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PHOTODEGRADATION KINETICS OF 4-NITROPHENOL IN TiO_2 SUSPENSION

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Abstract—A new two-phase swirl-flow monolithic type reactor was designed to study the kinetics of heterogeneous photocatalytic processes on semiconductor catalysts. Most of the earlier work investigated the effects of various parameters on the initial degradation rate (or the formation of CO_2) of the pollutants. In the present study, photomineralization of 4-nitrophenol (4-NP) sensitized by Degussa P25 TiO_2 in aqueous solution has been investigated as a function of the following different experimental parameters: initial concentration of pollutant (C_{S0}), light intensity (I_a), partial pressure of oxygen (p_{O_2}), catalyst concentration, pH, chloride ion and temperature. The kinetic expression obtained can be described by the following formula $r_s = k_0 \exp(-E/RT) I_\alpha^\beta K_{O_2} p_{O_2}/(1 + K_{O_2} p_{O_2}) K_s C_s/(1 + K_s C_{s0})$. The apparent overall activation energy for 4-NP obtained was 7.42 kJ mol^{-1} by fitting the above equation with experimental data and the values for β, K_{O2} and K_s were 0.84, 9.98 atm^{-1} and 0.075 ppm^{-1} respectively. The kinetic equation can predict the concentration of 4-NP during the entire degradation process at pH value of 4.3 and TiO_2 concentration of 2 g l^{-1}, and is therefore, more meaningful. It can be used in the development of large-scale photocatalytic reactor and optimization of experimental conditions for any particular studies. Furthermore, the photodegradation of 4-NP on two different catalysts (P25 and UV100) was compared and the photonic efficiency of the process has also been investigated. © 1998 Elsevier Science Ltd. All rights reserved

Key words—semiconductor photocatalysis, advanced oxidation, water treatment, titanium dioxide, 4-nitrophenol, slurry reactor, kinetic reactor, photocatalytic degradation

INTRODUCTION

Water purification by semiconductor photocatalysis has been attracting an immense research interest in recent years. A growing interest in the purification of water by semiconductor photocatalysis, especially in the removal of toxic organic pollutants, is evidenced by the ever-increasing number of different studies in this area (Ollis *et al.*, 1989, 1991, Matthews, 1988; Mills and Morris, 1993; Inel and Okte, 1996). The semiconductor photocatalytic process is based on aqueous phase hydroxyl radical chemistry and couples low energy UV-A light with semiconductors acting as photocatalyst. It has been proved that this process can completely destroy many toxic organic compounds in wastewater into carbon dioxide (Ollis *et al.*, 1989; D'Oliveira *et al.*, 1990; Okamoto *et al.*, 1985). The overall process can be summarized by the following reaction equation:

$$\text{Organic Pollutants} + O_2 \xrightarrow{\text{Semiconductor+ UV–A light,}} CO_2 + H_2O + \text{mineral acid} \quad (1)$$

The most suitable semiconductor photocatalyst for sensitizing above reaction is TiO_2. Although there are many different sources of TiO_2, Degussa P25 TiO_2 has effectively become a research standard due to its reasonably well-defined nature and considerable photocatalytic activity. The adopted wavelength of UV light for TiO_2 is about 365 nm in order to avoid the direct photolysis of organic compounds. Organic pollutants in above equation include alkanes, haloalkanes, aliphatic alcohols, carboxylic acids, alkenes, polymers, surfactants, herbicides, pesticides, and dyes as well as aromatics and haloaromatics which are commonly present in industrial wastewater.

It has been demonstrated (D'Oliveira *et al.*, 1990; Al-Sayyed *et al.*, 1991; Inel and Okte, 1996) that various parameters have effects on the degradation rate of compounds. A few degradation kinetic expressions of different compounds have been reported in literature (Lu *et al.*, 1993; Chen and Chou, 1993). Unfortunately, almost all these studies investigated the effects of various parameters on the initial degradation rate rather than the degradation rate during the whole photomineralization process. The degradation kinetic rate expressions have so far focused on the initial disappearance rate of organic compounds (Inel and Okte, 1996) or the initial for-

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mation rate of CO_2 (Matthews, 1988, Mills and Morris, 1993). Meanwhile, initial rate data are tedious to obtain and prone to variation, this will reduce the reliability of the results. For the design of large-scale reactor, these kinetic expressions are not always meaningful, and therefore, not useful.

In this study 4-nitrophenol (4-NP) was chosen as model compound. It is one of the 114 organic pollutants listed by EPA in U.S.A. and its maximum allowed concentration is 20 ppb. So far only a few papers (Augugliaro *et al.*, 1991, 1993; Palmisano *et al.*, 1989; Dieckmann *et al.*, 1992; Dieckmann and Gray, 1996) have reported the photodegradation of 4-NP. In this work, effects of initial pollutant concentration, light intensity, partial pressure of oxygen, TiO_2 catalyst concentration, pH value of suspension, temperature and chloride ion on the degradation rates of 4-NP have been studied. A kinetic expression, which can be used in the development of large-scale photocatalytic reactor and optimization of experimental conditions, has been obtained. Furthermore, the photodegradation of 4-NP on two different catalysts (P25 and UV100) was compared and the photonic efficiency of the process has also been investigated.

EXPERIMENTAL DETAILS

Materials

Two different brand TiO_2 catalysts, Degussa P25 provided by Degussa Company and Hombikat UV 100 provided by Sachtleben Chemie GmbH (Germany), were used throughout this work. The physiochemical properties of these two titanium dioxide catalysts were listed in Table 1. Hydrochloric acid (37%) and nitric acid (65% by weight) were obtained from Merck chemicals, 4-nitrophenol (4-NP; 98 + %) from BDH chemicals, sodium hydroxide (98 + %) from Baker chemicals. All chemicals were used as received. Water used to make up solutions in this work was Milli-Q water.

Table 1. Physicochemical properties of the two different brand of titanium dioxide

Property	Degussa P-25 TiO_2	Hombikat UV100 TiO_2
Physical state	White powder	White powder
Composition (%)	≈80% anatase, ≈20% rutile	100% anatase
Density ($g\,cm^{-3}$)	3.8	3.9
BET surface area ($m^2\,g^{-1}$)	≈55	> 250
Average primary particle size (nm)	≈30	< 10
pH in aqueous solution	3–4	≈6
Contents		
SiO_2 (%)	< 0.2	–
Al_2O_3 (%)	< 0.3	–
Fe_2O_3 (%)	< 0.01	–
TiO_2 (%)	> 97	> 99
HCl (%)	< 0.3	–
Porosity	nonporous	porous (mesopores, about 5.6 nm in diameter)

Photoreactor and light source

The batch photoreactor consists of two circular glass plates that are placed between soft padding housed within stainless steel and aluminum casings. The TiO_2 aqueous solution, which was circulated by a peristaltic pump, was introduced tangentially between the two glass plates, and exited from the center of the top plate. The tangential introduction of liquid created a swirl-flow, thereby making the liquid solution well mixed. The lamp (Philips BPR 125 W high-pressure mercury vapour) was placed about 10 cm underneath the bottom glass plate on a holder that could be moved to create a different angle of incidence of light on the bottom glass plate. Primary radiation of this lamp is emitted at 365 nm and the incident light intensity is $213\ W\ m^{-2}$. The lamp and reactor were placed inside a wooden box painted black so that no stray light can enter the reactor. The lamp was constantly cooled by compressed air to keep the temperature down and protect the lamp from overheating. Provision was made for placement of several metal screens of different mesh size between the lamp and bottom glass plate to obtain variation in light intensity.

Experimental procedures

The reaction solution was made by adding 145 ml of Milli-Q water at natural pH containing the target concentration of 4-NP into the beaker with a water jacket. Then 0.29 g (0.2%) powder photocatalyst was dispersed into above solution and in some cases, hydrochloric acid or nitric acid or sodium hydroxide was used to adjust the solution to the desired pH. The mixture was magnetically stirred and circulated in the system by peristaltic pump for about 20 min. About 5 ml sample was taken to determine its initial concentration prior to illumination. The temperature of the photodegradation system was adjusted by a water bath in which heating or cooling water was recirculated through the jacket of the beaker.

Analyses

In order to remove particulate before analyses, all water samples were filtered by Millex-HA filter (Millipore, 0.45 μm). A SHIMADZU TOC-5000A analyzer with an ASI-5000 autosampler analyzed the total organic carbon (TOC) in samples. Analysis of 4-NP was carried out by using a Shimadzu UV 3101 PC spectrophotometer.

REACTION MECHANISM AND RATE EXPRESSIONS

It has been well demonstrated that when TiO_2 is illuminated by light ($\lambda < 380$ nm) in the presence of water containing dissolved oxygen and organic compounds, photodegradation of the organic compounds will occur. Many organic compounds are known to be degraded to CO_2 under these conditions. The primary step in photodegradation is certainly the generation of electrons and holes within the TiO_2 particle.

$$TiO_2 \xrightarrow{h\nu,\ \lambda < 380\ nm} TiO_2(e^- + h^+) \qquad (2)$$

The majority of these recombine with the liberation of heat. However, in the presence of dissolved oxygen and an electron donor, $OH^{\cdot}$ radical is formed by the reaction between the valence band holes (h^+) and the TiO_2 surface active $OH^{\cdot}$ group or H_2O.

$$h^+ + OH^-_{ad} \longrightarrow OH^{\cdot}_{ad} \qquad (3)$$

$$h^+ + H_2O_{ad} \longrightarrow OH^{\cdot}_{ad} + H^+ \quad (4)$$

The photogenerated conduction band electron (e^-) is trapped by the dissolved oxygen to form a superoxide ion O_2^-.

$$e^- + O_2 \longrightarrow O_2^{\cdot-} \quad (5)$$

4-NP will be attacked by hydroxyl radicals formed in above equations and generates organic radicals or some other intermediates. NO_2^- was found and oxidized to NO_3^- (Augugliaro *et al.*, 1991). Eventually all the parent compounds and intermediates will be oxidized into CO_2 with an overall reaction stoichiometry:

$$C_6H_4OHNO_2 + 7O_2 \longrightarrow 6CO_2 + 2H_2O + HNO_3 \quad (6)$$

In the photomineralization of 4-NP sensitized by TiO_2, it is postulated that oxygen, 4-NP and its intermediates are adsorbed at different sites on the surface of TiO_2 (Augugliaro *et al.*, 1993) and the rate-determining step is the reaction between the primary oxidizing species $OH^{\cdot}$, and the adsorbed 4-NP. In terms of Langmuir–Hinshelwood kinetics the second-order decomposition rate of 4-NP may be expressed as

$$r_s = k'\theta_{OH}\,\theta_s, \quad (7)$$

The number of electron–hole pairs that escape from recombination significantly influences concentration of hydroxyl radical. Oxygen adsorbed on the TiO_2 surface inhibits the recombination process by trapping the electrons. In addition, the generation of hole–electron pairs is affected by the light intensity. Therefore, equation 7 can be rewritten as

$$r_s = k_P I_\alpha^\beta \theta_{O_2}\theta_s, \quad (8)$$

where

$$\theta_{O_2} = \frac{K_{O_2}P_{O_2}}{1 + K_{O_2}P_{O_2}} \quad (9)$$

$$\theta_s = \frac{K_sC_s}{1 + K_sC_s + \sum_i K_iC_i} \quad (10)$$

θ_{O_2} and θ_s, are the fractions of the sites covered by oxygen and 4-NP. I_a is light intensity, subscripts s and i are 4-NP and intermediates, K_{O_2}, K_s, and K_i are equilibrium adsorption constants for O_2, s and i respectively. Augugliaro *et al.* (1991) made the following assumption:

$$K_sC_s + \sum_i K_iC_i = K_sC_{s0}, \quad (11)$$

where C_{s0} is the initial concentration of 4-NP. That is, the adsorption constants for the decomposition intermediates were same as that of the parent compound. Substituting equations 9–11 into equation 8 and rewriting the apparent rate constant as a function of temperature, more complete photodegradation kinetics is obtained

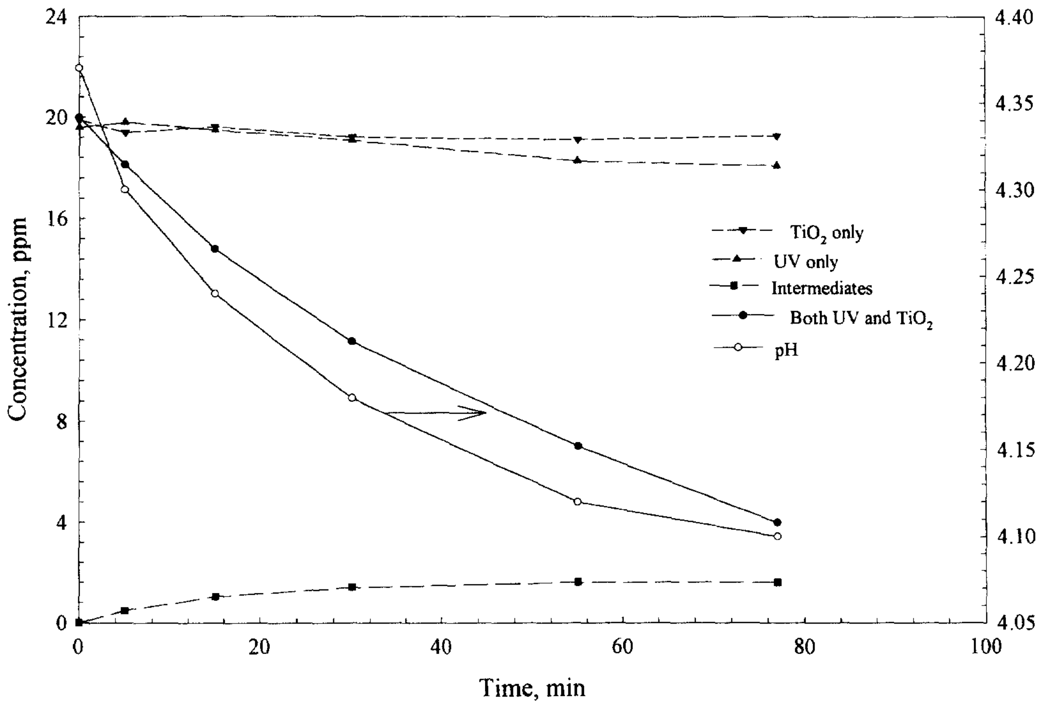

Fig. 1. 4-NP, intermediates and pH profiles during degradation. [C_{S0} = 20 ppm; pH = normal; TiO_2 dosage = 2 g l^{-1}; flowrate = 250 ml min^{-1} and O_2 saturated].

with the following expression.

$$r_s = -\frac{dn_s}{S\,dt} = k_0 \exp\left(-\frac{E}{RT}\right) I_\alpha^\beta \frac{K_{O_2}p_{O_2}}{(1+K_{O_2}p_{O_2})} \times \frac{K_s C_s}{1+K_s C_{s0}} \tag{12}$$

Here, the photodegradation rate ($g\,m^{-2}\,s^{-1}$) is defined as the mole (n_s) reduction of pollutant per irradiated reactor window area (S).

RESULTS AND DISCUSSIONS

As shown in Fig. 1, a very small decrease in the concentration of 4-NP was observed when only UV-A is present or when only TiO_2 is present. However, 4-NP could be degraded quickly by illuminated TiO_2. The pH value of the solutions decreased as the reaction proceeded due to the formation of HNO_3 or HNO_2. Two aromatic intermediates (4-nitrocatechol and hydroquinone) were identified during the degradation of 4-NP (Dieckmann and Gray, 1996). In this work, some intermediates during the reaction were also found (Fig. 1) and the total maximum concentration of these intermediates was less than 8% of the initial concentration of 4-NP. However, in this study no attempt was made to identify these intermediates.

As described in the experimental section, an UV absorption experiment of the reaction solution was carried out after the filtration of photocatalyst. In order to monitor the gradual disappearance of 4-NP, a series of UV spectra were recorded in the 200–500 nm range with the increasing illumination time. Typical spectra are shown in Fig. 2. The characteristic absorption of 4-NP almost disappeared after 95 min of irradiation. No peak for intermediates was detected due to the low concentration of intermediates.

Effect of mass of TiO_2

The variation in degradation rate constant of 4-NP against the concentration of TiO_2 was determined (Fig. 3) over the [TiO_2] range 0.2–4 $g\,l^{-1}$. As expected, the rate constant was found to increase with the increasing concentration of TiO_2 and approaching a limiting value at high concentration. The limiting value (2 $g\,l^{-1}$ for 4-NP) mainly results from following two factors: (a) aggregation of TiO_2 particles at high concentrations, causing a decrease in the number of surface active sites, and (b) increase in opacity and light scattering of TiO_2 particles at high concentration leading to a decrease in the passage of irradiation through the sample. Similar results have been reported in previous studies (Al-Sayyed *et al.*, 1991; Mills and Morris, 1993; Terzian and Serpone, 1995) and the amount of catalyst at the beginning of the plateau was between 0.5 and 2 $g\,l^{-1}$ for different photosystem. When the experimental data was fitted with a Langmuir-type expression: $k_p = k_{p0}\ K_{app}[TiO_2]/(1 + K_{app}[TiO_2])$, values of k_{p0} and K_{app} were obtained from the linear transform of the

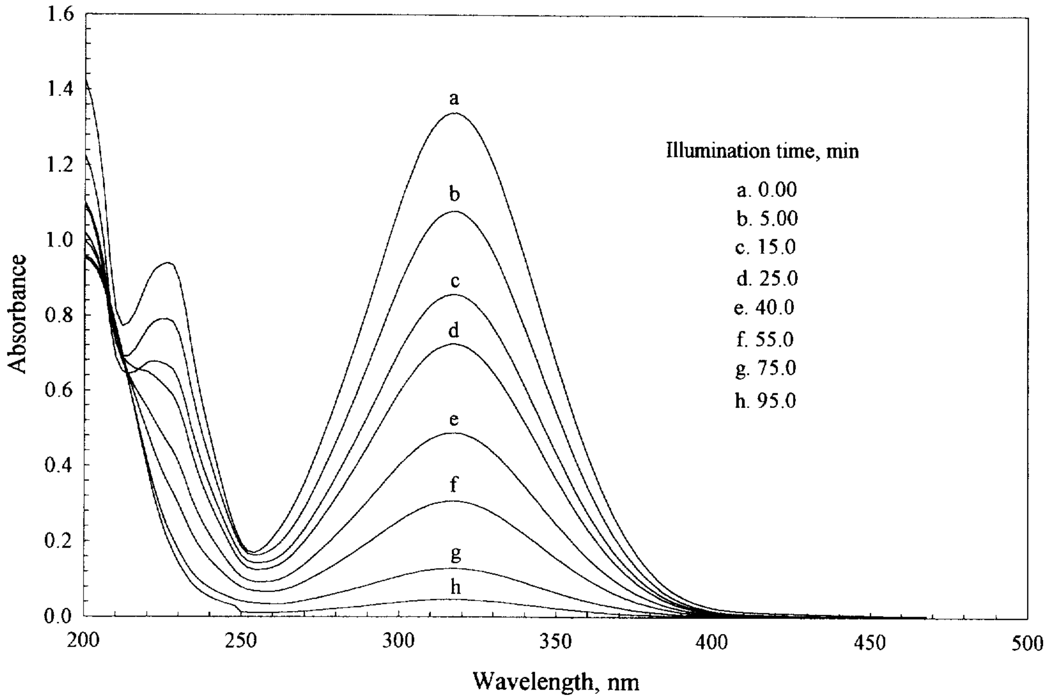

Fig. 2. Typical UV spectrum profiles during degradation of 4-NP on P25 catalyst.

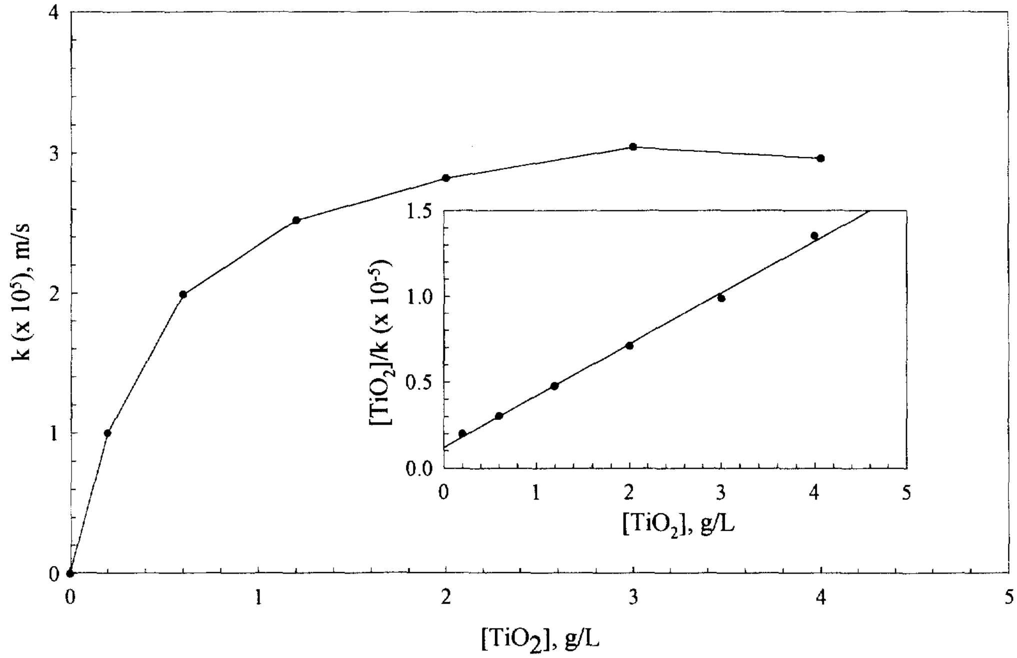

Fig. 3. Effect of TiO_2 dosage on the degradation rate. [C_{S0} = 20 ppm; pH = natural; T = 303 K; flowrate = 250 ml min^{-1} and O_2 saturated].

expression as $k_{p0} = 3.33 \times 10^{-5}$ m s^{-1} and $K_{app} = 2.48$ l g^{-1}.

Effect of initial concentration

As the effect of pollutant concentration is of importance in any process of water treatment, it is necessary to investigate its dependence. The effect of initial concentration on the photocatalytic degradation of 4-NP is shown in Fig. 4. Different concentration profiles were observed during the degradation for different initial concentrations. Furthermore, degradation rates at same concen-

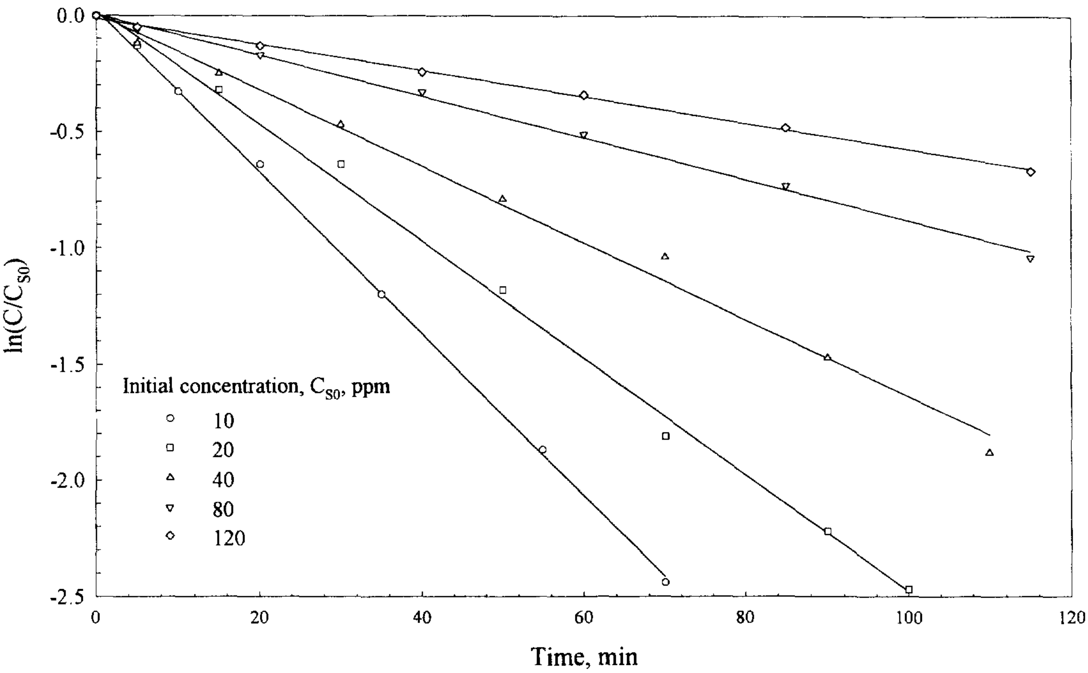

Fig. 4. Effect of initial concentration on the degradation rate. [pH = 4.3; TiO_2 dosage = 2 g l^{-1}; T = 303 K; flowrate = 250 ml min^{-1} and O_2 saturated].

tration with different initial concentrations were different. This is quite different from ordinary thermal reaction. But, all the concentration profiles could be correlated by the following exponential function with good agreement.

$$C_s = C_{s0} \exp(-k_s t) \qquad (13)$$

The apparent rate constant k_s ($\mathrm{l\,min^{-1}}$) in above equation decreased with the increasing of initial concentration of 4-NP when other parameters are kept unchanged. Therefore, the degradation rate was pseudo-first-order with respect to the concentration within the experimental range.

In recent years the Langmuir–Hinshelwood rate expression has been used successfully for heterogeneous photocatalytic degradation to describe the relationship between initial degradation rate and initial concentration (Al-Sayyed *et al.*, 1991; Lu *et al.*, 1993). A linear expression can be conveniently obtained by plotting reciprocal initial rate against reciprocal initial concentration

$$\frac{1}{r_{s0}} = \frac{1}{k} + \frac{1}{kK_s}\frac{1}{C_{s0}} \qquad (14)$$

A reasonable fit of above equation was obtained with values of $0.072\ \mathrm{ppm^{-1}}$, $9.55 \times 10^{-4}\ \mathrm{g\,m^{-2}\,s^{-1}}$ for K_s and k respectively. This indicates that the degradation of 4-NP occurred mainly on the surface of TiO_2. However, Turchi and Ollis (1990) investigated the photodegradation of organic pollutants in illuminated TiO_2 slurries and found it plausible that the reaction occurs not only on the TiO_2 surface but also in solution.

Effect of light intensity

Previous studies (D'Oliveira *et al.*, 1990; Ollis *et al.*, 1991; Al-Sayyed *et al.*, 1991) on photodegradation rate vs illumination intensity indicated that the reaction rate increases with the square root of intensity at high intensity level when mass transfer limit is not reached. At sufficiently low levels of illumination (catalyst dependent), on the other hand, degradation rate is of first-order in intensity. Increased illumination results in an increase in volumetric reaction rate, until the mass transfer limit is encountered. The transition points between these regimes, however, will vary with the photosystem. In the degradation of 3-CP in TiO_2 aqueous suspensions, the initial degradation rate was reported to be proportional to radiant flux for values smaller than $20\ \mathrm{mW\,cm^{-2}}$ while above this value it was proportional to its square root (D'Oliveira *et al.*, 1990). The initial degradation rate of 4-CP against radiant flux was also investigated in the range of 2–$50\ \mathrm{mW\,cm^{-2}}$ (Al-Sayyed *et al.*, 1991), where similar rate shift from first-order to halforder in intensity was observed. Other investigations on the photodegradation of phenol (Okamoto *et al.*, 1985), isopropanol, pesticides, xylenols and malonic acid (Inel and Okte, 1996) also reported similar results. However, no report on 4-NP was found in literature. Figure 5 shows the result of the effect of light intensity on the degradation rate constant of 4-NP in this study. Following equation correlated the effect

$$k \propto I_\alpha^\beta \qquad (15)$$

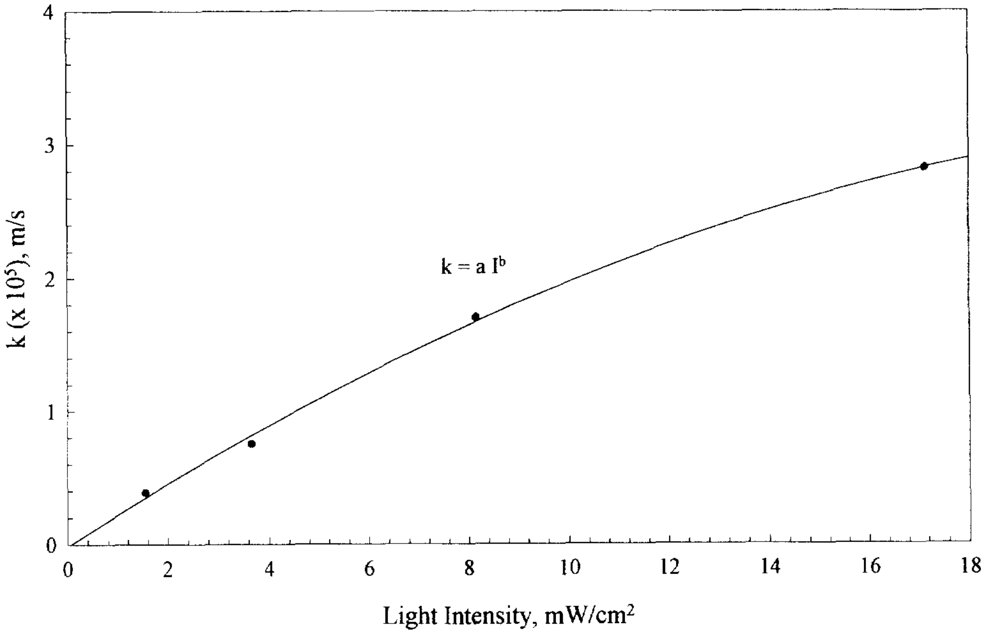

Fig. 5. Effect of light intensity on the degradation rate. [$C_{S0} = 20$ ppm; pH = 4.5; TiO_2 dosage = $2\ \mathrm{g\,l^{-1}}$; $T = 303$ K; flowrate = $250\ \mathrm{ml\,min^{-1}}$ and O_2 saturated].

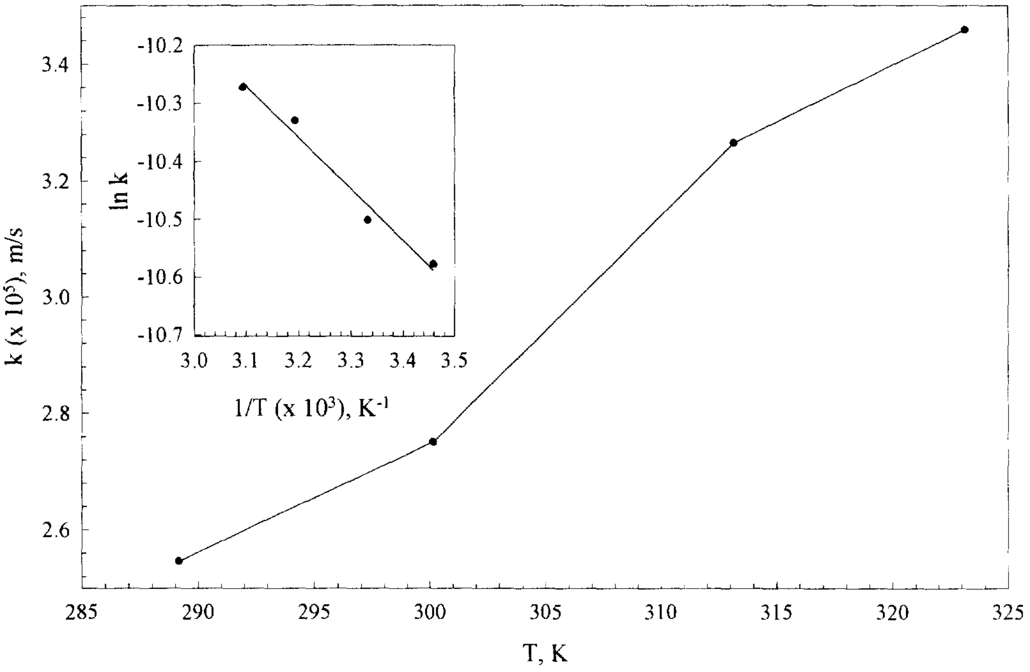

Fig. 6. Effect of temperature on the degradation rate. [$C_{S0}=20$ ppm; pH = 4.3; TiO_2 dosage = 2 g l^{-1}; flowrate = 250 ml min^{-1} and O_2 saturated].

with the β value 0.84. The value is quite close to reported value of 0.74 in the photodegradation of 4-CP (Mills and Morris, 1993). It indicated that the degradation rate was neither catalyst dependent nor mass transfer dominated. Several studies (D'Oliveira *et al.*, 1990; Ollis *et al.*, 1991; Al-Sayyed *et al.*, 1991; Inel and Okte, 1996) attributed the $I_\alpha^{1.0}$ to $I_\alpha^{0.5}$ rate transition to the recombination of photogenerated electron–hole pairs at high light intensity. This is obviously detrimental to the photocatalytic process as the quantum efficiency decreases. Recombination process may be slowed possibly by the addition of better electron acceptors, such as H_2O_2, Cu^+ and Ag^+ (Ollis *et al.*, 1991).

Effect of temperature

The overall process of semiconductor photocatalysis is usually not very temperature sensitive. The dependence of degradation rate constant on temperature of 4-NP is shown for the temperature range from 288 to 323 K in Fig. 6. It was observed that the rate constants increased with increasing temperature. The Arrhenius plot yielded a straight line from which the overall apparent activation energy obtained was 7.42 kJ mol^{-1} (Fig. 6). Obviously, this value was smaller than that of ordinary thermal reactions and the photocatalytic reaction was less temperature dependent. Although no activation energy of 4-NP photodegradation was reported in literature, the value is comparable with those listed in Table 2. The value is also quite close to that for a hydroxyl radical reaction (Matthews, 1987), suggesting that the photodegradation of 4-NP was governed by hydroxyl radical reaction. However, for TiO_2 photocatalysis, irradiation is the primary source of electron–hole pair generation at ambient temperature as the band gap energy is too high to be overcome by thermal activation. Therefore, the increase in rate constant was most

Table 2. Comparison of activation energy, *E*, obtained in this study with those in literature

Reactant	TiO_2 catalyst	*E* (kJmol^{-1})	*T* (K)	Investigator(s)
4-CP	deposited	20.6	283–333	Hofstadler *et al.*, 1994
4-CP	suspension	16	288–328	Mills and Morris, 1993
4-CP	suspension	5.5	283–318	Al-Sayyed *et al.*, 1991
Methyl orange	suspension	18	300–318	Chen and Chou, 1993
Dichlorvos	deposited	28.4	293–313	Lu *et al.*, 1993
Malonic acid	suspension	9.99	294–324	Inel and Okte, 1996
Phenol	suspension	10	293–323	Okamoto *et al.*, 1985
Salicylic acid	deposited	11	298–318	Matthews, 1987
Xylenols	suspension	8.8	279–333	Terzian and Serpone, 1995
4-NP	suspension	7.42	288–323	this work

likely due to the increasing collision frequency of molecules in solution that increases with increasing temperature.

Effect of dissolved oxygen concentration

Photomineralization of organic compounds will cease unless sufficient oxygen is present in the solution. The partial pressure of oxygen was adjusted by mixing the oxygen stream with a nitrogen stream while the total flowrate of gas was maintained at a constant value.

Figure 7 shows that the degradation rate constant of 4-NP increased with increasing oxygen partial pressure and it has reached about 70% of its maximum value when the partial pressure of oxygen was 0.2 atm. This indicates that in commercial application it is possible to replace pure oxygen with air. The effect of oxygen partial pressure on the degradation of 4-NP could be well described by noncompetitive Langmuir kinetic equation as follows.

$$k_p \propto \frac{k_{O_2} p_{O_2}}{1 + k_{O_2} p_{O_2}} \tag{16}$$

Straight line was obtained with good correlation coefficient by plotting p_{O_2}/k against p_{O_2}. The main influence of the dissolved oxygen is to enhance the separation of photogenerated electron–hole pairs, hereby increasing hydroxyl radical concentration.

Effect of pH value and chloride ion

The pH value is an important parameter in photodegradation that takes place on the surface of photocatalyst. The point of zero charge (pzc) for TiO_2 is at pH between 5.6 and 6.4 (Lu *et al.*, 1993; Terzian and Serpone, 1995). Hence, at more acidic pH values, the catalyst surface is positively charged, while at pH values above 5.6, it is negatively charged

$$\mathrm{Ti^{IV} - OH + H^+ \longrightarrow Ti^{IV} - OH_2^+} \tag{17}$$

$$\mathrm{Ti^{IV} - OH + OH^- \longrightarrow Ti^{IV} - O^- + H_2O} \tag{18}$$

Therefore, pH value will have significant effect on the adsorption–desorption properties at the catalyst's surface.

The effect of pH on the degradation of 4-NP is shown in Fig. 8. The result indicates that pH value has a significant effect and at both low and high pH values photodegradation rates are quite slow. The best pH value for the degradation is near the pzc point of TiO_2. This probably explains that the effect of pH on degradation rate is perhaps due to its effect on TiO_2 particle itself This includes the charge separation on the particles. The high OH^- ion content of the system enhances the e–h separation. However, the photogenerated CO_2 will be trapped in the solution, and bicarbonate, carbonate are formed in alkaline system. Both bicarbonate and carbonate are efficient scavengers of hydroxyl radicals due to their very high rate constants with the hydroxyl radicals ($k = 3.9 \times 10^8\ M^{-1}\ s^{-1}$ for carbonate and $k = 8.5 \times 10^6\ M^{-1}\ s^{-1}$ for bicarbonate) (Buxton *et al.*, 1988). On the other hand, according to equation 3 low OH^- in acidic system hinders the formation of hydroxyl radicals and subsequently reduces the degradation rate. Maximum degra-

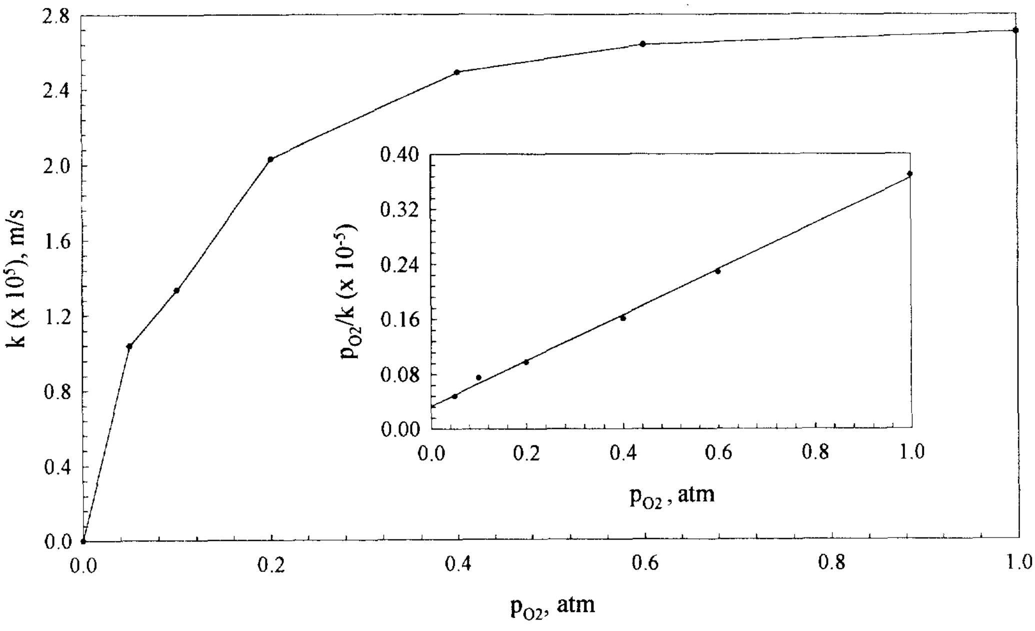

Fig. 7. Effect of dissolved oxygen on the degradation rate. [$C_{S0} = 20$ ppm; pH = 4.5; TiO_2 dosage = 2 g l^{-1}; T = 303 K; flowrate = 250 ml min^{-1}; O_2 saturated].

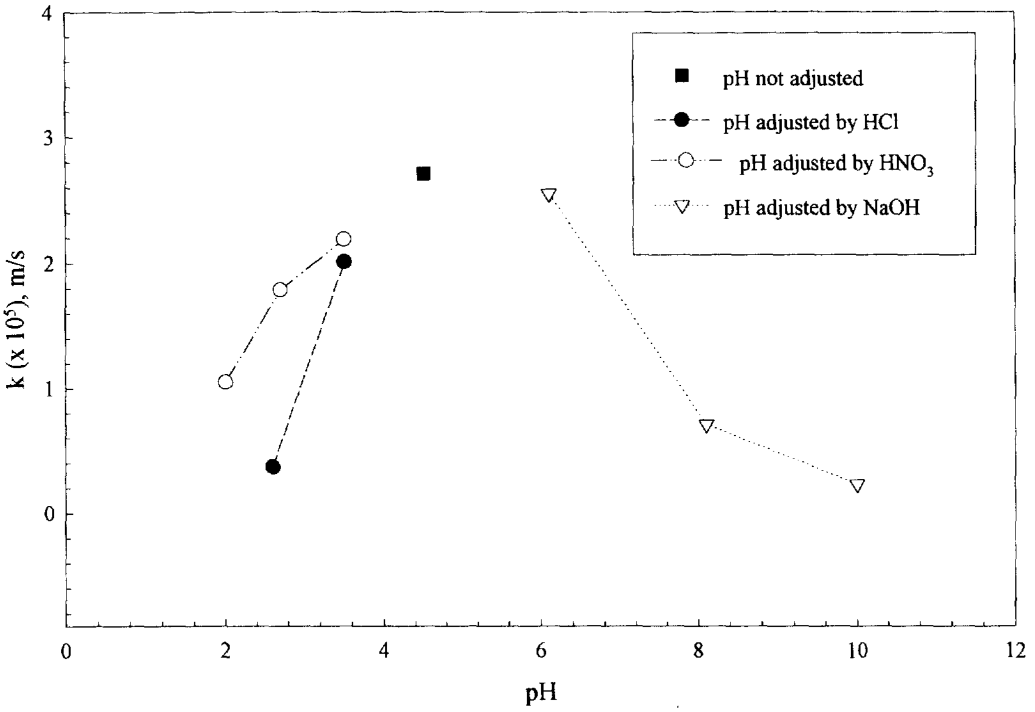

Fig. 8. Effect of pH and chloride ion on the degradation rate. [C_{S0} = 20 ppm; TiO_2 dosage = 2.0 g l^{-1}; T = 303 K; flowrate = 250 ml min^{-1} and O_2 saturated].

dation rate of 4-NP at pH 4.5 was reported (Palmisano *et al.*, 1989), but the degradation rate increased a little bit with the increasing pH value beyond 10. Augugliaro *et al.* (1993) investigated the effect of pH in the range of 3–11 on the degradation of 4-NP in TiO_2 suspension and found that the degradation rate decreased slightly with the increasing pH value. In order to investigate the chloride effect on the degradation, HCl and HNO_3 were used to adjust the pH value of solution. The result in Fig. 8 shows that chloride had substantial inhibitory effect on the degradation of 4-NP, particularly at low pH value. One possible explanation is that chloride ion can competitively adsorb on the surface of TiO_2 with big adsorption constant. Similar result was reported elsewhere (Augugliaro *et al.*, 1991).

Degradation kinetics of 4-NP

In literature, no perfect degradation kinetics has been reported that could predict the concentration profiles during photoreaction. A perfect degradation kinetic expression is very useful in the design of large-scale photoreactor. In this study, a series of experiment has been carried out for 4-NP at natural pH value of 4.3 and constant TiO_2 concentration of 2 g l^{-1}. While other parameters are varied as follows: T = 288–323 K, I = 1.5–18 mW cm^{-2}, C_{S0} = 10–120 ppm, p_{O_2} = 0.05–1.0 atm. The following kinetic expression was obtained with satisfactory agreement.

$$r_s = -\frac{dn_s}{S\,dt} = 1.87 \times 10^{-3} \exp\left(-\frac{7415.3}{RT}\right) \times I_a^{0.84} \cdot \frac{9.98p_{O_2}}{1 + 9.98p_{O_2}} \cdot \frac{0.075C_s}{1 + 0.075C_{s0}} \qquad (19)$$

Above equation indicates that equilibrium adsorption constants for oxygen (K_{O_2}) and 4-NP (K_s) on TiO_2 surface are 9.98 atm^{-1} and 0.075 ppm^{-1} respectively. Literature reported (Augugliaro *et al.*, 1991) values of K_{O_2} and K_s for 4-NP-TiO_2 suspension are 1.82 atm^{-1} and 0.064 ppm^{-1} respectively.

Comparison of the two different TiO_2 catalysts

Although Degussa P25 TiO_2 catalyst has been extensively used in most of the photocatalytic processes, recently it was reported that a novel TiO_2 photocatalyst (Hombikat UV100) has a good performance in the photodegradation of some model compounds. The physiochemical data of these two titanium dioxide catalysts were listed in Table 1. In the present study, the photomineralization of 4-NP has been carried out under otherwise identical conditions using both P25 and UV100 photocatalyst. The disappearance of 4-NP on both catalysts is illustrated in Fig. 9. The photodegradation is via apparent first order kinetics: $k_p = 1.54 \times 10^{-3}$ m s^{-1} and $k_p = 6.03 \times$

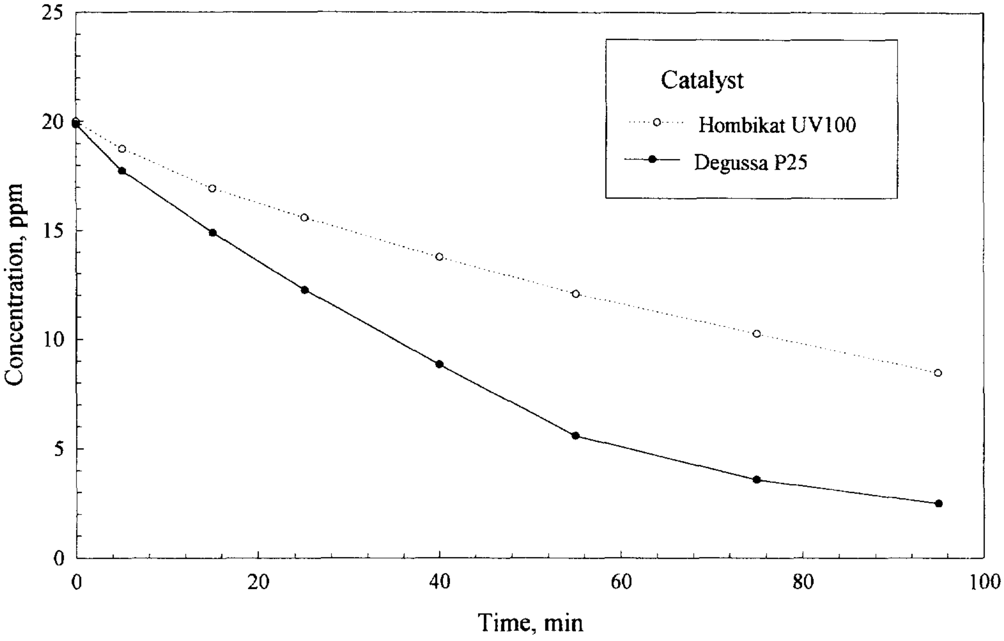

Fig. 9. Comparison of degradation rate for 4-NP on Hombikat UV100 and Degussa P25 catalysts. [pH = natural; TiO_2 dosage = 2 g l^{-1}; T = 303 K; flowrate = 250 ml min^{-1} and O_2 saturated].

10^{-4} m s^{-1} for Degussa P25 and Hombikat UV100 respectively. Obviously, P25 is more active than UV100 in the photomineralization of 4-NP under given experimental conditions.

Efficiency of the photocatalytic process

So far, many photocatalytic processes have been investigated in laboratory scale. It is obviously

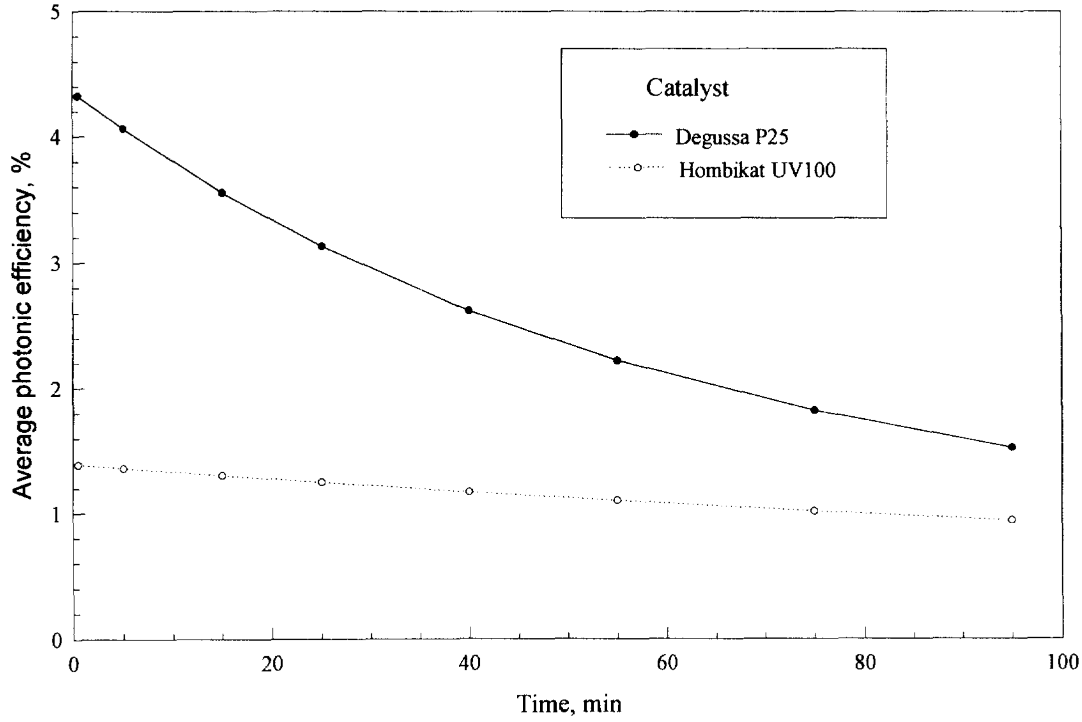

Fig. 10. Average photonic efficiency for the degradation of 4-NP on P25 and UV100 catalysts. [C_{S0} = 20 ppm; pH = natural; TiO_2 dosage = 2 g l^{-1}; T = 303 K; flowrate = 250 ml min^{-1} and O_2 saturated].

necessary to compare the photocatalytic efficiencies of different processes. In homogeneous photochemistry, quantum yield has been extensively used as it provides a means of comparing two or more photochemical events. By contrast, a similar description in heterogeneous photochemistry is further complicated by many fundamental unknown quantities.

In this work, we use the relative photonic efficiency to describe the efficiency of the photocatalytic process. The relative photonic efficiency is defined as the number of molecules converted relative to the total number of photons incident on the reactor window, i.e.

$$\varphi_{(t)} = \frac{\text{rate of reaction(mol s}^{-1})}{\text{rate of photon incident on window(mol s}^{-1})} \tag{20}$$

For our system (batch reactor):

$$\varphi_{(t)} = \frac{r_s}{\phi} \tag{21}$$

where ϕ is light intensity (mol photon $m^{-2}\,s^{-1}$). When the reaction is first order, i.e.:

$$C_{(t)} = C_{(0)}\exp(-k_{TOC}t) \tag{22}$$

The relative photonic efficiency is

$$\bar{\varphi}_{(t)} = \frac{V_R C_{(0)}[1-\exp(-k_{TOC}t)]}{\phi S t}, \tag{23}$$

where V_R is the volume of the reaction solution and $\bar{\varphi}_{(t)}$ is the average value within reaction time t. In above equations k_{TOC} is the degradation rate constant measured in terms of the TOC reduction. C is the concentration of carbon (mol l^{-1}) and we assume that one photon required per carbon atom. Typical values of the relative photonic efficiency are indicated in Fig. 10 for the degradation of 4-NP on both P25 and UV100 photocatalysts. The reasons for the very low relative photonic efficiencies are mainly due to the recombination of photogenerated electron–hole pairs and the light absorption by the reaction solution. equation 23 can also be used to compare the degradation of different compounds on the photocatalyst.

CONCLUSIONS

In this study, a meaningful perfect kinetic expression for the degradation of 4-NP was obtained. equation 19 can predict the concentration of 4-NP during the photodegradation in addition to the initial degradation rate, and is therefore, more reliable because it was obtained under a variety of different experimental conditions. The degradation rate of 4-NP was found to be pseudo first-order with respect to its concentration within the experimental concentration range. The apparent rate constant decreased with the increasing initial concentration. It indicates that the photodegradation of 4-NP has a saturate behavior. The influence of pH was remarkable for 4-NP and photodegradation was not suitable at both low and high pH values. Chloride ion had a negative effect on the degradation. The overall apparent activation energy was 7.42 kJ mol^{-1}, implying that the degradation of 4-NP was less temperature sensitive. Equilibrium adsorption constants for oxygen and 4-NP on TiO_2 P25 obtained in this work were 9.98 atm^{-1} and 0.075 ppm^{-1} respectively.

Although P25 is more active for the photodegradation of 4-NP than UV100, at the current state of development the degradation efficiency on both two catalysts is very low. Therefore prior to commercializing this process, a significant progress in the improvement of the photo-efficiency must be made by modifying currently used photocatalysts or developing a novel photocatalyst.

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