

Wastewater Treatment Using Photocatalysis: Destruction of Methylene Blue Dye from Wastewater Streams

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ABSTRACT

Photocatalytic processes have been suggested as an alternative treatment for water pollutants. Although presently many treatment methods are being used, most of them do not completely destroy the pollutants but only offer phase transfer or partial degradation of the pollutants. In photocatalytic processes, a semiconductor photocatalyst is activated with ultraviolet (UV) irradiation. The activated photocatalyst promotes the formation of hydroxyl radicals, which in turn completely degrades the pollutants. In the present study, an ultraviolet irradiated photoreactor system was used to degrade methylene blue dye in aqueous solutions. The photocatalyst used was titanium dioxide (TiO_2). Experiments were performed with varying catalyst loading, initial concentration of dye, circulation flow rate and air flow rate. Initial reaction rates of dye degradation were used to compare the effect of varying the above variables. The effect of increasing the catalyst loading from 0 to 0.4 wt% showed that an increase in the initial reaction rate, reaching an optimum at catalyst loading of 0.2 wt%. Effect of initial concentration has proven that lower initial concentration resulted in more efficient degradation of the dye. The increase in the initial reaction rate degradation with increasing circulation flow rate confirmed the significant role played by external mass transfer. Introduction of air to the system did not significantly increase in the initial reaction rate when the air flow rate was increased from 0 to 4.0 liter min^{-1} .

Keywords: Effluent treatment, kinetics, photocatalytic process, titanium dioxide, UV irradiation

ABSTRAK

Proses foto-pemangkinan telah dicadangkan sebagai kaedah alternatif terhadap perawatan air sisa. Walaupun terdapat banyak kaedah perawatan air sisa pada masa kini, kebanyakannya tidak memusnahkan bahan pencemar secara lengkap, tetapi hanya menyebabkan perubahan fasa atau pemusnahan bahan pencemar secara separa sahaja. Dalam proses foto-pemangkinan, foto-mangkin semikonduktor diaktifkan dengan radiasi sinaran ultra lembayung (UV). Foto-mangkin yang telah diaktifkan akan menghasilkan radikal hidroksil yang berkebolehan untuk mendegradasikan bahan pencemar. Dalam kajian ini, sistem foto-reaktor yang diaktifkan oleh radiasi sinaran ultra lembayung digunakan untuk mendegradasikan pewarna metil biru

dalam larutan akues. Foto-mangkin yang digunakan adalah titanium dioksida (TiO_2). Ujikaji dilaksanakan dengan mengubah jumlah mangkin yang digunakan, kepekatan awal larutan pewarna, kadar aliran larutan pewarna dan kadar aliran udara. Kadar tindak balas awal proses degradasi pewarna digunakan untuk membandingkan kesan perubahan pembolehubah yang dinyatakan di atas. Peningkatan jumlah mangkin yang digunakan daripada 0 ke 0.4% (peratus berat) telah menyebabkan peningkatan kadar tindak balas awal dan nilai optimum dicapai apabila 0.2% (peratus berat) mangkin digunakan. Kesan kepekatan larutan awal telah membuktikan bahawa pada kepekatan larutan awal yang lebih rendah, proses degradasi pewarna dapat berlaku dengan secara lebih efisien. Peningkatan kadar tindak balas awal proses degradasi dengan peningkatan kadar aliran pewarna, mengesahkan bahawa pemindahan jisim luaran memainkan peranan yang penting dalam proses ini. Pengaliran udara kepada sistem ini tidak meningkatkan kadar tindak balas awal secara signifikan apabila kadar aliran udara dinaikkan daripada 0 ke 4.0 liter min^{-1} .

Kata kunci: Rawatan sisa, kinetik, proses foto-pemangkinan, titanium dioksida, radiasi sinaran ultra lembayung

INTRODUCTION

The rise in water and air pollution throughout the century is the result of toxic chemicals and gases emitted from the various industries. Among the industries involved are petroleum refining, organic chemicals and synthetic industries, milling and coal conversion, pulp and paper manufacturing and textile processing industries (Ollis 1988). Even the use of fuel for heating and transportation, the use of agricultural and domestic pesticides, insecticides, detergents and aerosol sprays have contributed to this ever-growing problem (Serpone 1995). Water pollution, however, has been given more attention by environmentalists and researchers probably due to the large number of publications reporting its effects and damages to human health, animals and the environment.

Currently, there are many processes that are being employed to remove these pollutants. Figure 1 summarizes the various waste treatment technologies for polluted water streams either currently available or in the stages of development. Air stripping, which is commonly employed for the removal of volatile organics while carbon adsorption is usually used for removal of both volatile and non-volatile components. However, air stripping only transfers the pollutants from the water phase to the air phase while in granular carbon adsorption process, the spent carbon emerges as a new pollutant which needs further treatment (Chen & Ray 1998).

Biodegradation is currently the most frequently used method where microorganisms are used to degrade the pollutants or toxins. However, many toxic mixtures are known to be lethal to microorganisms which limit the applicability of the method to cases where well-defined and constant pollutant mixtures can be expected (Bahnemann et al. 1991). Moreover, aerobic biological degradation of pollutants is reported to be inadequate because of the low degradation rate and also due to a non-biodegradable fraction that remains in the contaminated water following the treatment

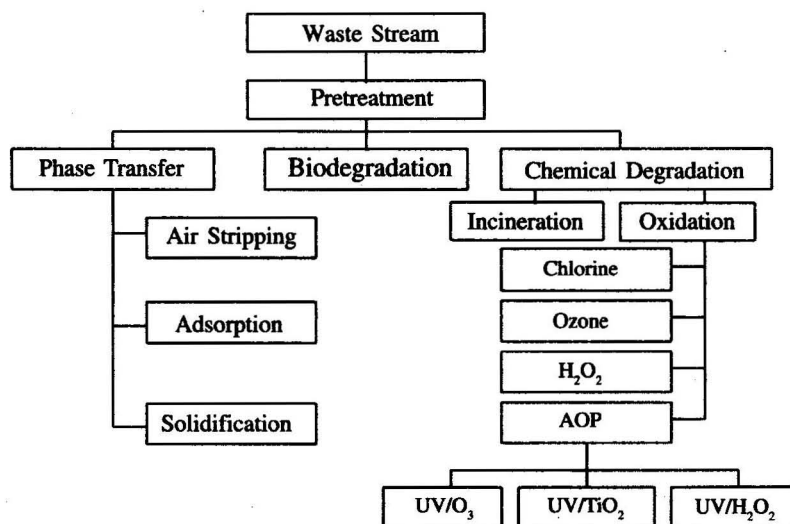


FIGURE 1. Various wastewater treatment technologies

(Donlagic & Levec 1997). Incineration of waste although has been widely used especially by the municipality, is not an ideal treatment as it releases toxic gases into the air.

Oxidation processes that use oxidants such as chlorine, ozone or hydrogen peroxide that do not suffer from the limitations of biodegradation, are generally too expensive for the treatment of vast volumes. Moreover, the formation of side products are often encountered when polluted water is chemically oxidized (Ollis 1988). However, the ultimate goal for any disposal or treatment technique of polluted wastewater should be the elimination of all environmental toxicities. The treatment strategy should be engineered to provide complete mineralization of the pollutants such that the only products that remain are carbon dioxide, salts, water, phosphates, nitrates or other non-toxic material. Due to the set backs of the current available wastewater treatment processes, engineers and scientists face significant challenges in searching for alternative processes.

Among the alternative processes available as shown in Figure 1 are Advanced Oxidation Processes (AOPs) including three photochemical technologies namely, UV-Ozonation, UV-Peroxidation with hydrogen peroxide (H_2O_2) and heterogeneous photocatalysis which have been reported to completely destruct numerous organic pollutants. However, the high cost of generation of ozone and hydrogen peroxide (H_2O_2) has made photocatalysis very attractive, as it requires only an inexpensive photocatalyst such as titanium dioxide (TiO_2), ultraviolet irradiation and atmospheric oxygen rather than ozone or hydrogen peroxide (H_2O_2).

Photocatalysis can be very easily carried out under ambient conditions and leads to the total mineralization of organic carbon to carbon dioxide (CO_2), without the formation of significant photocatalyzed intermediate products (Ollis et al. 1991).

APPLICATIONS OF PHOTOCATALYSIS

Photocatalyzed dehalogenation has been suggested by Carey and co-workers in 1976, who observed the liberation of chloride ions upon illumination of TiO_2 in the presence of chlorinated biphenyls. However, between 1976 and 1983, no progress was made in the field of water treatment using heterogeneous photocatalysis. Pruden et al. in 1983 reported the total mineralization of chloroform (CHCl_3) in aqueous suspensions of TiO_2 to carbon dioxide (CO_2) and hydrochloric acid (HCl). For the first time, the stoichiometric equation for the photocatalytical degradation was written as:

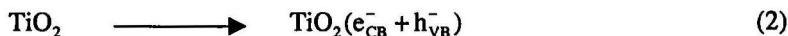


Since then, many classes of compounds including chlorinated aromatics, surfactants, pesticides and herbicides have been reported to undergo photocatalytic degradation (Bahnemann et al. 1994). Some of the organic pollutants that have been successfully degraded using photocatalysis include halogenated hydrocarbons such as chloroform, chlorobenzene, trichloroacetic acid, pentachlorophenol and m-fluorophenol (Serpone 1995). The s-triazine herbicide family such as atrazine, simazine, trietazine, prometon and prometryne were reported to be degradable by Pelizzetti et al. (1990). However, in all cases, the herbicides were singularly resistant to complete mineralization due to the formation of cyanuric acid, which is very stable. Degradations of highly toxic dioxins such as, 2,7-dichlorodibenzo-p-dioxin have also been reported in the literature (Serpone 1995). Textile dyes such as methylene blue, methyl orange, Congo Red, Malachite Green have been reported to have undergone photocatalytic de-colourisation (Reeves et al. 1992). Studies have also proven that anionic, cationic and non-ionic surfactants can be fully mineralized by photodegradation (Ollis 1988).

PHOTOCATALYSIS THEORY

In a solid, the electrons will occupy energy bands due to the extended bonding networks. However, for the case of semiconductors, a band gap, E_{bg} , which is a region devoid of energy levels separates the highest occupied energy band (Valence Band, VB) and the lowest occupied energy band (Conduction Band, CB). This specific electronic structure possessed by semiconductors enable them to act as photocatalysts in the photodegradation processes. (Mills et al. 1993)

A semiconductor can be activated by photons with of energy, $h\nu$ equal or greater than the band gap energy, E_{bg} , of the semiconductor. Upon illumination, the semiconductor absorbs a photon onto its surface, causing excitation of an electron from the Valence Band to the Conduction Band (CB) thereby forming a positive hole, h^+ in the Valence Band (Bahnemann et al. 1991). This process is illustrated by the following equation using titanium dioxide as the photocatalyst.



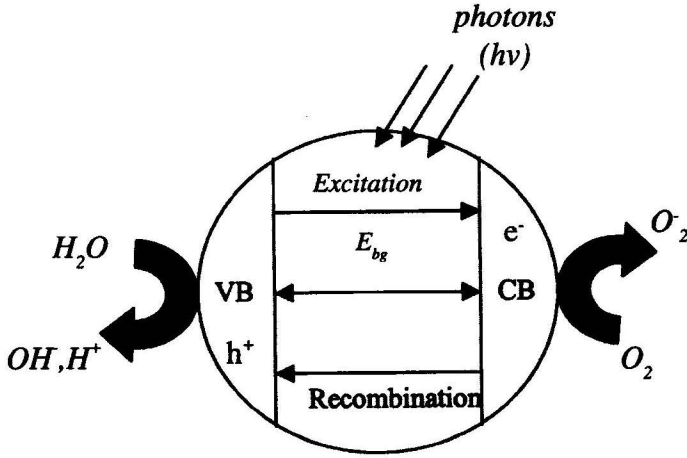


FIGURE 2. Electron-hole pair generation in an irradiated TiO_2 particle and consecutive reactions.

The electron-hole pair generation in an irradiated semiconductor photocatalyst is illustrated in Figure 2.

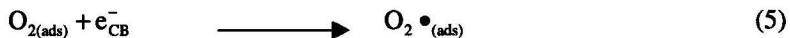
The concentration of the electron-hole pair in the semiconductor particle depends on the illumination intensity and the electronic characteristics that prevent the recombination of the holes and electrons and release of the absorbed energy. The threshold wavelength required for the excitation of the semiconductor can be determined from the following equation:

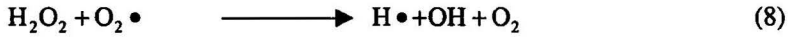
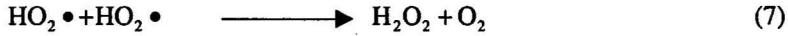
$$\lambda_{bg}(\text{nm}) = \frac{1240}{E_{bg}(\text{eV})} \quad (3)$$

The positive holes that are generated have very high affinity for electrons and therefore are very strong oxidizing agents. However, the recombination process as described below occurs due to absence of suitable electron and hole scavengers, thus dissipation the input energy only in a few nanoseconds (Chen & Ray 1997).

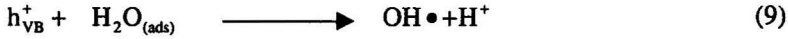


Therefore to keep the holes available for oxidation, the recombination process must be prevented. The electrons that are formed must be promptly removed by an electron acceptor such as oxygen which reacts with the photogenerated electron through the following equations (Chen & Ray 1997):





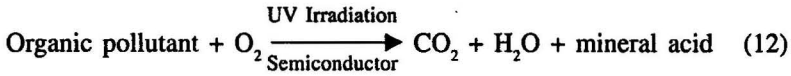
After migrating to the surface of the semiconductor, the photogenerated holes oxidize and absorb water molecules or hydroxide ions according to the following reactions (Gerischer and Heller, 1991):



The photogenerated hydroxyl radical ($\text{OH} \bullet$) is very reactive and reacts rapidly and non-selectively in the oxidation of organic compounds. Its high oxidation potential (2.8V) enables it to oxidize most of the organic species into carbon dioxide and their mineral acids as shown below (Chen & Ray 1997):



Therefore, the overall equation of the photocatalytic reaction can be written as:



KINETIC MODEL

The photocatalytic degradation of organics has been modeled using different kinetic models. However, the most common rate equation is given by equation (13) (Ollis 1988).

$$r = \frac{kKC}{1 + KC + \sum K_i C_i} \quad (13)$$

For initial stages of the reaction, where intermediate or product formation (C_i) is not significant, the term $\sum K_i C_i$ can be neglected, thus reducing the above model to a rate model represented by equation (14).

$$r_o = \frac{kKC_o}{1 + KC_o} \quad (14)$$

where r = rate of reaction ($\text{mol liter}^{-1} \text{min}^{-1}$)
 r_o = initial rate of reaction ($\text{mol liter}^{-1} \text{min}^{-1}$)
 k = reaction rate constant ($\text{mol liter}^{-1} \text{min}^{-1}$)
 K = adsorption equilibrium constant ($\text{mol}^{-1} \text{liter}^{-1}$)
 C_o = initial concentration (mol liter^{-1})

The objective of the present work is to study the photocatalytic degradation of methylene blue dye using a photocatalytic reactor that was

fabricated. Various parameters affecting the degradation process such as catalyst loading, initial concentration of dye, circulation flow rate and air flow rate were also studied.

EXPERIMENTAL

EXPERIMENTAL SETUP

Many photoreactor designs have been reported in the literature. Many of the earlier studies were carried out in recirculating differential conversion photoreactors (Pruden & Ollis 1983), batch photoreactors (Chen & Chou 1993) and glass spiral photoreactors (Hua et al. 1995). Reactor design is now taking an important role in photocatalysis studies as researchers aim to improve the photocatalytic efficiency by addressing parameters such as light distribution. Among the new reactor designs are the swirl-flow reactor (Ray & Beenackers 1997) and the distributive type photoreactor (Ray & Beenackers 1998).

In the present study, an ultraviolet photocatalytic reactor system was constructed as shown in figure 3. The photoreactor in this system is an annular photoreactor consisting of an outer shell constructed using stainless steel having a diameter of 10.2 cm, illuminated length of 74.5 cm and volume of 1.14 liters. The UV Light was placed in the axis of a reactor and is separated from the solution by a quartz sleeve (22 mm diameter, 1.5 mm thickness). The UV unit consisted of a UV Ballast and Fluorescent Tube provided by Aquafine Corporation and was modified from an Ultraviolet Water Treatment Unit. The unit produced UV irradiation at a constant wavelength of 254 nm at an intensity of 13.5 mW cm^{-2} . A 20 liter stainless steel tank was used to store the feed solution. A magnetic drive pump was used for circulation of the solution through the system. The circulation flow rate was controlled using a rotameter. Stainless steel piping was used in the system. The solution was agitated using a laboratory mixer. Temperature of the solution was constantly monitored using a thermocouple.

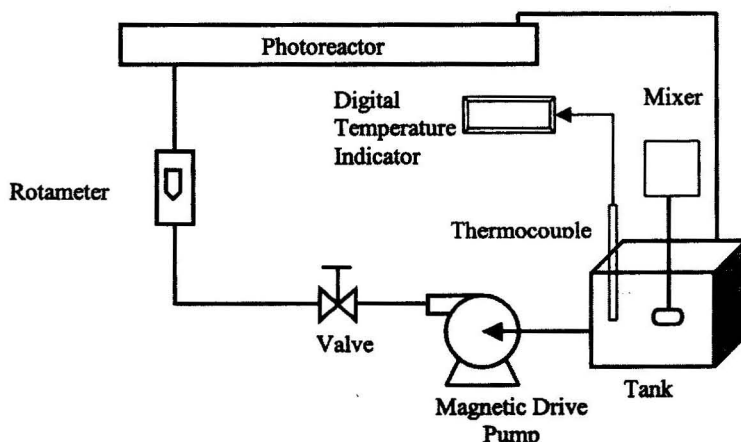


FIGURE 3. Schematic diagram of the experimental setup

MATERIALS

The model dye component used was methylene blue, a water-soluble heterocyclic textile dye obtained from Fluka Chemie. Laboratory grade TiO_2 with average particle size of less than 1.2 μm and surface area of 7.7 m^2/g obtained from BDH Laboratory Supplies was used as the photocatalyst.

ANALYSIS

Methylene blue dye concentration was measured using a Hitachi U-2000 Spectrophotometer. The calibration curve was prepared using solutions of known concentration with an analytical wavelength of 664 nm. The plot obtained obeyed the Beer-Lambert with high precision from 0 to 20 ppm. For higher concentrations, samples were first diluted. Samples were taken at suitable time intervals by removing 5 ml samples from the tank. The samples were then centrifuged before measurement of concentration. Light intensity was measured using a Cole-Parmer Digital Radiometer fitted with a 254 nm UV Sensor.

EXPERIMENTAL PROCEDURE

Experiments were carried out using the system described earlier. Before each experiment the system was flushed with water. For each run, 2.5 liters of dye solution was used. The UV Unit was switched on for at least 20 minutes before the start of the experiment to ensure ample time for the fluorescent tube to be heated up in order to produce UV irradiation at a constant intensity. After the start of the experiment, the system was then left to circulate as samples were taken at appropriate intervals. The parameters varied were catalyst loading, circulation flow rate, initial dye concentration and air flow rate.

RESULTS AND DISCUSSION

EFFECT OF PHOTOCATALYSIS ON METHYLENE BLUE DYE

The effect of photocatalysis was studied by carrying out an experiment with an initial methylene blue dye concentration of 25 ppm, catalyst loading of 0.1 wt% TiO_2 and circulation flow rate of 1.6 $\text{liter}\cdot\text{min}^{-1}$. Figure 4 illustrates the results of a typical experiment when the reactor system was flushed and all the piping were thoroughly cleaned to remove any adsorbed dye. In the first section of the graph, where no catalyst or UV irradiation is introduced, the decrease in concentration is caused by the adsorption of the dye onto the system. In the next section, where the catalyst was added to the system, without the presence of UV irradiation (dark reaction), the degradation was caused by the adsorption of the dye onto the surface of the catalyst. In the following part, where UV irradiation is introduced, a rapid decrease was observed. In this part, the actual photocatalytic reaction took place.

REACTION SCHEME

The photocatalytical degradation of methylene blue dye can be illustrated by equation (15). From the reaction scheme, the photocatalytic degradation of

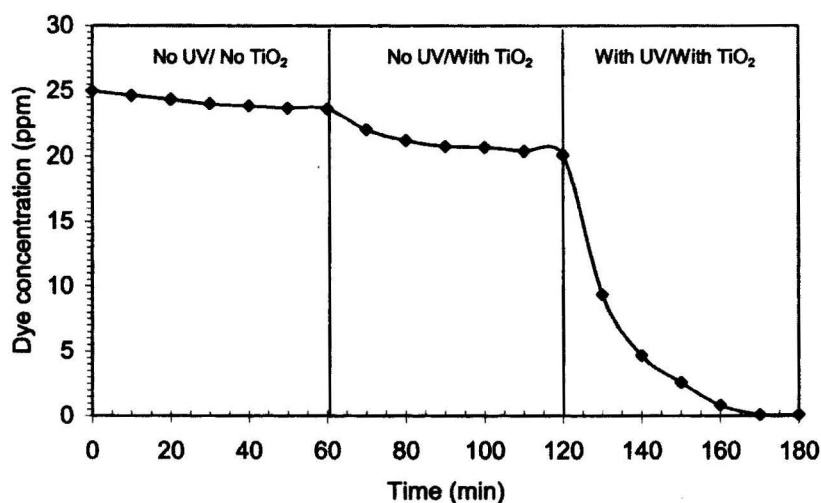
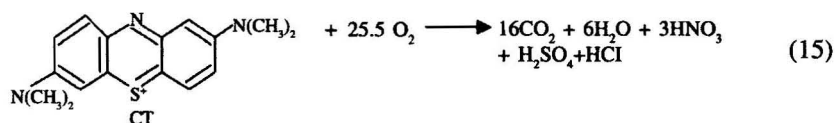


FIGURE 4. Degradation profile showing dye adsorption by the system, dark reaction (no UV) and photocatalytic reaction.

methylene blue dye will liberate hydrochloric, sulfuric and nitric acids. However, the acids formed are only in concentration of ppm level since the initial dye pollutant is at ppm level. Therefore if there is any environmental consideration for the acids formed, then products may be first neutralized with low concentration of alkali before being released.



EFFECT OF CATALYST LOADING

Since the photocatalytic reaction takes place on the surface of the catalyst, the number of available sites for the adsorption of the pollutants will affect the photodegradation process. To study the effect of catalyst loading on the photocatalytic system, the catalyst loading was varied from 0.025 to 0.4 wt%. It can be observed from figure 5 that the initial reaction rate increased as the catalyst loading was increased from 0 to 0.2 wt% due to the increase in the number of available sites for dye adsorption. Further increase in catalyst loading did not result in higher initial reaction rates. Although increasing the loading above 0.2 wt% increased the available sites for dye adsorption, the irradiation intensity remained constant. Therefore, there was no increase in hydroxyl radical formation as the incident photons were almost absorbed. As the hydroxyl radicals were responsible for the degradation of dyes, consequently, there was no increase in the initial reaction rate. In previous studies, the optimum loading of the photocatalyst usually ranges from 0.05 to 0.5 wt% for different pollutants, light intensities and reactor configurations (Chen & Ray 1997).

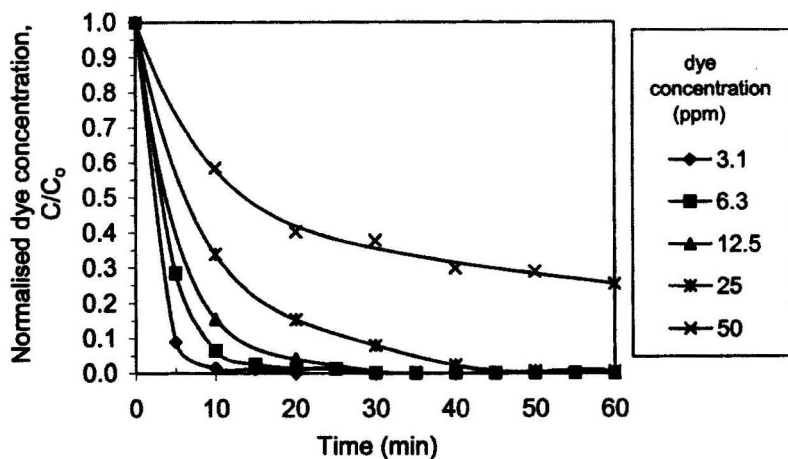


FIGURE 5. Effect of catalyst loading. Initial concentration of methylene blue = 25 ppm, Circulation flow rate = 1.6 liter min^{-1}

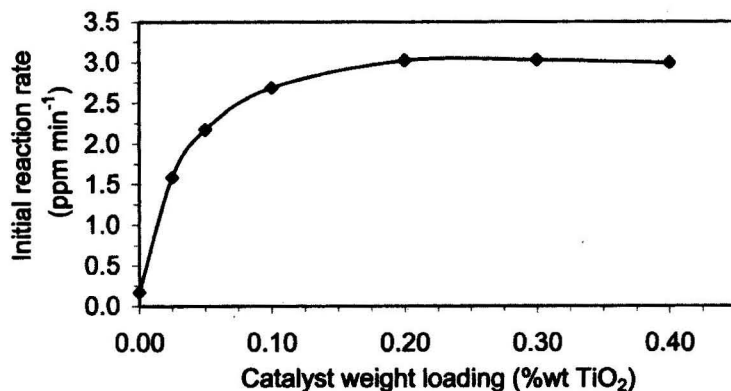


FIGURE 6. Effect of initial concentration of methylene blue. Catalyst loading = 0.1 wt% TiO_2 , Circulation flow rate = 1.6 liter min^{-1} .

EFFECT OF INITIAL CONCENTRATION

In the treatment of pollutants, the initial concentration of the pollutant is an important parameter as it may affect the efficiency of the treatment process. Therefore to investigate the effect of initial concentration on the photodegradation of methylene blue, experiments were carried out with varying the initial concentration from 3.1 to 50.0 ppm. Figure 6 shows the decrease of normalized methylene blue dye concentration against time at various initial concentration of the dye. It is clear, from the figure that the increase in initial concentration of methylene blue dye resulted a drop in the photodegradation efficiency of the dye.

This observation could be explained by considering that when the initial concentration is increased, the amount of dye molecules adsorbed onto the surface of the catalyst also increases. However, the light intensity and

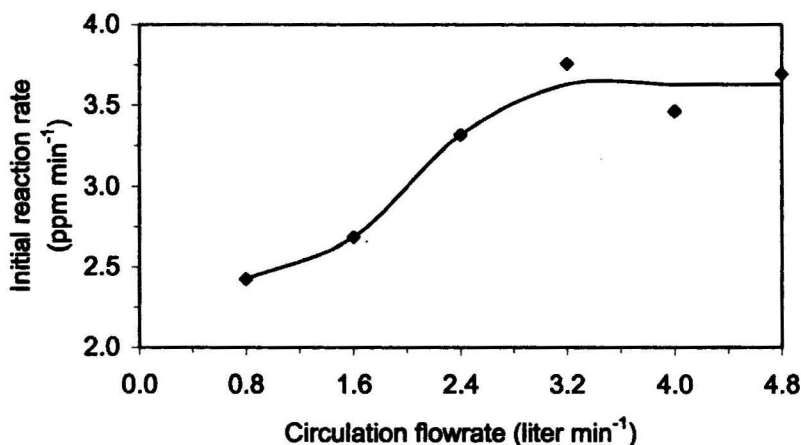


FIGURE 7. Effect of circulation flow rate. Initial concentration of methylene blue = 25 ppm, Catalyst loading = 0.1 wt% TiO_2 .

irradiation time remained the same resulting the number of hydroxyl radicals needed for photocatalytic activity formed on the surface of the catalyst to remain constant.

Therefore, if the initial concentration is increased, the relative ratio of hydroxyl radicals attacking the dye molecules decrease, thus decreasing in the photocatalytic efficiency (Mengyue et al. 1995).

EFFECT OF CIRCULATION FLOW RATE

Kinetics studies using photocatalysis are usually carried out in recirculating systems, therefore the effect of circulation flow rate must be investigated. The effect of circulation flow rate was investigated by varying the circulation flow rate from 0.8 to 4.8 liter min^{-1} . From figure 7, the initial reaction rate was found to increase almost linearly when the solute flow rate was increased from 0.8 to 3.2 liter min^{-1} and reached a plateau at 3.2 liter min^{-1} . Further increase in circulation did not have any substantial effect on the initial rate. These results show that at low circulation flow rates, mass transfer resistance played an important role and the rate was found to be dependent on the flow rate. At higher flow rates, more than 3.2 liter min^{-1} , the external mass transfer resistances were absent.

EFFECT OF AIR FLOW RATE

Dissolved oxygen is essential to continue the Redox reaction in photocatalytic processes in order to maintain the electro-neutrality of the reacting system. If no oxygen is present in the system, the positive holes formed on the catalyst particle will recombine with the electron to produce heat resulting in energy loss. An electron scavenger is needed and oxygen is the most common scavenger used in photocatalytic processes (Wang et al. 1992). Considering commercial applicability, air instead of pure oxygen can be used as it has been reported that in closed systems, the degradation rate saturated by air was about 70% of that saturated by pure oxygen.

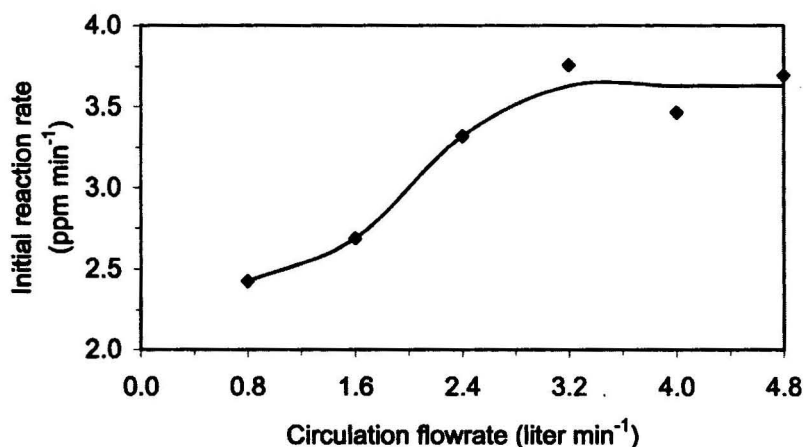


FIGURE 7. Effect of circulation flow rate. Initial concentration of methylene blue = ppm, catalyst loading = 0.1 wt% TiO_2

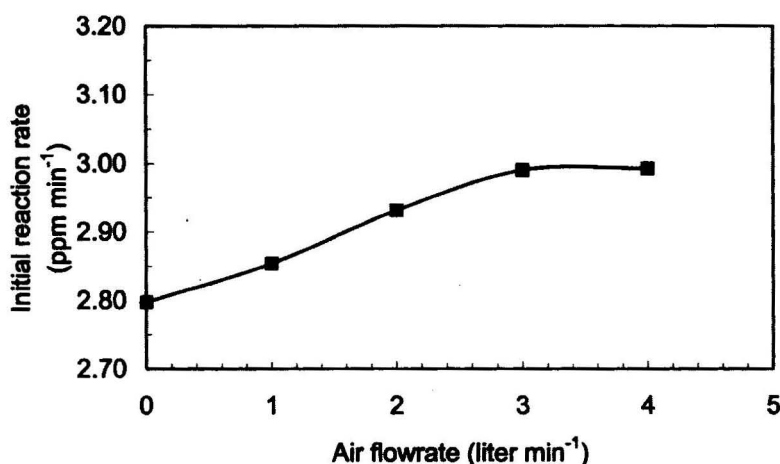


FIGURE 8. Effect of air flow rate. Initial concentration of methylene blue = 25 ppm, Catalyst loading = 0.1 wt% TiO_2 , Circulation flow rate = 1.6 liter min⁻¹.

However, no reports have been made for the effect of introduction of air or oxygen for the case of open systems. Therefore, the above effect was investigated by bubbling air instead of pure oxygen into the system using an air pump that delivers air at a constant air flow rate. In this study, the air flow rate was varied from 0 to 4 liter min⁻¹ using a variable flow meter. It is clear from Figure 8 that the initial reaction rate slightly increased when the air flow rate was increased from 0 to 3 liter min⁻¹ but further increment had no effect on the initial reaction rate. However, the increase was found to be insignificant.

This observation suggests that the concentration of dissolved oxygen in the dye solution was already at saturation. Hence, it can be established that for open systems, no introduction of air or oxygen is necessary.

CONCLUSIONS

Photocatalysis has proven to be a promising technology in the treatment of wastewater contaminated with organic pollutants. The photocatalytic process involves the excitation of a semiconductor particle using UV irradiation, which generates an electron-hole pair. The photogenerated hole through a series of reactions produces a hydroxyl radical, which due to its high oxidation potential, degrades organic pollutants in wastewaters. In the present study the optimum catalyst weight loading for the degradation of methylene blue dye was 0.2 wt %. Any further increase in catalyst weight loading did not enhance the photocatalytic degradation of the dye. The circulation flow rate was found to affect the initial rate of reaction for the photocatalytic degradation of methylene blue dye. The increase in circulation flow rate from 0.8 to 3.2 liter min⁻¹ increased the initial reaction rate showing the presence of external mass transfer. The initial concentration of the methylene blue dye was found to affect the degradation of the dye. Higher initial concentration resulted in lower degradation efficiencies. Introduction of air to the system did not show any significant enhancement to the degradation of the dye.

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NOTATIONS

<i>C</i>	Concentration (mol.liter ⁻¹)
<i>E</i>	Energy (eV)
<i>e⁻</i>	Electron
<i>h</i>	Planck's constant, 6.6 x 10 ⁻³⁴ J.s
<i>h⁺</i>	Positive hole
<i>l</i>	Wavelength (nm)
<i>k</i>	Reaction rate constant (mol.liter ⁻¹ .min ⁻¹)
<i>K</i>	Adsorption equilibrium (mol ⁻¹ .liter ⁻¹)
<i>r</i>	Rate of reaction (mol.liter ⁻¹ .min ⁻¹)
<i>n</i>	Frequency, s ⁻¹

Subscript

<i>bg</i>	band gap
<i>ads</i>	adsorption
<i>0</i>	initial
<i>i</i>	product species

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