Photocatalytic degradation of methyl orange as a model compound

Siham Al-Qaradawi, Salman R. Salman*

Faculty of Science, Chemistry Department, University of Qatar, P.O. Box 2713, Doha, Qatar

Abstract

Titanium dioxide (TiO_2) was used as a photocatalyst for the detoxification of water containing methyl orange (MO), which was used as a model compound. Solar radiation was used as an irradiation source. It was found that there was no degradation for the MO in the dark and in the presence of TiO_2. Also no degradation was observed for MO when the solution placed under solar radiation but without TiO_2. Several experiments were used to optimize the experimental parameters. In the first set of experiments variable amounts of TiO_2 were used with a fixed concentration of MO. It was found that 0.4% of TiO_2 gave the highest degradation rate constant, $0.619\,h^{-1}$. In the second set of experiments TiO_2 concentration was fixed at 0.4% and the MO concentration was varied, the highest rate constants was obtained when the concentration of MO was $4 \times 10^{-5}\,M$ and it was found to be $0.639\,h^{-1}$. The degradation became negligible in the presence of high concentrations of MO. The highest degradation rate was obtained at pH = 3 with a rate constant $\kappa = 2.6683\,h^{-1}$, followed by that at pH = 9 where the calculated $\kappa = 0.7585\,h^{-1}$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Titanium dioxide; UV–visible spectroscopy; Methyl orange; Solar radiation; Degradation rate constant; Photocatalysis; First order kinetics; Effect of concentration; Effect of solar energy; Effect of changing pH

1. Introduction

Water resources are limited in developing countries and there is a great need to recycle water and to reuse it in agriculture and industry. Solar energy is abundant in most developing countries. Solar energy intensity in the gulf region is quite suitable and can be used as a source for the photocatalytic detoxification of polluted water. This process may prove to be economically and technologically feasible [1–3] for water treatment and detoxification of wastewater [4].

Photocatalysis has received growing interest over the last few years. Titanium dioxide (TiO_2) is generally considered to be the best photocatalyst, and has the ability to detoxificate water from a number of organic pollutant [5]. Anatase TiO_2 has a wide band gap, $E_g \approx 3.2\,eV$ [6], thus, only light below 400 nm is absorbed and capable of forming the e^-/h^+ pair [7].

Photocatalysis is a potential technology for the destruction of organic contaminants in water such as aromatic compounds which present a potential hazard to the environment. Oxidation of organic compounds in aqueous solution is achieved by the reactive hydroxyl radical.

Different compounds have been mineralized by using photocatalysts, among them are hydrocarbons [8], phenols [9,10], chlorinated phenols [11,12], and chlorinated aliphatic compounds [13,14]. Carboxylic acid [15], and herbicides [16]. The primary oxidant responsible for most heterogeneous photocatalytic oxidation (HPCO) processes is the hydroxyl radical, which is formed by the reduction reactions of holes with water or hydroxide ions. The mechanism of the formation of the hydroxyl radical is well discussed in the literature [17–22].

In the case of TiO_2 the photocatalytic activity is influenced by a wide variety of factors such as, specific surface area, the adsorption affinity and capacity for organic contaminants, electron–hole recombination processes in the bulk and on the surface of the catalyst, intensity and spectral distribution of the illuminating light [14,23] crystal morphology, intrinsic solid state defects, stoichiometry of the catalyst oxide [24], pH [25,26], the presence of electron acceptors [13] and the concentration of the pollutants. In addition, photo-reactor design, operational conditions, and constituents in the water matrix also influence the overall efficiency of HPCO processes.

The aim of the present work is to explore the possibility of using solar radiation for the detoxification of different pollutants. Methyl orange (MO) was used as a model compound because it was possible to use UV–visible spectroscopy to monitor the degradation under different conditions such as MO concentration, pH, TiO_2 concentration and solar intensity.

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* Corresponding author.
E-mail address: srsalman@qu.edu.qa (S.R. Salman).

2. Experimental

MO was chosen as a model compound. This compound is orange in basic medium and red in acidic medium. When dissolved in water the UV–visible spectrum show two maxima. The first at 270 nm and the second at 465 nm. Different concentrations of MO were prepared ranging between 2×10^{-3} and 1×10^{-5} M. Those concentrations were within Lambert–Beers's law. 0.5 l three neck round bottom flasks were used as reactors. Optimum amount of TiO$_2$ was sonicated using Camlab Transonic T460/H and placed in the reactor. An optimum concentration of MO was placed in the reaction vessel and the mixture was placed at the same position all the time and the solar intensity was measured. The solution was stirred and the solution was left to exchange oxygen with the environment. The pH variation was measured at definite intervals and at the end of the reaction. After the elapse of 1–5 h a small quantity of the solution was taken and left in the refrigerator for TiO$_2$ to settle down.

The measurements were performed for the clear solution. TiO$_2$, anatase (Aldrich) was used through out this work and it was heated at 120 °C for 1 day before use. MO was of pure grade (BDH) and was used without purification. Double distilled water was used in this work. pH was measured using (Elico LI 120). The UV/Vis spectra were recorded on a Perkin-Elmer lambda 2S spectrophotometer, using 1 cm fused silica cells. TiO$_2$ was heated and homogenized with distilled water using sonification techniques. The solar intensity was measured using Solar Data Pomona, California, USA, Model 815 W, time integrated, W h/m^2.

3. Results and discussion

To standardize our procedure the same concentration of MO was used with the same type of reaction vessel. The vessel was situated at the same site through out this work.

The UV–visible for MO in distilled water show two absorption maxima (Fig. 1). The first band observed at 270 nm and the second band at 465 nm. The band at 465 nm was used to monitor the effect of the photocatalysis on the degradation of MO.

To study the optimum conditions and the effect of different parameters on the degradation of MO under solar radiation the following experiments were performed. Degradation decay follow a first order kinetics. From the slopes of ln (concentration vs. time) the apparent first order rate constants have been determined and presented in Tables 1–5.

3.1. Effect of solar radiation without TiO$_2$

The reaction vessel was exposed to solar radiation for 5 h in the absence of TiO$_2$. It was noticed that MO is quite stable under solar conditions and the rate constant for the decay of MO was calculated to be 0.0072 h^{-1}.

Table 1
Rate of degradation (h^{-1}) under different conditions

	MO		
	Mixture A	Mixture B	Mixture C, December 2000
TiO$_2$	2 g	–	2 g
Sunlight	Yes	Yes	Dark
κ (465 nm)	0.3491	0.0078	−0.0075
κ (270 nm)	0.1099	0.0072	0.0031

Table 2
The effect of different quantities of TiO$_2$ on the rate constant κ of degradation, July 1999, amount of sunlight in 5 h: 4480 W h/m^2

Amount per 0.5 l	κ (465 nm)	R^2
20 g TiO$_2$	0.3728	0.96
10 g TiO$_2$	0.3988	0.96
5 g TiO$_2$	0.2886	0.96
4 g TiO$_2$	0.4009	0.90
3 g TiO$_2$	0.5937	0.98
2 g TiO$_2$	0.6196	0.97
1 g TiO$_2$	0.5363	0.98

Table 3
The rate constant κ of degradation of TiO$_2$ (h^{-1}) in different time with different solar intensities W h/m^2

Month	First order rate constant	Solar intensity
July 1999	0.6195	4480
November 1999	0.367	2535
December 1999 (cloudy)	0.2455	2177
January 2000	0.3314	3060
February 2000	0.6489	3419
March 2000	0.7953	4255
April 2000 (cloudy)	0.3657	2760
May 2000	0.5445	4814
June 2000	0.4645	3969
October 2000	0.3491	3970
November 2000 (cloudy)	0.3855	2173
December 2000	0.3134	3955
January 2001	0.4923	3474
February 2001	0.7045	3022
March 2001 (cloudy then sunny after 3 h)	0.4861	2800
April 2001	0.2009	2990
May 2001	0.4456	4325
June 2001	0.9449	4270

Table 4
Effect of pH on the rate of degradation (h^{-1}) during May 2001

pH of reaction mixture	κ (465 nm)	R^2
pH = 3	2.6683	0.98
pH = 5	0.547	0.90
pH = 7	0.6377	0.95
pH = 9	0.7585	0.94
Normal experiment, pH = 6.5	0.4456	0.97
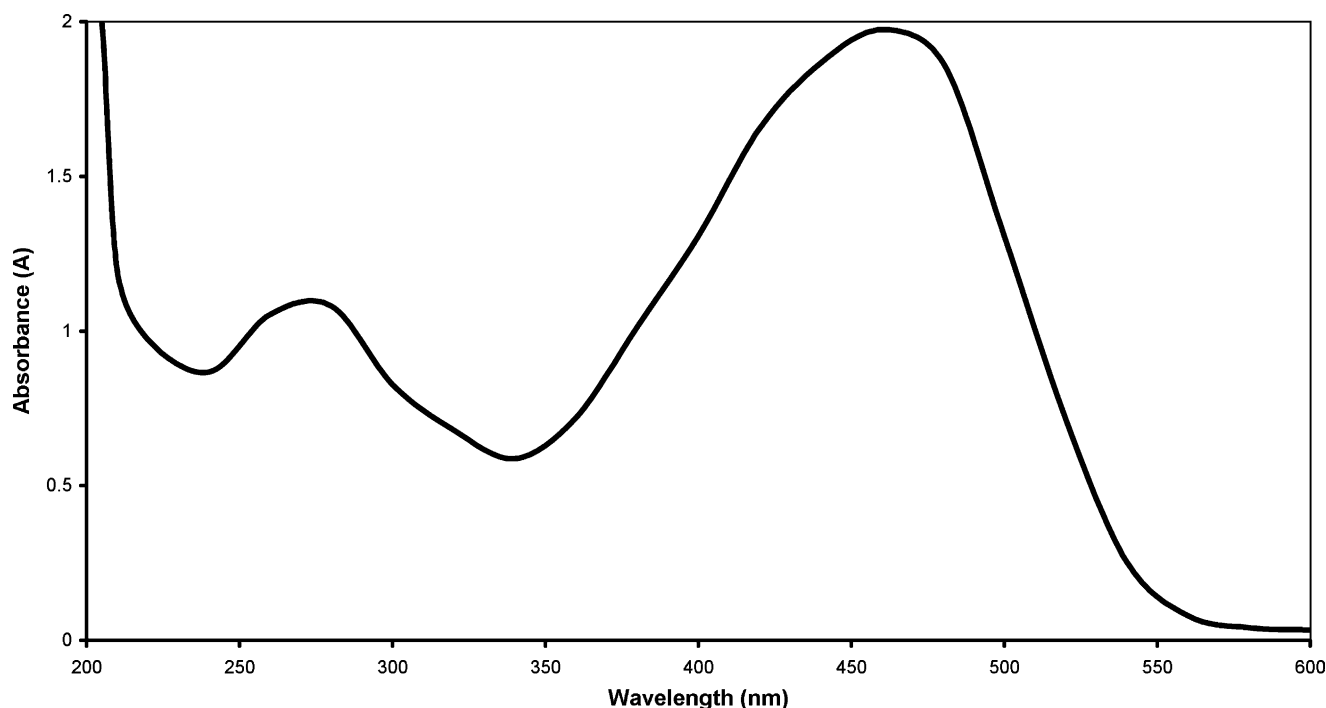
Fig. 1. The UV–visible spectrum of MO.

Table 5
Variation of pH after the reaction

	pH					
	Before irradiation	After 1 h	After 2 h	After 3 h	After 4 h	After 5 h
pH = 3	3.0	3.2	3.1	3.2	3.2	3.0
pH = 5	5.2	6.8	4.7	4.5	4.5	4.2
pH = 7	6.8	7.2	5.5	4.6	4.7	5.9
pH = 9	8.6	7.4	6.7	6.1	6.4	6.4
Normal experiment	6.8	6.3	6.0	5.5	5.0	4.8

3.2. Effect of TiO₂ in the absence of solar radiation

The reaction vessel containing TiO_2 was kept in the dark for 10 h. No decay was observed under these conditions (Table 1).

3.3. TiO₂ concentration optimization

To optimize the concentration of TiO_2 needed for the highest degradation rate the following quantities were used starting from 20 g/0.5 l (Table 2). It was noticed that the best results were obtained when the ratio of TiO_2 to solution was 2 g/0.5 l was used (0.4%) (Fig. 2). This quantity will be used throughout this work.

It is interesting to note from Fig. 3 that the absorption of the visible band at 465 nm decreased with time and that a new band started to form at 320 nm and another at 270 nm.

After 1 h the band intensity at 465 nm started to decrease and the band intensity at 270 nm increased. After 3 h the band intensity at 465 and 270 nm started to decrease. After 5 h the bands at 465 and 270 nm disappeared and only one strong band at 254 nm increased with time, decreasing after 3 h.

This trend suggests that the extended aromatic MO absorbs at 465 nm and the aromatic ring absorb in the range 200–270 nm. In the first period the polyaromatic rings in MO start to degrade creating a mono substituted aromatics thus the band at >200 nm increase in intensity and a new band at 320 nm appear. After 2 h both bands at 270 and 465 nm start to decrease and the band at >200 decrease also. This indicates that MO starts to degrade and that CO_2 and H_2O start to form.

3.4. Effect of time and solar intensity

It was observed that a complete degradation of MO was achieved within 5 h using 0.4% of TiO_2. This concentration was used throughout the course of the investigation. The experiments were repeated each month for a period of 1.5 year. The radiation intensity received by the sample was measured (Table 3). It is interesting to note that the degradation rate reach its maximum in March 2000 and June 2001. It is notice from Table 3 that there is no direct correlation between radiation intensity and rate constant of degradation, but in general the high rate of degradation needs a limiting number of photons and that even on cloudy days the rate of degradation is high. It has been reported, that the photon efficiency of the photocatalytic DCA degradation
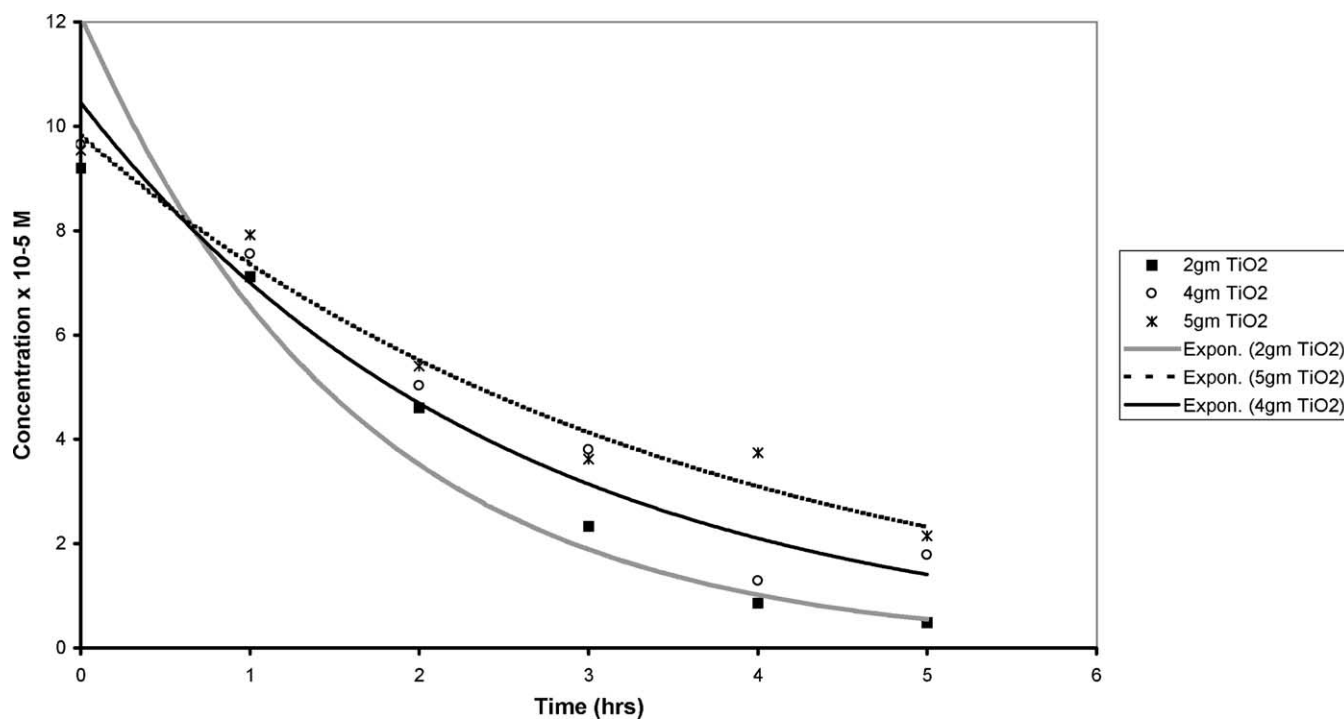
Fig. 2. Decay curves for different concentration of TiO_2 in 0.5 l of solution.
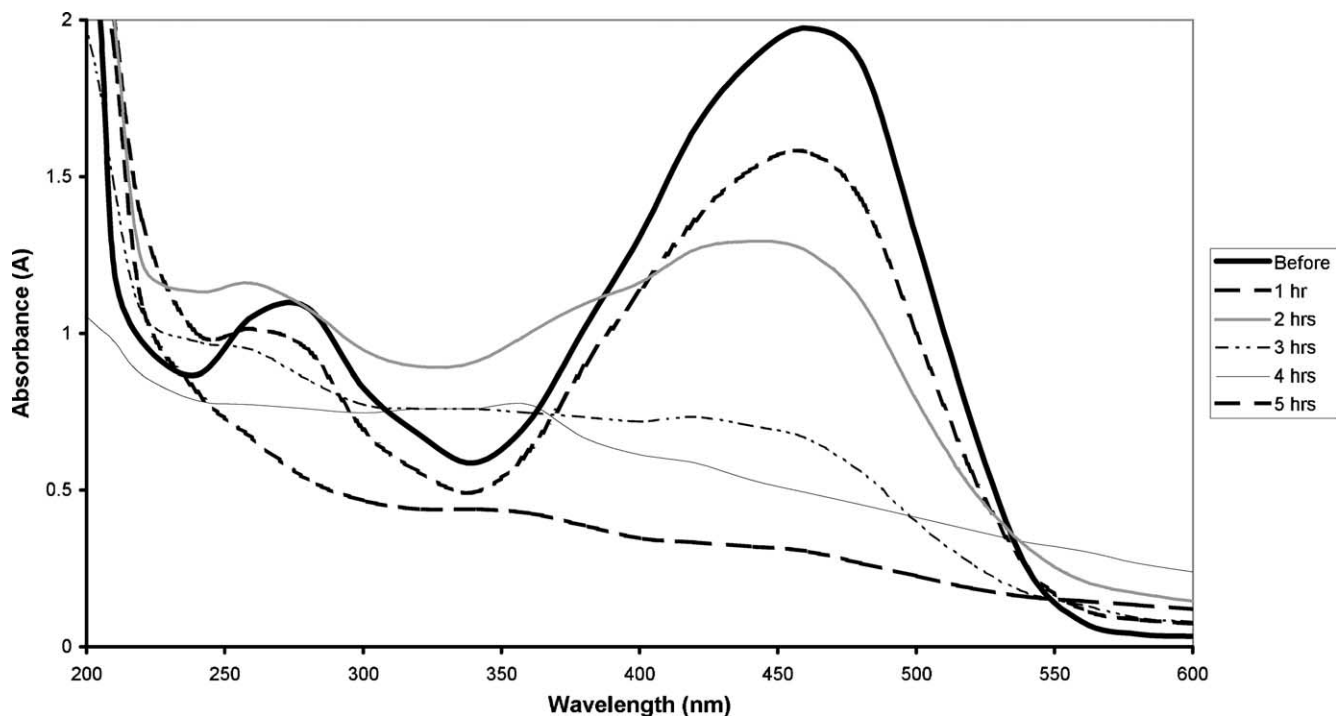

Fig. 3. The UV–visible spectra of MO at different time intervals.

considerably decreases as the light intensity is increased [27,28]. It is observed that this reaction is very sensitive to time, therefore two flasks containing the same amount of TiO_2 and MO were exposed to solar energy in the same day in June 2001. The first was exposed in the morning at 8:00 h and the rate constant κ was $0.9448 \, h^{-1}$ and the measured solar intensity was $4270 \, W \, h/m^2$. The second reactor was exposed to light in the morning at 11:00 h, and the measured rate constant κ was $0.6819 \, h^{-1}$ and the solar intensity was $3700 \, W \, h/m^2$.
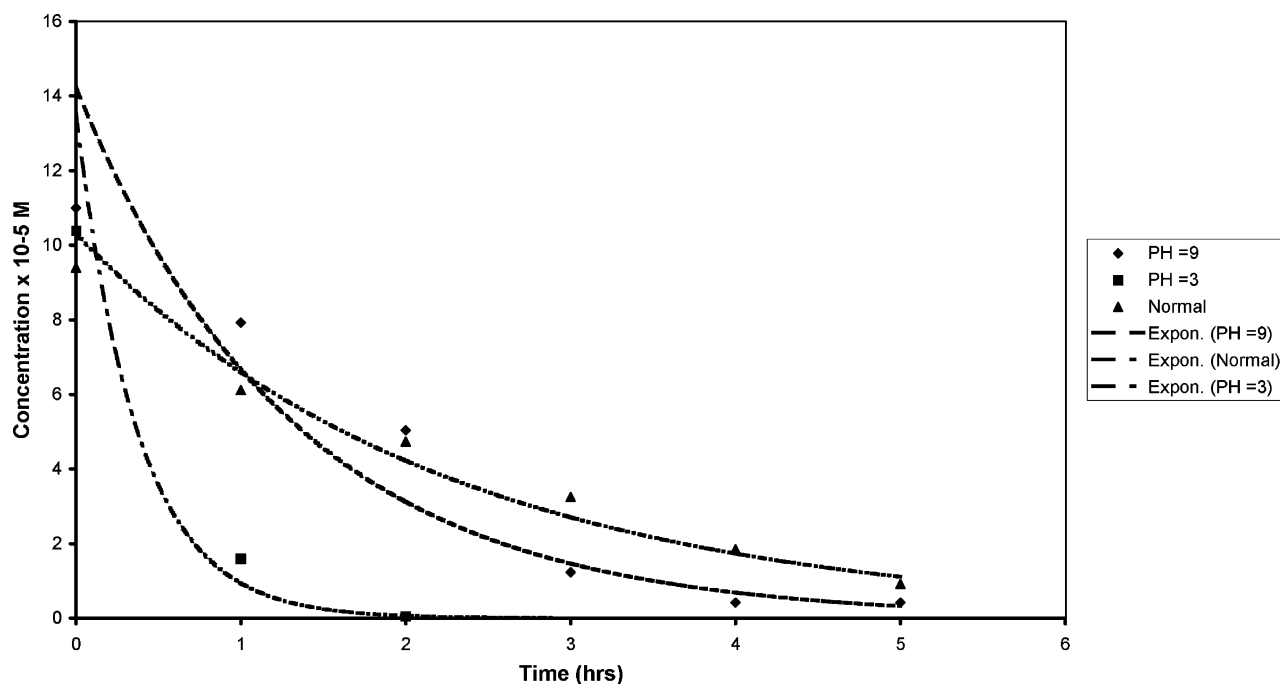
Fig. 4. The decay curves for MO at different pH.

3.5. Effect of changing pH

The pH of the solutions which include 2 g TiO$_2$ and a fixed concentration of MO (8×10^{-5} M) were varied. The experiments were performed at the same time. Best degradation was obtained with pH = 3 followed by pH 9 (Table 4, Fig. 4). The pH changed during irradiation toward a more acidic solution, except at pH 3 where there was no pH change (Table 5).

It appears that the effect of pH on the degradation of the pollutants is variable and controversial [29], for example the photocatalytic degradation rate of CHCl$_3$ at pH 8–9 is about 10 times higher than that at pH 3.8 [30]. Similar results were obtained for CCl$_4$ when the degradation is much higher at pH 10 and 11 than that at pH = 2.

It is expected that the degradation rate increases with high pH value, therefore at basic medium the number of hydroxyl radical in solution will increase at the surface of TiO$_2$ particles by trapping photo induced holes [31].

In our case the highest degradation rate was achieved at pH = 3. Similar results were previously observed for the photodecomposition of 3-chlorophenol which was explained on the basis that at low pH HO$_2$ radicals will form, and this will compensate for the effect of decreasing hydroxyl ions concentration [29]. Also if it is assumed that the oxidation attack of the hole is the rate determining step then this will lead to an increase oxidation at low pH [30].

3.6. Effect of MO concentration

Different MO concentration were used ranging from 2×10^{-3} to 1×10^{-5} M. It was found that the best degradation

Table 6
Effect of concentration on the degradation rate (h^{-1}) during April 2001

[MO] April 2001	κ (465 nm)	R^2	pH (before reaction)	pH (after reaction)
2×10^{-3} M	0.0412	0.94	6.4	6.1
4×10^{-4} M	0.1329	0.96	6.4	6.0
8×10^{-5} M	0.2010	0.98	6.5	6.1
4×10^{-5} M	0.6393	0.92	6.5	6.4
1×10^{-5} M	0.2912	0.90	5.9	6.2

was obtained with 4×10^{-5} M (Table 6, Fig. 5). The degradation efficiency increased with decreasing concentration of MO. This is different from the results which were obtained for the degradation of CCl$_4$ where the degradation increase with increasing the initial concentration of CCl$_4$ [32]. It seems that in our case MO degradation reaches a saturation limit at high concentration of the reactant.

3.7. Increase in photocatalytic oxidation activity of reused TiO$_2$

In all the above experiments it was difficult to isolate TiO$_2$ from the solution and it needed more than 1 day for TiO$_2$ to settle down. At pH = 3 it is noticed that the TiO$_2$ settled immediately after we stopped stirring the solution. The used TiO$_2$ was washed, heated to dryness and used in new experiments with fresh MO (Fig. 6). It was noticed that MO degradation was faster compared to the experiment where fresh TiO$_2$ was used. The rate constant κ for the degradation of MO using fresh catalysts was 0.7127 h^{-1} and it increased to 0.8490 h^{-1} in the case of reused catalysts. This increase
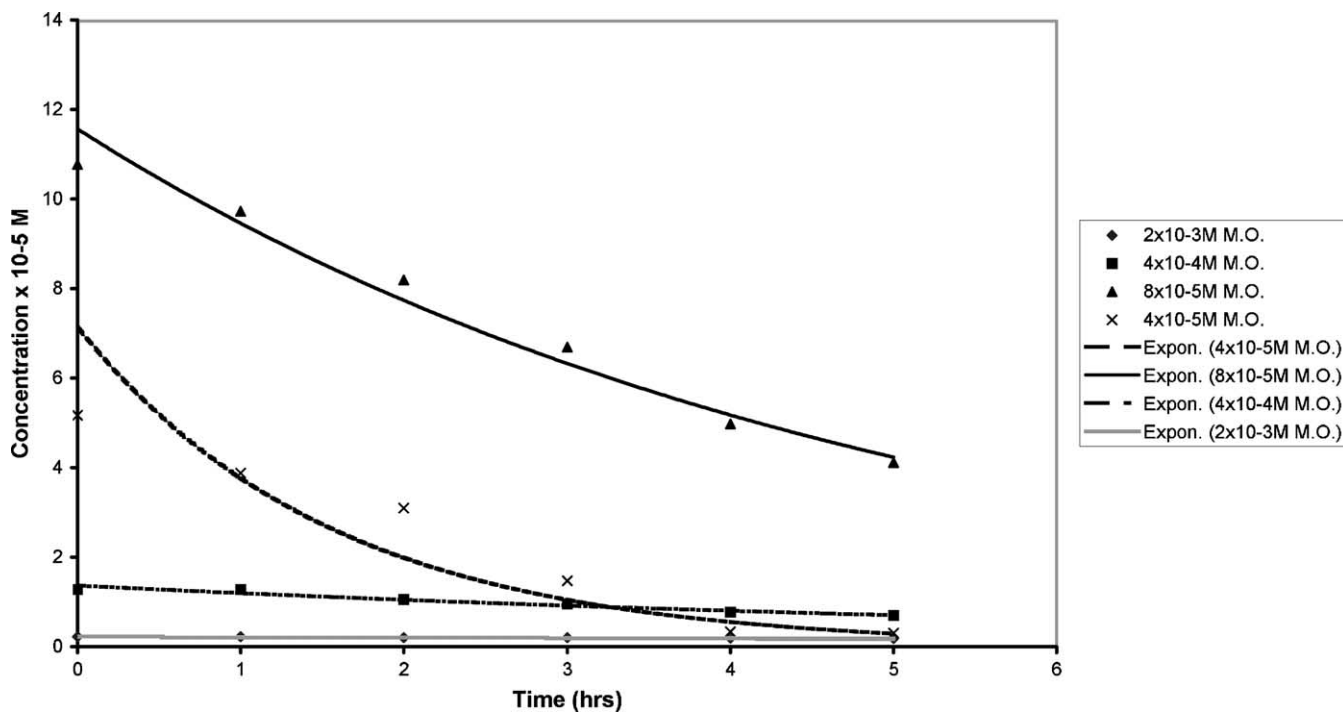
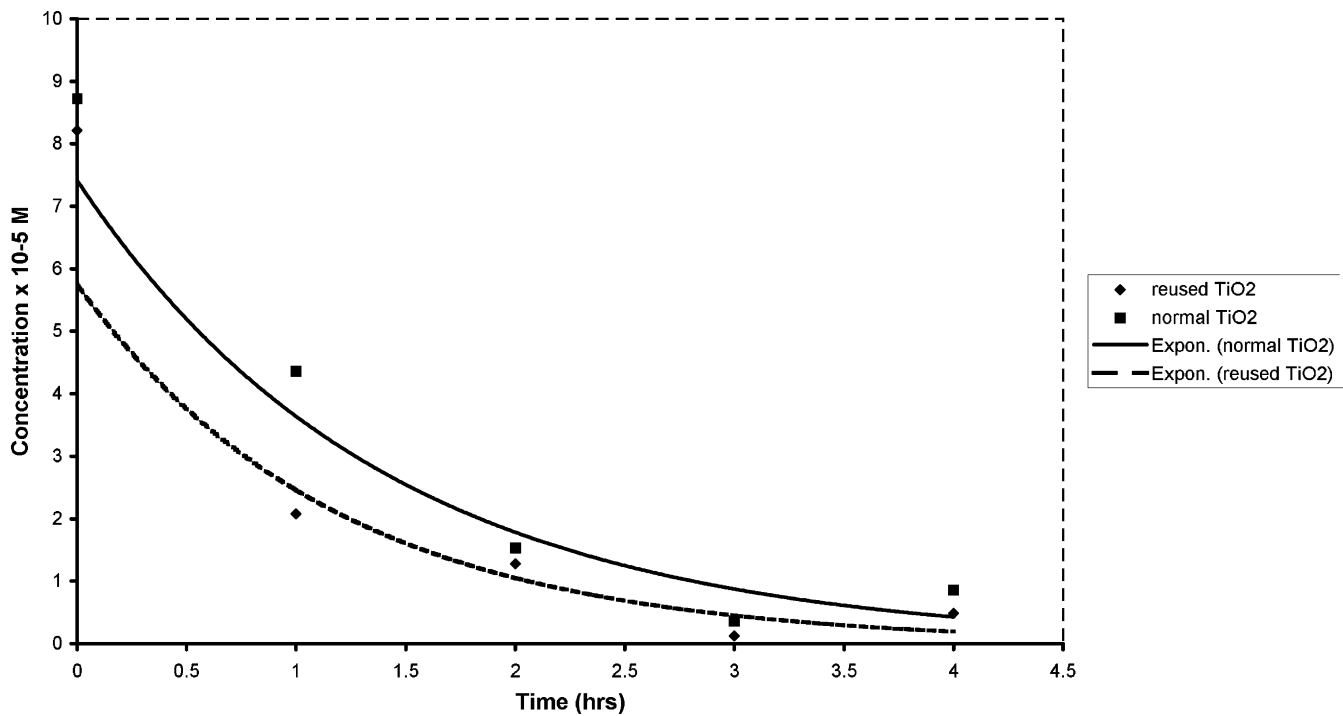Fig. 5. The decay curves for different concentrations of MO.

Fig. 6. The decay curves for MO using virgin and reused TiO_2.

in photocatalytic activity was noticed by other authors [33]. The fast settlement of TiO$_2$ at pH = 3 may be explained on the bases that to the TiO$_2$ particles aggregate together. The increase in reused TiO$_2$ may be explained [33] on the bases that there were an increase in the surface, chemical composition and the presence of bound water in the reused catalysts. Further work will be performed to characterize the changes in the catalysts after use.

4. Conclusion

TiO$_2$ was used as a photocatalysts for the detoxification of MO which was used as a model compound. One can conclude the following.

The degradation of the MO is not directly related to the solar radiation intensity, but in general high rate of degradation needs a limited number of photon. The pH has a large effect on the degradation rate constant, therefore the highest degradation rate was obtained when the pH = 3, and the pH of all solutions changed toward lower value (more acidic) after 5 h. It was noticed that TiO$_2$ settled immediately when the solution pH = 3. The optimum concentration of MO was 4×10^{-5} M, and increasing the concentration cause the degradation rate to decrease this might be to catalysts saturation by MO. In general complete degradation of the model compound was achieved after 5 h. It was found that reused TiO$_2$ is more active than the virgin one.

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