table 2). Comparing the effect of the fluorescent lamp on the photodegradation of the Methyl Orange with that of the Halogen lamp 1000 W for the same concentration and time interval, it is clear that the photodegradation velocity for the 10^{-4} M methyl orange is higher in presence of irradiation with fluorescent lamp than for the same concentration with Halogen lamp 1000 W.

Also the photocatalyzed degradation of Methyl Orange in TiO₂ suspensions was carried out for one concentration, 10^{-4} M, with the aid of sunlight irradiation. The experiment was performed in dark and in irradiation with time interval of 9 h (Figure 7). This figure shows the greatest vertical shift of the absorption spectrum with respect to the above two cases and resulted in higher degradation percentage of the dye (99.6%) than using the other irradiation sources. Also, it is clear that:

i) The photodegradation velocity for the 10^{-4} M Methyl Orange is the highest in the presence of irradiation with sunlight among that for the same concentration at the irradiation with Halogen lamp 1000 W and fluorescent lamp.

ii) Photo-degradation of Methyl Orange in TiO₂ suspensions is the best at sunlight irradiation for high concentrated Methyl Orange dye.

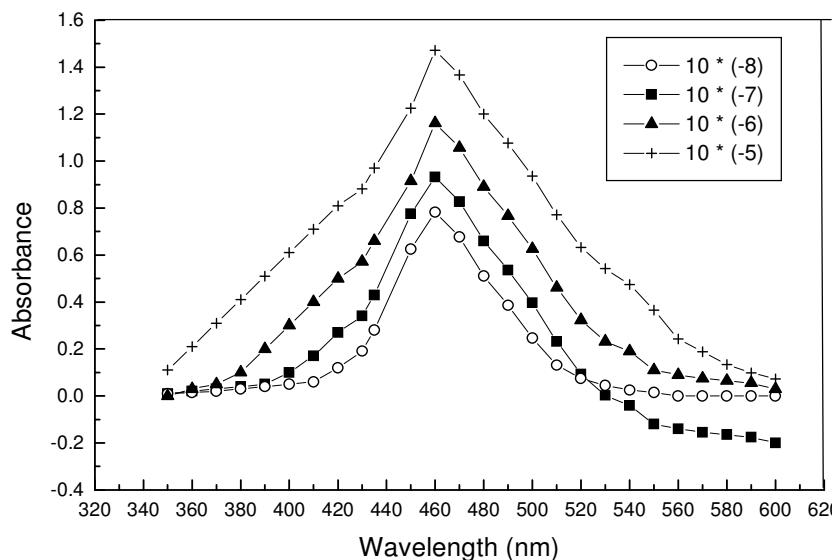


Figure 4. Effluence of initial dye concentrations on rate degradation of methyl orange dye using halogen irradiation

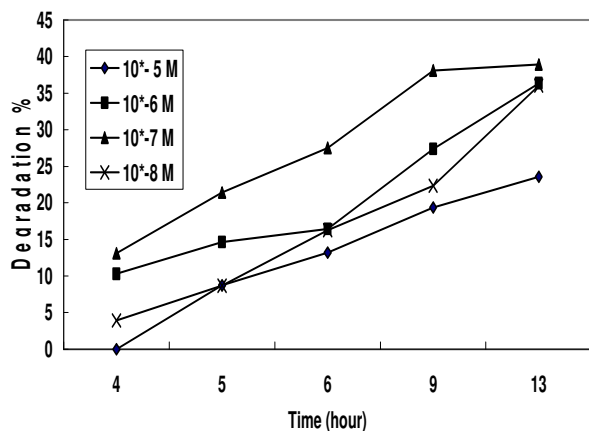


Figure 5. Time effect on photocatalytic degradation of MeO at different concentrations

Kinetic study

The kinetics of disappearance of MeO at different concentrations is illustrated in Figure 8. The results show that the photocatalytic decolorization of MeO dye can be described by the first order kinetic model, $\ln(C_0/C) = kt$, where C_0 is the initial concentration and C is the concentration at time t . The plots of the concentration data gave a straight line. The correlation constant for the fitted line was calculated to be $R^2 = 0.992, 0.912, 0.961$ and 0.822 for MeO concentrations $10^{-5}, 10^{-6}, 10^{-7}$ and 10^{-8} respectively. The rate constants were calculated to be $0.056, 0.084, 0.094$ and 0.135 for the previous MeO, respectively (Table 3).

DISCUSSION

Effect of the initial dye concentration on photodegradation

It is generally noted that the degradation rate increases with the increase of dye concentration to a certain concentration and a further increase leads to a decrease in the dye degradation rate (Sakthivela et al., 2003). The decrease of dye degradation as the dye concentration increase is as a result that the generation of OHO radicals on the catalyst surface is reduced since the active sites are covered by dye ions (Poulios and Tsachpinis, 1999). Our results agree with those reported with Li et al. (2005) that at irradiation of methyl orange by UV source, the degradation of the dye decreases 34.1% as the dye concentration increase. Also Kansal et al. (2006) concluded that the photocatalytic degradation of methyl orange, using TiO_2 as a catalyst and UV source, decrease as the dye concentration increase. They explained this decrease as the result of increasing the number of photon absorption by the catalyst in lower concentration (Davis et al., 1994).

Effect of irradiation sources on photodegradation

Light intensity is a major factor in photocatalytic degradation because electron-hole pairs are produced by light energy. Augugliaro et al. (2002) reported that the heterogeneous photocatalytic method can be successfully used not only for the colour abatement, but also for the complete degradation of methyl orange from waste water

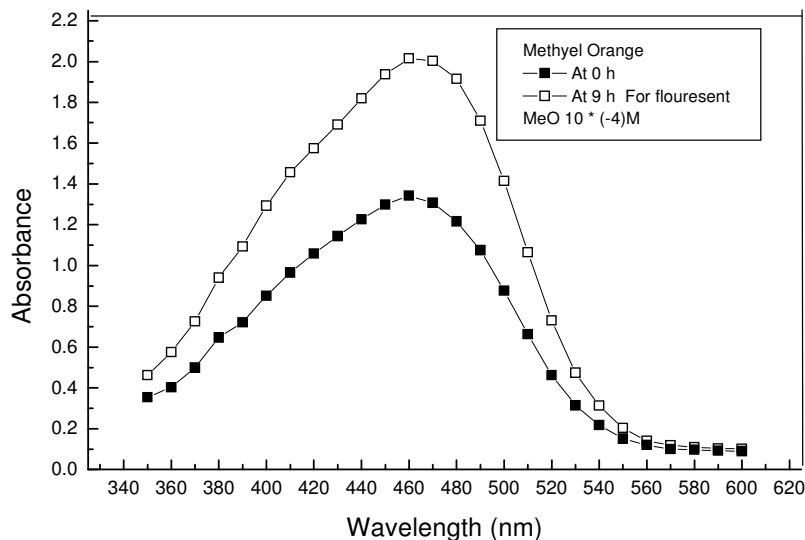


Figure 6. Time effect on photocatalytic degradation of methyl orange dye using fluorescent irradiation.

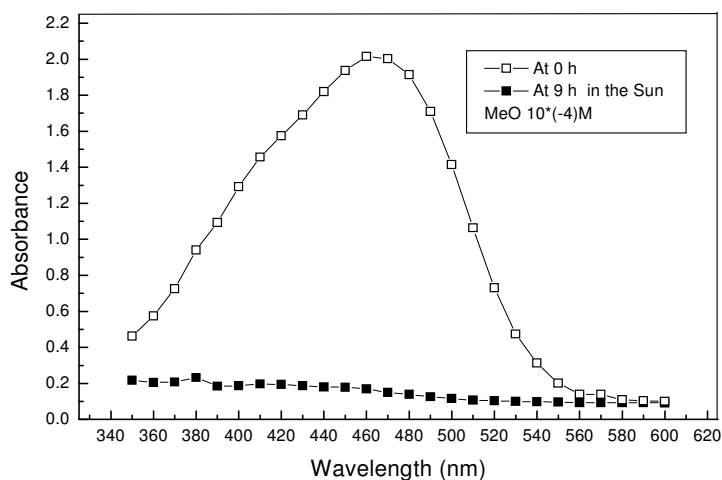


Figure 7. Time effluence on photocatalytic degradation of methyl orange dye using sun light irradiation.

containing suspended polycrystalline TiO_2 particles under sunlight irradiation. Kansal et al. (2006) found that the decolorization of MeO occur at a faster rate with solar light in comparison to UV light. In the case of MeO, 98.92% decolorization efficiency was observed at 90 min irradiation time under solar light, whereas in the presence of UV irradiation for the same duration, only 50% decolorization efficiency was recorded Yang et al. (2006) reported that Anatase TiO_2 nanoparticles of about 16 nm in crystal size have been successfully used for degradation of Methyl Orange under ultraviolet (UV) illumination. Li et al. (2006) reported that TiO_2 coated activated carbon

was shown high photoactivity for the photodegradation of Methyl Orange dyestuff in aqueous solution under UV irradiation. The kinetics of photocatalytic MeO dyestuff degradation was found to follow a pseudo-first-order rate law.

At upper Egypt intense sunlight is available throughout the year and hence, it could be effectively used for photocatalytic degradation of pollutants in wastewater. Moreover there is no material deterioration in case when sunlight is used as a radiation source. Kamat and Vinodgopal (1993) have reported that only the dye molecules that were in direct contact with the TiO_2 surface (the molecu-

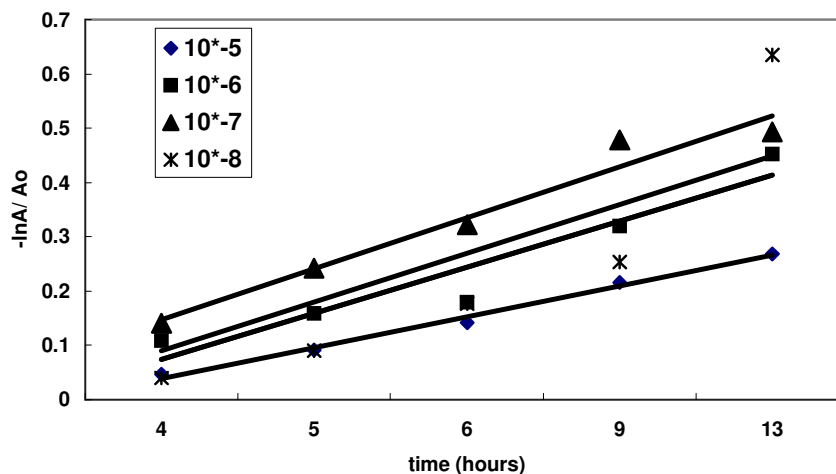


Figure 8. Pseudo-first-order kinetics for methyl orange photocatalyzed degradation.

les at minelayer or submonolayer coverage) undergo photodegradation with visible light.

Effect of light intensity on photodegradation

Ollis et al. (1991) reviewed the studies reported for the effect of light intensity on the kinetics of the photocatalytic process of dye and stated that:

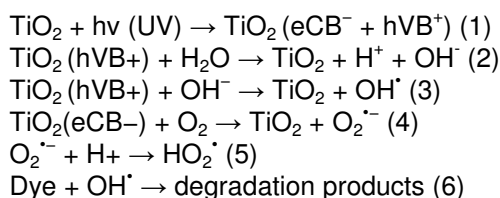
- i) At low light intensities ($0\text{--}20\text{ mW/cm}^2$), the rate would increase linearly with increasing light intensity (first order).
- (ii) At intermediate light intensities beyond a certain value (approximately 25 mW/cm^2), the rate would depend on the square root of the light intensity (half order).
- (iii) At high light intensities the rate is independent of light intensity.

This is likely; because at low light intensity reactions involving the electron-hole formation are predominant and the electron-hole recombination is negligible. However, at increased light intensity electron-hole pair separation competes with recombination, thereby causing lower effect on the reaction rate. In our study, the enhancement of the rate of decolorization as the light intensity increased was also observed and agreed with the other studies (Hermann, 1999; Konstantinou and Albanis, 2004). It is evident that the percentage of decolorization and photodegradation increase with the increase in irradiation time. The reaction rate decreases with irradiation time since it follows apparent first-order kinetics.

Photocatalytic degradation mechanisms

Photocatalytic oxidation

The detailed mechanism of MeO dye catalyzed degradation states that conduction band electrons (e^-) and valence band holes (h^+) are generated when aqueous TiO_2 suspension is irradiated with light energy greater than its band gap energy ($E_g=3.2\text{ eV}$). The photo-generated electrons could reduce the dye or react with electron acceptors such as O_2 adsorbed on the Ti(II) -surface or dissolved in water reducing it to superoxide radical anion $\text{O}_2^{\cdot-}$. The photogenerated holes can oxidize the organic molecule to form R^+ , or react with OH^- or H_2O oxidizing them into OH^\cdot radicals. Together with other highly oxidant species (peroxide radicals) they are reported to be responsible for the heterogeneous TiO_2 photodecomposition of organic substrates as dyes. According to this, the relevant reactions at the semiconductor surface causing the degradation of dyes can be expressed as follows:



The resulting OH^\cdot radical, being a very strong oxidizing agent (standard redox potential $+2.8\text{ V}$) can oxidize most of methyl orange dye the mineral end-products. Substrates not reactive toward hydroxyl radicals are degraded employing TiO_2 photocatalysis with rates of decay highly influenced by the semiconductor valence band edge position (Hoffman et al., 1995).

Photocatalytic degradation kinetics

Pervious results of photocatalytic degradation kinetics indicated that the destruction rates of photocatalytic oxidation of various dyes over illuminated TiO₂ fitted the Langmuir–Hinshelwood (L–H) kinetics model (Cunningham et al., 1994; Oliveira-Campos et al., 2003)

$$r = \frac{dC}{dt} = \frac{kKC}{1 + KC}$$

where r is the oxidation rate of the reactant (mg/l min), C is the concentration of the reactant (mg/l), t the illumination time, k the reaction rate constant (mg/l min), and K is the adsorption coefficient of the reactant (l/mg). When the chemical concentration C_o is small the above equation can be simplified to an apparent first-order equation:

$$\ln\left(\frac{C_o}{C}\right) = kt$$

A plot of $\ln C_o/C$ versus time represents a straight line, the slope of which upon linear regression equals the apparent first-order rate constant k . Generally, first-order kinetics is appropriate for the entire concentration range up to few ppm and several studies were reasonably well fitted by this kinetic model. It has been agreed that the expression for the rate of photomineralization of organic substrates such dyes with irradiated TiO₂ follows the Langmuir–Hinshelwood (L–H) law for the four possible situations:-

- The reaction takes place between two adsorbed substances.
- The reaction occurs between a radical in solution and an adsorbed substrate molecule.
- The reaction takes place between a radical linked to the surface and a substrate molecule in the solution.
- The reaction occurs with both species being in the solution.

In all cases, the expression for the rate equation is similar to that derived from the L–H model, which has been useful in modeling the process, although it is not possible to find out whether the process takes place on the surface, in the solution or at the interface (Tanak and Reddy, 2002).

Conclusion

The photocatalyzed degradation of methyl orange in TiO₂ suspension was carried out using three sources of irradiation Halogen lamp, fluorescent lamp, and sunlight irra-

diation. Five concentrations of methyl orange were used with halogen lamp irradiation and one concentration was used with both fluorescent lamp and sunlight irradiation. The photo-catalytic processes were influenced by the initial concentrations of methyl orange. Color change from orange to colorless is irreversible and the degradation rate of the methyl orange followed the pseudo-first order kinetics. For all irradiation sources used in this study, the photocatalytic degradation of methyl orange using sun light turns out to be the best one.

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