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Photocatalytic Degradation of 4-Chlorophenol: The Effects of Varying TiO_2 Concentration and Light Wavelength

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The effects of TiO_2 surface loading and light conditions on the photocatalyzed degradation of 4-chlorophenol (4-CP) were examined, in order to address deficiencies in previous studies in which these issues were not examined satisfactorily. It is proposed that these factors explain differences in the reported reaction intermediate concentrations. Increasing the loading of TiO_2 in a slurry has little effect on the rate of 4-CP disappearance. However, the concentration of 4-chlorocatechol (4-CC), a primary degradation product, decreases with increasing TiO_2 loading. Zero order kinetics in terms of 4-CP were observed for 4-CP degradation. The rate of mineralization increased with increasing TiO_2 concentration. The rate of mineralization relative to 4-CP degradation was more rapid under conditions of lower light intensity. Significant adsorption of 4-CC on Degussa P25 TiO_2 was measured and these data are fitted well by a Langmuir isotherm. Adsorption of 4-CC accounts for most of the changes in 4-CC concentration at different TiO_2 loadings. An increased proportion of surface oxidation reactions at higher TiO_2 loadings and lower light intensity may explain the higher rates of mineralization in thicker slurries. The quantum yield of reaction of 4-CP increased with decreasing wavelength of light from $\phi = 0.01$, at $\lambda = 360$ nm to $\phi = 0.07$, at $\lambda = 300$ nm. A relationship of $d[\text{4-CP}]/dt \propto I^{0.8}$ was measured.

INTRODUCTION

The photocatalytic degradation of 4-chlorophenol (4-CP) using titanium dioxide and ultraviolet light has been the topic of many recent investigations (1–16). The successful mineralization of 4-CP to CO_2 has been demonstrated, and in a number of the studies intermediates *en route* to mineralization have been identified and quantified. However, in some of these photocatalytic studies hydroquinone (HQ) was found to be the predominant aromatic intermediate (2–4, 11), while in others 4-chlorocatechol (4-CC) was predominant (7, 8, 12). The maximum total intermediate concentration relative to the initial 4-CP concentration varied from 1% (4) to 26% for degradation with TiO_2 (7) and 31% for degradation with ZnO as the photocatalyst (12). In an earlier study we demonstrated that 4-CC and HQ were the predominant intermediates formed when 4-CP was radiolytically degraded in conditions favoring ·OH attack (14). Adsorption of intermediates to TiO_2 has not been considered in previous studies of the photocatalytic degradation of 4-CP. However, in a study of the photocatalytic degradation of 4-CP using ZnO, it was found that 30% of the reaction intermediate, 4-CC, adsorbed to the surface (12).

To understand the reasons for differences in intermediate concentrations, a study of TiO_2 photocatalytic degradation of 4-CP was undertaken in which the effect of TiO_2 loading on reactant disappearance and intermediate concentration, and on the reduction of TOC (total organic carbon) was examined. An adsorption isotherm of 4-CC was also measured, and can be related to solution concentrations. Detailed actinometry measurements were made using two lamps of different intensities to gain a better understanding of quantum yield measurements, and the role light intensity may play in by-product yields and reaction pathways. A study of the effect of wavelength on the rate of reaction was made using monochromatic light.

EXPERIMENTAL

Chemicals. 4-Chlorophenol (4-CP) (Aldrich, 99%+), 4-chlorocatechol (4-CC) (Tokeo Kasei), 4-chlororesorcinol (4-CR) (Aldrich, 98%), phenol (Fluka, >99.5%), and 1,2,4-trihydroxybenzene (Tokyo Kasei) were used without further purification. Hydroquinone (HQ) (Aldrich, 99%+) was recrystallized from water/ethanol prior to use, and benzoquinone (Alfa) was purified by sublimation. Fumed titanium dioxide (P25, mostly anatase (17)) was obtained from Degussa Corporation (50 ± 2 m^2 g^{-1}) (18).

Quantum yield measurements were made using potassium ferrioxalate actinometry, the procedure for which is outlined elsewhere (19). Ferrous sulfate (Fisher), 1,10-phenanthroline (Aldrich), potassium oxalate (Matheson, Coleman, and Bell), ethylenediamine dihydrochloride (Sigma), and sodium acetate (Fisher) were used to prepare the necessary solutions. The nitrogen and oxygen used

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were high purity. Milli-Q water was used to prepare all samples.

Photoreactor. A borosilicate glass annular photoreactor (800 ml capacity) was used for photocatalytic degradation reactions. The reactor has three ports used for monitoring pH, dissolved oxygen, and sampling. The reaction mixture was illuminated using either a 450 W medium pressure mercury lamp (Hanovia) (20), or an 8 W blacklight lamp (New England Ultraviolet Products, Inc., $\lambda_{\max} = 350$ nm) (21) within the borosilicate glass thimble. Short wavelength ultraviolet light and lamp heat were removed by a filter solution (330 nm cutoff, 60 g dm^{-3} $CuSO_4$ (Fisher), 0.25 g dm^{-3} 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate (Eastern Chemical)) constantly circulated through this thimble from a reservoir that was cooled by cold water circulating through copper coils. The reaction temperature was 25 ± 0.5°C when the 8 W lamp was used, and 29 ± 1.0°C when the 450 W lamp was used. Dissolved oxygen concentration, pH, and temperature were monitored constantly.

Solutions of 250 μM 4-CP were prepared by diluting a stock solution with Milli-Q water and saturating with oxygen. TiO_2 addition made no significant change to either the 4-CP or dissolved oxygen concentration. Samples for HPLC analysis were removed from the reactor with a syringe at regular intervals and filtered using Gelman 0.2 μm PVDF syringe filters to remove the catalyst particles (samples that were analyzed using TOC were filtered with PTFE syringe filters, because organic material eluting from PVDF filters interfered with TOC analysis). Comparisons of light transmission were made using a long wave UV meter (by Ultraviolet Products, Inc., San Gabriel, CA). A fuller description of the experimental details is available elsewhere (18).

Monochromator. Experiments were conducted to study the effect of wavelength on quantum yield. In this series 5 ml aliquots of 250 μM 4-CP solutions with 0.125 g dm^{-3} of TiO_2 in suspension, saturated with oxygen, were degraded for 10 min using monochromatic light (250 W xenon lamp, SLM Instruments, and Bausch and Lomb monochromator). Light transmittance was monitored using a Scientech light-meter, and the output of the system at each wavelength was measured using potassium ferrioxalate actinometry (19). Aliquots of 5 ml of the actinometry solution (0.2 M $Fe_2(SO_4)_3$, 1.2 M $K_2Cr_2O_4$) were irradiated using the same monochromatic light for a measured time, and light intensity was calculated using the procedure detailed in Murov (19).

Analysis. HPLC (Waters 600E system controller, 712WISP auto sample injector, 990 Photodiode array detector) was used to analyze for 4-CP and aromatic intermediates in the samples. Aliquots of 50 μl were injected onto a reverse-phase C-18 column (Waters Nova-Pak or Supelco Supelcosil), and eluted with acidified water-methanol (60 : 40 with 1 ml/liter of acetic acid). Absorbance at 280 nm was used to measure the concentrations of 4-CP and aromatic intermediates (except benzoquinone whose concentration was measured at 254 nm).

TOC (total organic carbon) analysis was conducted using a Dohrmann DC-180 carbon analyzer, which employs the low temperature UV/persulfate oxidation method (22). Filtered samples (using PTFE syringe filters) were stored in 4 ml sample vials sealed with septa, to allow measurement of dissolved inorganic carbon, without CO_2 diffusing into or out of the sample prior to analysis. The IC (inorganic carbon) of total carbon of 400 μl aliquots were measured. TOC is the difference.

RESULTS

TiO_2 Concentration

Photocatalytic degradation of 250 μM 4-CP solutions was carried out with Degussa P25 TiO_2 catalyst loadings of 0.050–1.00 g dm^{-3} under UV-irradiation ($\lambda > 340$ nm). The concentrations of 4-CP, O_2, and the reaction intermediates. HQ and 4-CC, measured over the course of some experiments are shown in Fig. 1. The rate of consumption of 4-CP was zero order initially. The values for the initial rates of 4-CP disappearance are listed in Table 1. The initial rate of 4-CP disappearance showed a small increase with

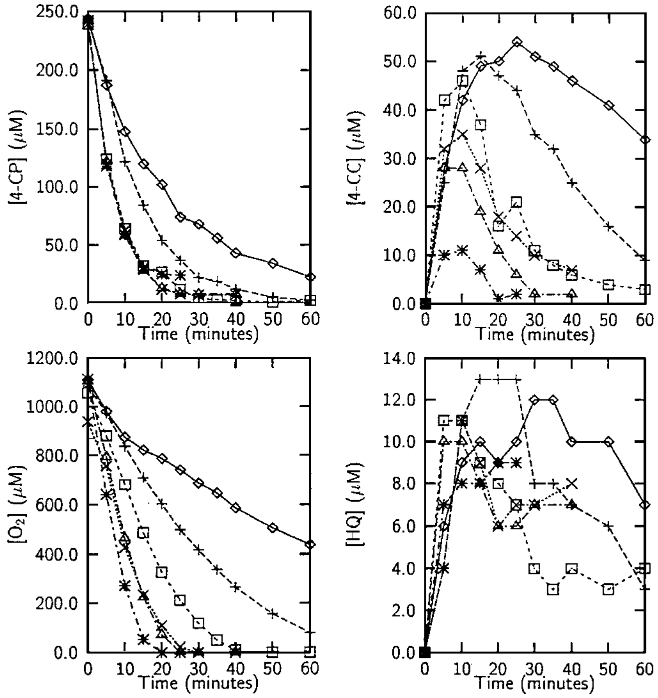

FIG. 1. The effect of varying the TiO_2 loading on the concentrations of 4-CP, oxygen, and intermediates, during the photocatalytic degradation of 4-CP using a 450 W medium pressure mercury lamp. The TiO_2 loadings used were 0.025 g dm^{-3} (◇), 0.050 g dm^{-3} (+), 0.125 g dm^{-3} (□), 0.250 g dm^{-3} (×), 0.500 g dm^{-3} (△), and 1.000 g dm^{-3} (∗).

TABLE 1

The Effect of TiO_2 Loading on Initial 4-CP Reaction Rates Using a 450 W Hg

TiO_2 concentration (g dm^{-3})	Trans-mittance through slurry, T^a	Initial rate of 4-CP reaction $k(\mu M\ min^{-1})^b$	Initial rate of 4-CP reaction corrected for light absorptance $(k/(1-T))^c$	Initial rate of oxygen consumption ($\mu M\ min^{-1}$)
0.025	0.71	10	35	24
0.050	0.57	12	28	25
0.125	0.23	23	30	28
0.250	0.08	24	26	51
0.500	0.02	24	25	64
1.000	0.00	25	25	84

[a] The ratio of the reading from a long wavelength ultraviolet meter through the slurry to the reading with no TiO_2 in solution.

[b] The initial zero order rate for 4-CP disappearance which is the slope of the initial linear part of the 4-CP curves in Fig. 1.

[c] The initial rate corrected for light absorption. Calculated by dividing the previous column values by $(1-T)$, where T is transmittance from column 2.

increasing TiO_2. At lower catalyst loadings much of the light was transmitted through the slurry in the annular reactor, while at higher catalyst loadings all the incident photons were absorbed by the slurry. Measurements of transmission of the slurry suggest that ~95% of the incident light is absorbed in the quarter of the reactor closest to the illuminated wall. To correct for the amount of light actually absorbed (not transmitted) the initial rate values were divided by the absorptance (23) and the corrected zero order rate values are listed in Table 1. There was little difference in this corrected rate at different TiO_2 loadings, with the exception of the lowest TiO_2 loading. The slightly faster corrected rate at this loading (0.025 g dm^{-3}) is discussed later.

Increased TiO_2 loading significantly decreases the concentration of the reaction intermediate, 4-CC, measured during the reaction (Fig. 1). HQ concentration is only slightly effected. The ratios of the maximum 4-CC and HQ concentrations relative to the initial 4-CP concentration are reported in Table 2. The ratio of the two reaction intermediate concentrations is also reported in the last column of Table 2. It is evident, that as the loading of TiO_2 was increased, the ratio of $[HQ]_{max}$ to $[4\text{-}CC]_{max}$ also increased.

TABLE 2

Maximum Intermediate Concentrations for the Photocatalytic Degradation of 250 μM 4-CP Using a 450 W Hg Lamp

TiO_2 concentration (g dm^{-3})	$[4\text{-}CC]_{max}$ (μM)	$[HQ]_{max}$ (μM)	$\frac{[HQ]_{max}}{[4-CC]_{max}}$
0.025	54	12	0.22
0.050	51	13	0.25
0.125	46	11	0.24
0.250	35	11	0.29
0.500	28	10	0.36
1.000	11	9	0.82

Initial rates of oxygen consumption are listed in Table 1. The rate increased considerably with increased TiO_2 loadings, and was greater than three times the initial rate of consumption of 4-CP at the highest TiO_2 loading (1.000 g dm^{-3}). This suggests that while the rate of 4-CP reaction increased little with increased TiO_2, the rate of its mineralization increased.

Reaction with an 8 W blacklight lamp. A similar series of reactions was completed using an 8 W blacklight lamp instead of the 450 W Hg lamp (shown previously in our work comparing radiolytic and photocatalytic oxidation) (14). The trends were similar to those seen using the 450 W lamp, although the rates were slower because of the lower lamp intensity. The only difference of note was the lower maximum concentration of 4-CC. The significance of this observation will be discussed later.

TOC analysis. Solutions of 4-CP were photocatalytically degraded in Degussa P25 TiO_2 slurry, and TOC (total organic carbon) and IC (inorganic carbon) were measured over the course of the experiments. In Fig. 2 the rate of consumption of 4-CP is compared with the rate of decrease in TOC concentration for the degradation of ~170 μM 4-CP solutions using a 450 W Hg lamp, in TiO_2 slurries with loadings of 0.125 g dm^{-3} and 1.000 g dm^{-3}. The initial zero order rate of degradation of 4-CP was 20 $\mu M\ min^{-1}$ in 0.125 g dm^{-3} TiO_2 slurry, and 17 $\mu M\ min^{-1}$ in 1.000 g dm^{-3} slurry. In comparison the initial rates of decline of TOC, expressed in terms of six carbon atoms (by dividing the TOC in ppm of carbon by 72), were 5 $\mu M\ min^{-1}$ for 0.125 g dm^{-3} TiO_2 slurry, and 11 $\mu M\ min^{-1}$ for 1.000 g dm^{-3} TiO_2 slurry. This indicates that while the degradation rate of 4-CP is similar in both slurries, the rate of overall degradation of organic species is over twice as fast in the thicker slurry.

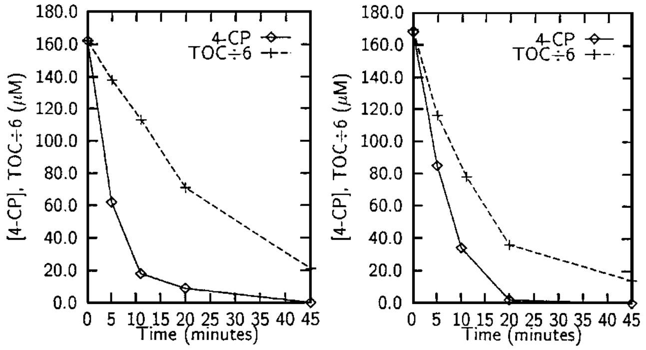

FIG. 2. The photocatalytic degradation of ~170 μM 4-CP solution using a 450 W Hg lamp, in 0.125 g dm^{-3} (left) and 1.000 g dm^{-3} (right) slurries of TiO_2 compared with the decline in total organic carbon TOC. The TOC is presented in terms of μM of carbon divided by 6, for easy comparison with 4-CP.

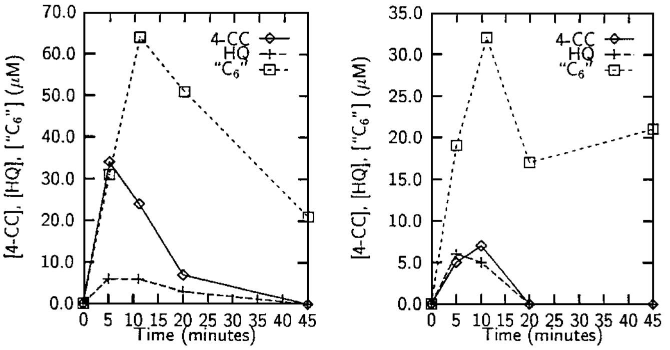

FIG. 3. Intermediates detected during the degradation of ~170 μM 4-CP solution in 0.125 g dm^{-3} (left) and 1.000 g dm^{-3} (right) slurries of TiO_2 (Fig. 2). "C_6", the unidentified intermediates, is the difference between the measured TOC and the quantities of 4-CP, 4-CC, and HQ. "C_6" represents six carbon species.

The intermediate concentrations are shown in Fig. 3. 4-CC concentrations are higher in the 0.125 g dm^{-3} slurry (as previously seen, Fig. 1). Intermediates other than 4-CC and HQ are represented by "C_6," a term for unidentified intermediates in terms of six carbon species (24). The concentration of "C_6" is higher in the thin slurry (0.125 g dm^{-3}), and lags in value behind the concentration of the other intermediates, suggesting that it represents subsequent degradation steps on course to complete mineralization (Reaction 1).

$$\text{4-CP} \rightarrow \text{4-CC, HQ} \rightarrow \text{“C}_6\text{”} \rightarrow\rightarrow CO_2, HCl, H_2O \qquad [1]$$

TOC and IC data are shown in Fig. 4. AC is an estimate of carbon adsorbed to TiO_2. It is the difference between the total carbon (sum of TOC and IC^{25}) at time t, and the initial total carbon. A peak is visible at around 5–10 min in the 1.000 g dm^{-3} slurry, which suggests that under these conditions concentrations of adsorbed intermediates are high when concentrations of intermediates in solution are highest (comparison of Fig. 4 with Fig. 3).

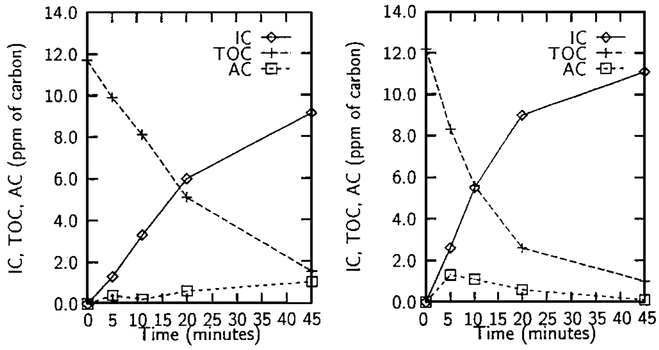

FIG. 4. Total organic carbon (TOC), total inorganic carbon (IC), and adsorbed carbon (AC) measured during the degradation of ~170 μM 4-CP solution in 0.125 g dm^{-3} (left) and 1.000 g dm^{-3} (right) slurries of TiO_2 (Fig. 2). IC is accounted for by dissolved CO_2, and AC is the difference between the initial TOC and the sum of TOC and IC.

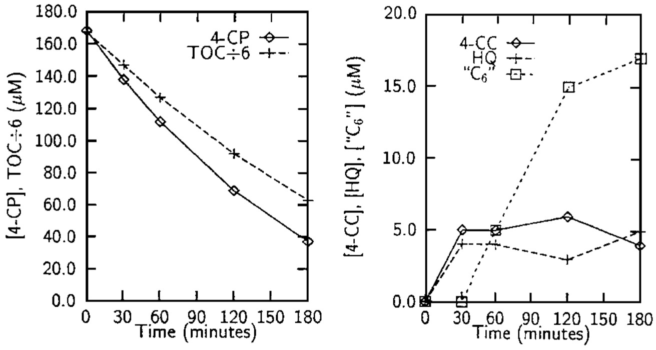

FIG. 5. The degradation of ~170 μM 4-CP solution in 0.125 g dm^{-3} slurry of TiO_2 with an 8 W blacklight lamp. Total organic carbon (TOC) is presented in terms of μM of carbon divided by 6, for easy comparison with 4-CP (left). Intermediate concentrations are also shown (right). The term "C_6" represents unknown intermediates in terms of 6 carbon unit species (24).

The TOC was also measured for a run using an 8 W blacklight lamp and 0.125 g dm^{-3} TiO_2 slurry (Fig. 5). The initial 4-CP degradation rate was 1.0 μM min^{-1} and the initial decline of TOC was 0.67 μM min^{-1}. The ratio of the rate of TOC decline to 4-CP disappearance was greater than for reaction with the 450 W Hg lamp. Intermediate concentrations are presented in the second part of Fig. 5. Concentrations are lower than for the reaction with the 450 W lamp. For this experiment, IC measurements were unreliable because the long time over which the reaction was run allowed CO_2 to equilibrate between the liquid and the gas headspace.

Adsorption of Intermediates

In the photocatalytic degradation of 4-CP the maximum concentration of 4-CC detected in solutions decreased when the loading of TiO_2 was increased (Fig. 1). This decrease may be due to 4-CC adsorption. While the amount of 4-CP adsorbed to TiO_2 from aqueous solutions has been measured and is reported as low or negligible (<2 μmole g^{-1}) (7–10, 26), adsorption isotherms of intermediate compounds such as 4-chlorocatechol on TiO_2 have not yet been reported.

An adsorption isotherm of 4-CC was measured by adding 1–5 g dm^{-3} of Degussa P25 to 104 μM 4-CC solutions and stirring for 1 h to allow equilibration. The final 4-CC liquid concentration as measured by HPLC was then plotted against the amount adsorbed per gram of TiO_2 (Fig. 6). This resembles a Langmuir–Hinshelwood isotherm and the correlation coefficient for the plot of C_s against C_s/C is 0.96. Using the equation for the Langmuir isotherm

$$C_s = -\frac{1}{K}\frac{C_s}{C} + C_{s_{max}} \qquad [2]$$

values of the equilibrium adsorption constant, K,

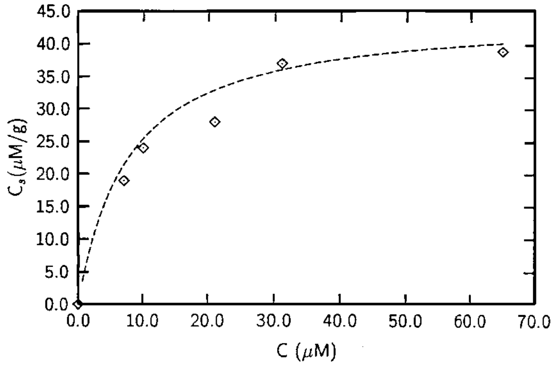

FIG. 6. Equilibrium isotherm for the adsorption of 4-chlorocatechol to TiO_2 (Degussa P25) (data points, ◇, and adsorption curve, $C_{s_{max}} = 45$ μ mole g^{-1}, and K, is 0.13 μM^{-1}).

$0.13 \times 10^6\ M^{-1}$, and maximum adsorbed concentration of 4-CC, $C_{s_{max}}$, 45 μmole g^{-1} were calculated.

Attempts were made to measure the adsorption isotherm for hydroquinone, but its adsorption was negligible. It is probable that the amount adsorbed to TiO_2 would be similar to the amount of adsorbed 4-CP (i.e., $C_{s_{max}} < 2$ μmole g^{-1}) (10).

Quantum Yield Measurements

Quantum yield in the annular photoreactor. Potassium ferrioxalate actinometry was used to measure the output of the 450 W medium pressure mercury lamp and the 8 W blacklight lamp in the annular photoreactor. Actinometry measurements were made under the same conditions, as the series of degradation reactions with varied TiO_2 concentrations were conducted. Detailed calculations are reported elsewhere (18). Corrections were made for the considerable output of the 450 W lamp in the blue visible region of the electromagnetic spectrum, which is sufficiently energetic to cause the photoreaction between ferric and oxalate ions that is the basis of the actinometer (19), but is not sufficiently energetic to cause charge separation in anatase TiO_2 ($\sim 400 < \lambda < 500$ nm). The long-UV ($\sim 300 < \lambda < 400$ nm) output of the 450 W lamp, that is transmitted by the filter solution into the photoreactor, was found to be 47 μerg s^{-1} (2.8 merg min^{-1}). Approximately 91% of the photons were at 366.0 nm, with the remainder being more energetic (302.5 nm, 313.0 nm, 334.1 nm). All other peaks are insufficiently energetic to cause TiO_2 photocatalysis, or were filtered out. The output of the blacklight lamp was mostly long-UV with a broad peak at 350 nm. Its output in the reactor was 1.85 μerg s^{-1} (0.111 merg min^{-1}).

Quantum yields of 4-CP and O_2 consumption, were calculated by dividing initial rates of consumption (Fig. 1 and Ref. (14)) by the rate at which photons were absorbed in the reactor. Corrections were made for absorptance (23) and quantum yields are reported in Table 3.

TABLE 3

Quantum Yields of Consumption of 4-CP and O_2 for Photocatalytic Reactions in Fig. 1 and Previously Published Work (14), Corrected for Light Absorptance

TiO_2 (g dm^{-3})	8 W blacklight lamp[14]		450 W Hg lamp[a]	
	$\phi^0_{[4CP]}$	$\phi^0_{[O_2]}$	$\phi^0_{[4CP]}$	$\phi^0_{[O_2]}$
0.025	0.029	0.078	0.012	0.029
0.050	0.026	0.056	0.010	0.020
0.125	0.017	0.046	0.011	0.013
0.250	0.016	0.055	0.009	0.020
0.500	0.017	0.062	0.009	0.023
1.000	0.018	0.073	0.009	0.030

[a] From Fig. 1.

Dependence of quantum yield on wavelength. Anatase has a band gap of 3.23 eV (27). This corresponds to the photon energy of 387 nm light. In order to assess wavelength dependence of the quantum yield, an experiment was conducted in which a 5 ml cuvette containing 250 μM 4-CP, 0.125 g dm^{-3} TiO_2 slurry was illuminated with monochromatic light. The data for this experiment are shown in Table 4, and the quantum yield plotted against wavelength is shown in Fig. 7. The quantum yield increased significantly with decreasing wavelength.

DISCUSSION

The effects of many different reaction parameters, such as the effect of initial 4-CP concentrations, oxygen concentrations, pH, and temperature, on the rate of the photocatalytic degradation of 4-CP have been previously reported (2, 4, 7, 8). This study examines in detail other experimental

TABLE 4

Quantum Yields for the Photocatalytic Degradation of 4-CP Using 0.125 g dm^{-3} TiO_2 Slurry at UV Wavelengths from 300–400 nm

λ (nm)	%T	$I \times 10^6$ (E)	$I \times (1 - \%T)$	[4-CP][a] (μM)	r[b] (μM min^{-1})	ϕ^{0}[c]
400	12	1.14	1.00	228	1.7	0.007
390	11	1.39	1.19	234	1.1	0.004
380	9	1.35	1.23	235	1.0	0.003
370	16	1.17	0.98	239	0.6	0.002
360	7	1.17	1.09	213	3.2	0.012
350	5	1.12	1.06	211	3.4	0.013
340	3	0.75	0.73	200	4.5	0.025
330	0	0.76	0.76	200	4.5	0.024
320	0	0.68	0.68	191	5.4	0.032
310	0	0.48	0.48	175	7.0	0.058
300	0	0.45	0.45	163	8.2	0.073

[a] Concentration after 10 min reaction. $[4\text{-CP}]_0$ was 245 μM.

[b] Zero order rate of disappearance of 4-CP, $r = ([4\text{-CP}]_0 - [4\text{-CP}]_{10})/t$.

[c] Quantum yield based on zero order disappearance of 4-CP over 10 min reaction. $\phi^0 = ([4\text{-CP}]_0 - [4\text{-CP}]_{10})V/tI$.

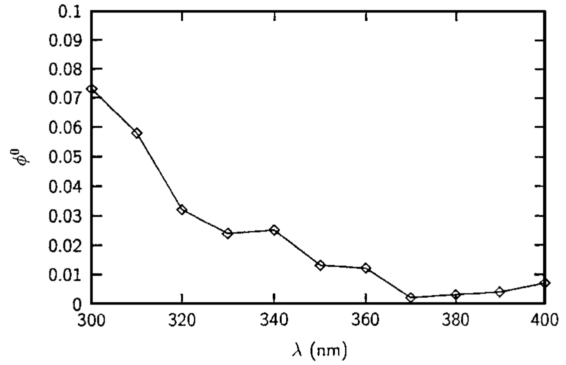

FIG. 7. Quantum yield for photocatalytic degradation of 4-CP with Degussa P25 TiO_2 plotted against wavelength.

parameters that have received little attention, in particular the effect of TiO_2 loading on intermediate concentrations and the effect of wavelength on the quantum yield. In addition, the effect of reaction conditions on the intermediate course of reaction is considered.

Effect of TiO_2 Loading

The concentration of aromatic intermediates during photocatalytic degradation of 4-CP varied significantly depending on the amount of TiO_2 added to the system. While the rate of disappearance of 4-CP, was relatively unaffected by the TiO_2 loading, its rate of mineralization, and the rate of oxygen consumption increased with increased TiO_2 concentrations.

Effect of TiO_2 loading on intermediate concentration. The concentration of aromatic intermediates, especially 4-CC, relative to the initial 4-CP concentration decreased considerably with increased TiO_2 loading during photocatalytic degradation of 4-CP in TiO_2 slurries. The effect was especially notable at higher concentrations (e.g. 1 g dm^{-3} of TiO_2) (see Table 2). The effect on the concentration of HQ was less significant, and at the highest TiO_2 catalyst loading (1 g dm^{-3}) the maximum concentration of HQ formed was similar to the maximum concentration of 4-CC.

Varied intermediate concentration values have been reported in previous studies of the photocatalytic degradation of 4-CP (2–4, 7, 11, 12, 14, 15). The TiO_2 loading was 2 g dm^{-3} in one study that reported a larger concentration of the intermediate HQ than 4-CC (4). The TiO_2 loading was 0.5 g dm^{-3} in a study that reported a larger concentration of 4-CC (7). The other reported studies in which HQ was the predominant intermediate used reactors of unique configuration that are not easily compared with the slurry reactors used in this study (14). In a study using ZnO instead of TiO_2 as the photocatalyst, it was reported that 4-CC was the predominant intermediate formed (12). Changes in pH have been proposed to be an explanation for these differences (7, 8). For example, no aromatic intermediates were detected when 4-CP was photocatalytically degraded at pH 9 (18). However, it is unclear if pH adequately accounts for all intermediate concentration and distribution differences. Rather, it is proposed that reactor configuration and catalyst loading have been found to have a significant influence on the product distribution, and thus account for most of the differences in the reported yields of reaction intermediates.

The decrease in intermediate concentrations, especially 4-CC, with increased TiO_2 loading suggests that surface reactions on TiO_2 particles, such as adsorption and oxidation of adsorbed intermediates, play an important role in the photocatalytic degradation of 4-CP. Adsorption experiments indicate that a significant amount of 4-CC adsorbs to TiO_2. Previous studies have shown that very small amounts of 4-CP are adsorbed to titanium dioxide from aqueous solution because it does not compete effectively with water for adsorption sites (7–10, 26). However, even a small amount of adsorbed 4-CP may be important in long-term irradiation experiments, especially at high surface loadings. As previously stated, when the photocatalytic reaction was carried out in a gas/solid system, 4-CP was chemisorbed to the TiO_2 surface and was degraded under ultra-violet irradiation to adsorbed HQ (13). No peaks consistent with adsorbed 4-CC were seen, indicating that transformation of adsorbed 4-CP is primarily to HQ (13). The increased ratio of [HQ]/[4-CC] (Table 2) with higher TiO_2 loadings is consistent with the possible contribution from such a surface reaction.

Adsorption of reaction intermediates. While previous research has shown that 4-CP is only sparingly adsorbed to Degussa P25 TiO_2 (<2 μmole g^{-1} of 4-CP are adsorbed to TiO_2 in slurries with <1 mM 4-CP in solution) (7–10, 26), very different behavior was observed for 4-CC. Langmuir isotherm data in the present study (Fig. 6) show that 4-CC is adsorbed strongly to TiO_2 ($K = 0.13\ \mu M^{-1}$, $C_{sat} = 45\ \mu$mole g^{-1}). Much less HQ is adsorbed under similar circumstances. The higher concentration of 4-CC in solution when using the powerful 450 W HG lamp instead of the blacklight lamp suggest that 4-CC is formed more rapidly than it is adsorbed, or that light energy is utilized differently depending on the intensity. The effect of light intensity on intermediate concentration will be discussed more fully below.

Effect of TiO_2 loading on the rate of mineralization. More rapid mineralization at higher TiO_2 loading is indicated by higher rates of oxygen consumption, lower overall concentration of intermediates (especially 4-CC) and higher rates of TOC reduction. The initial rate of decline of TOC was more than twice as rapid at a TiO_2 loadings of 1.000 g dm^{-3}, than at 0.125 g dm^{-3} (11 μM min^{-1} vs 5 μM min^{-1} in terms of six carbon atom molecules, see Fig. 2).

The initial rate of oxygen consumption was more rapid at the higher TiO_2 loadings. Earlier it was noted that maximum 4-CC concentrations were much lower in thick slurries.

These two facts, in addition to TOC data, support the thesis that in slurries in which significant quantities of intermediates are adsorbed to photocatalyst surfaces, mineralization is more rapid. Data presented by Al-Sayyed and co-workers are consistent with this observation (4).

Effect of TiO_2 loading on 4-CP reaction rate. The initial rate of 4-CP disappearance varies only slightly with TiO_2 loading as long as most of the incident light is absorbed along its path through the reactor (see Table 1). The decreased reaction rate at lower loadings has been explained by the fact that more light is transmitted through the reactor and the transmitted light is not utilized in photocatalytic reactions (4). However, a closer examination of the data in Table 1 indicates that when the initial rates of 4-CP degradation are corrected to account for transmitted light there is less variation in the rates. In fact, at the lowest TiO_2 loadings (0.025 g dm^{-3} and 0.050 g dm^{-3}) the corrected initial rate of 4-CP degradation increases. This is because when light is not limiting, a greater degree of excitation is by more energetic light.

Effect of Lamp Intensity

A comparison of the intermediate concentrations measured during reactions conducted using the 8 W blacklight lamp with reactions conducted using the 450 W medium pressure Hg lamp suggests that, when a lamp of lower light intensity is used, subsequent reactions of intermediates occur at a relatively faster rate than the initial degradation of 4-CP.

During the series of experiments in which TOC was measured, the initial rate of decline of TOC (in terms of six carbon units) was 67% of the rate of 4-CP degradation when the 8 W blacklight lamp was used to degrade 170 μM 4-CP, in a slurry with a TiO_2 loading of 0.125 g dm^{-3} (0.67 μM min^{-1} vs 1.0 μM min^{-1}). When using the 450 W Hg lamp under otherwise identical conditions, the initial rate of decline of TOC was 25% of the initial rate of degradation of 4-CP (5 μM min^{-1} vs 20 μM min^{-1}).

For the series of reactions conducted with 250 μM 4-CP and varied TiO_2 loadings, lower concentrations of aromatic intermediates were seen for the reactions conducted using the 8 W lamp than in those in which the 450 W lamp was used.

The lower concentrations of intermediates, and more rapid mineralization relative to initial substrate reaction, suggest that the relative proportion of reaction that occurs by the various reaction pathways is influenced by upon the light intensity. This enhanced rate of mineralization relative to initial substrate decay at lower light intensities suggests that surface reactions occur to a relatively greater extent at low light intensities. This may occur because the slower rate of hole production allows other species in solution to come into adsorption equilibrium with the TiO_2 surface.

Quantum Yield

Effect of wavelength. The bandgap of anatase TiO_2 is 3.23 eV (387 nm), but it appears that all photons more energetic than this are not equally efficient at causing photocatalytic degradation (Fig. 7). Quantum yields vary from 0.003 for 380 nm light to 0.07 for 300 nm light (Table 4). Quantum yield for 350–360 nm light, produced by the blacklight and medium pressure mercury lamps that are commonly used in photocatalytic studies, is ~0.013. This variation of quantum yield with wavelength indicates that care must be taken when comparing the reported quantum yields for photocatalytic degradation studies. This effect is the result of electrons that absorb more energetic photons being energized to an energy level higher than the conduction band minimum (LUMO—Lowest unoccupied molecular orbital). The higher energy electrons are less likely to recombine than electrons energized to the LUMO. Close to the band gap the efficiency of solar cell increases with decreasing wavelength (28). It is probable that a similar relationship would apply to TiO_2 photocatalyst particles, which in effect are minisolar cells.

Quantum yield in the photoreactor. In Table 3 quantum yields for the degradation of 4-CP and the consumption of oxygen in the annular photoreactor are reported. The data were extracted from the experiments conducted with different TiO_2 concentrations that are reported in Fig. 1 and our earlier work (14), and have been corrected for light transmission. The figures are similar to others previously reported for photocatalytic degradation of 4-CP with lamps of similar intensity ($0.009 < \phi < 0.013$) (4, 10). Quantum yields of 4-CP disappearance were higher at the lower TiO_2 concentrations. This is because a greater proportion of the absorbed photons have shorter wavelengths and are more energetic.

The quantum yield for oxygen consumption increased with increasing TiO_2 loadings, and reached a maximum of $\phi^0 = 0.073$ for the reaction with the 8 W blacklight lamp and 1 g dm^{-3} TiO_2 slurry. This is a further indication of the more rapid mineralization of 4-CP in thicker slurries.

The 8 W blacklight lamp is more efficient than the 450 W Hg lamp. It is widely accepted that less intense lamps have greater quantum officiencies for TiO_2 photocatalysis, and the relationship, $\phi \propto I^{0.5\text{–}0.74}$, has been reported (4, 8). Comparing the quantum yields in Table 3 with lamp intensities, relationships of $\phi^0_{[4CP]} \propto I^{0.8}$ and $\phi^0_{[O_2]} \propto I^{0.7}$ were calculated. The reason for variations in the exponent is discussed in greater detail in a subsequent paper (29).

CONCLUSIONS

4-CP in aqueous TiO_2 suspension was mineralized when the suspension was illuminated with long wavelength UV light (300 nm $< \lambda <$ 400 nm). While increased TiO_2 loading did not enhance the initial rate of 4-CP degradation in photocatalysis, increased TiO_2 loading did benefit the rate of mineralization of 4-CP. This was partly due to the significant adsorption of 4-CC to the surface, and to the increased importance of surface oxidation reactions. The quantum yield of mineralization also increased.

The rate of mineralization relative to initial substrate decay in TiO_2 photocatalysis is also enhanced at lower light intensities. This suggests that surface reactions occur to a relatively greater extent at low light intensities. This may occur because the slower rate of hole production allows other species in solution to come into adsorption equilibrium with the TiO_2 surface, and more surface sites are occupied by species other that hydroxyl groups.

The wavelength of UV-light has a great effect on the quantum yield of reaction with significantly faster rates of reaction being caused by 300 nm light than by light of longer wavelengths. This suggests that great care should be taken when reporting quantum yield measurements, and using shorter wavelength light may be a practical way of improving quantum yield and light utilization.

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23. Absorptance is the amount of light absorbed relative to the incident light. Its value is $1-T$, where T, the transmittance, is the amount of light transmitted through the reactor.
24. The term "C_6" does not mean that all unidentified organic carbon intermediates have six carbon atoms. Rather, it is likely that much of the "C_6" represents species with fewer carbon atoms, and is used here for mass balance purposes as the pool of unidentified carbon. "C_6" is calculated by subtracting the total 4-CP and known intermediates, from the TOC in terms of six carbon atoms.

$$[\text{“}C_6\text{”}] = \frac{\text{TOC}}{(12)(6)} - ([\text{4-CP}] + [\text{4-CC}] + [\text{HQ}])$$

25. If CO_2 in the headspace of the reactor, $\sim$100 cm^3, were in equilibrium with the CO_2 dissolved in solution, the total IC, calculated according to Henry's law would be aproximately 15% greater. However, due to the small liquid surface area in the annular reactor there is insufficient time for the liquid and headspace to come into equilibrium.
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