

The effect of UV absorption on the photocatalytic oxidation of 2-nitrophenol and 4-nitrophenol

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Abstract

Adsorption of 2-nitrophenol and 4-nitrophenol by titanium dioxide was measured and their photocatalytic oxidation was followed by both HPLC analysis and measurement of the total organic carbon content of the solution. The oxidation follows pseudo-first order kinetics with rate constants that decrease as the nitrophenol concentration increases. However the adsorption constants inferred from the reaction kinetics are inconsistent with those measured in the adsorption experiments, even though the relative amounts of reaction intermediates remain low. We conclude that the decrease in rate constant cannot be explained by a Langmuir–Hinshelwood model. Instead we suggest that the strong, but differing, UV absorption by nitrophenols lowers the effective UV flux at the catalyst surface and that the greater absorption of more concentrated solutions is primarily responsible for the apparent decrease in rate constant. A simple treatment of this absorption adequately describes the observed changes in rate. The quantitative effect of UV absorption depends on the lamp and on the reactor optics. It is suggested that variations are responsible both for differences in the reported relative oxidation rates of the two isomers, and for the different conclusions reported with respect to the effect of pH on oxidation rate.

1. Introduction

1.1. Mechanism

This paper describes the photocatalytic oxidation of nitrophenol by titanium dioxide. Photocatalytic oxidation by semi-conductors has been widely reviewed [11, 22]. It can occur either by direct transfer of a photo-generated positive hole to an organic molecule – direct hole transfer – or by reaction of the positive holes with hydroxyl ions, or surface hydroxyl groups, to form highly active hydroxyl radicals. Hydroxyl radical formation is believed to control the photocatalytic oxidation of nitrophenols, and during oxidation hydroxylated intermediates have been identified [33–55].

Nitrophenol by-products are representative of the substituted aromatics which may be present in a range of industrial effluents. In nitrophenols, hydroxyl substituents donate electrons to the aromatic ring whilst NO_2 withdraws electrons. Electron donating substituents increase the rate of the electrophilic bromination of benzene whilst electron-withdrawing- NO_2 groups

reduce the rate [66, 77]. The effect of the nitro substituent on the hydroxyl group is reflected in the dissociation constants of the three isomers. K_a for 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP) are similar (6.8×10^{-8} and 7×10^{-8} respectively) but both are greater than that for 3-nitrophenol (3-P), (5.3×10^{-9}); i.e. the ionization of the OH is much greater in the 2- and 4-isomers [88].

1.2. Apparent oxidation kinetics

The decrease in the concentration of nitrophenol during photocatalytic oxidation by TiO_2 generally follows pseudo-first order kinetics [33–55, 88–1212], despite the wide range of experimental conditions used in these studies (Table 1). However, an increase in the initial concentration of nitrophenol is reported [88, 99, 1111] to decrease the measured rate constant, k , even though the amount of nitrophenol oxidized either increases or goes through a maximum as the concentration is increased. Most authors [44, 55, 88, 99] consider the kinetics of nitrophenol oxidation to be represented adequately by an expression of the form

Table 1. A summary of previous work photocatalytic oxidation of nitrophenol

Reference & overall kinetics	TiO ₂ type, Surface Area/m ² g ⁻¹ & Catalyst loading/g dm ³	pH range	NP Conc./mm	Lamp type & analytical measurement method	Pseudo-first order rate constant $k_{\text{obs}} \times 10^4/\text{s}^{-1}$ & Langmuir adsorption constants, K
Tanaka et al. [33]	Fujititan (Anatase) 17, Loading of 3/g dm ⁻³	Natural	1	500 W Hg (HP), HPLC + TOC	1.2
Wang et al. [44] Langmuir-Hinshelwood	Degussa P25 55, Loading of 2/g dm ⁻³	3-11	0.1	125 W Hg (High P), HPLC + TOC	4.2-1.0
Cinar et al. [1212]	Degussa P25 55, Loading of 3/g dm ⁻³	5.1	0.035-0.093	5 × 8 W, Black light fluorescent lamps. 3.1 × 10 ⁻⁷ einstein s ⁻¹ UV spectra	0.7 × 10 ⁻⁴ at 0.1 mM
Chen et al. [55] Langmuir-Hinshelwood	Degussa P25 55, Hombikat > 250, 0.2-4/g dm ⁻³ , normally 2 /g dm ⁻³	2-10	0.14-1.7	125 W Hg (High P) UV/VIS + TOC	$K/(\text{Intensity})^{0.84} = 1.54$ $k/(\text{Intensity})^{0.84} = 0.6$ 5.8-0.84; $K_{4\text{NP}} = 10,400 \text{ M}^{-1}$ 0.28; $K_{2\text{NP}} = 7650 \text{ M}^{-1}$ $K_{4\text{NP}} = 8915 \text{ M}^{-1}$
Palmisano et al. [88] Langmuir-Hinshelwood assuming O ₂ and NP adsorb on different sites	Merck (Anatase) 11, Tiioxide -(Anatase) 14, Tiioxide (Rutile) 20, BDH (Anatase), 11 Montedison B5, Anatase 22, Normally 0.6/g dm ⁻³	pH 3 (b) Natural	0.7-7 Or (b) 0.22-2.2	1500 W Xe, 6.8 × 10 ⁻⁴ einstein s ⁻¹ Or 500 W Hg (HP), 1.5 × 10 ⁻⁴ einsteins ⁻¹ , UV/VIS. absorption	
Augugliamo et al. [99], Langmuir-Hinshelwood	Merck (Anatase) 11, Loading of 0.8/g dm ⁻³	3-11	0.2-1.4	500 W Hg (Med P), UV/VIS + TOC	2.77-0.21
Andreozzi et al [1010], Langmuir-Hinshelwood or Rideal Eley	Eurotitania 100, Loading of 0.2-6/g dm ⁻³	3 & 8.5 Phosphate-Buffer	0.25 to ~0.7	125 W Hg (High P) 0.88 kW dm ⁻³ HPLC	8, $K_{4\text{NP}} 1000 \text{ M}^{-1}$ at pH 3
Adesina et al. [1111]	Aldrich (> 99% anatase), 0.5-1.5, normally 1/g dm ⁻³		0.1-0.7	200, 300 or 400 W with a significant 250-310 nm component	

$$\begin{aligned} \text{Oxidation rate} &= \frac{-dc}{dt} = -kc_s \\ &= -k_{\text{surf}} \left(\frac{K_a c_s [\text{OH}^\bullet]_s}{1 + K_a c_s + \sum_p K_p P} \right) \quad (1) \end{aligned}$$

where c_s is the solution concentration of nitrophenol at time t and the observed rate constant k depends on the surface rate constant k_{surf} , the surface concentration of hydroxyl radicals $[\text{OH}^\bullet]_s$ and the surface concentration of nitrophenol. The nitrophenol surface concentration depends not only on its equilibrium solution concentration, c_s , and adsorption constant K_a , but also on adsorption of different intermediates and products—here represented as P . The detailed interpretation of Equation (1) varies. It may be derived for the Langmuir–Hinshelwood mechanism—i.e. a bimolecular surface reaction of two adsorbed reactants whose adsorption may be affected by the adsorption of one or more products species. However, Turchi and Ollis [1313] derived this form of equation from four different hypotheses, including the postulate that the hydroxyl radical may migrate from the TiO_2 surface and thus the two reactants need not be surface bound. By contrast Palmisano et al. [88] suggest that nitrophenol and oxygen adsorption occur independently on different sites. Despite differences in the detailed application of Equation (1), most authors consider that nitrophenol oxidation is consistent with the Langmuir–Hinshelwood (LH) model and that the decrease in the rate constant, k , with concentration is attributable to competition for specific surface sites by the initially formed products of reaction, i.e. different forms of P . It is usually assumed that the adsorption constants for P are similar to that of the nitrophenol isomer i.e. that $K_a c_s + \sum K_p P = K_a c_0$. In turn this approximation implies that the adsorption of substituted aromatics is relatively insensitive to the nature of the substituents. Although it is usually impractical to measure the concentration of either the many different adsorbed species or the hydroxyl radical concentration on the surface of working catalysts, the Langmuir–Hinshelwood concept, of a reaction rate controlled by reaction between adsorbed species whose concentration is modified by competition for limited sites, remains useful. The term, ‘Langmuir–Hinshelwood model’ is widely used in studies of photocatalysis [88, 1111, 1414] and is therefore adopted in this paper.

Andreozzi et al. [1010] applied the model to oxidation of 4-NP. They measured the adsorption of 4-NP, and evaluated K_{NP} , at pH 3, but at higher pH, 8.5, adsorption was undetected. This difference was attributed to the fact that, at pH 8.5, 4-NP ($\text{p}K_a$ 7) exists in the anionic form which cannot adsorb on the negatively charged (assuming pzc 6) TiO_2 surface. However, their measurements were made in the presence of a phosphate buffer and the effect of phosphate adsorption was not considered. Chen and Ray [55, 1515] fitted parameters for the adsorption constants of 4-NP and O_2 , and the

effect of light intensity and temperature to a more complete expression stated to be predict the concentration profiles throughout a photocatalytic oxidation. The maximum rate was found at pH \sim 5, but had fallen to \sim 1/3 of this maximum by pH 8. The reaction rate also decreased at low pH. Adesina and Lea [1111] reported a much smaller decrease, \sim 10%, in rate constant as the pH increases from 5.5 to 11. Chen and Ray [1515] later derived an expression, using the UV absorption coefficient of the TiO_2 , to predict the optimum catalyst loading. They concluded that the design of effective slurry reactors must take into account the dependence of UV penetration on catalyst loading. Cinar and co workers [1212] demonstrated that the enhanced photo-oxidation of 4-NP in the presence of H_2O_2 and the reduced photo-oxidation following addition of Cu^{2+} in solution both followed pseudo-first order kinetics. (They interpreted the reduced rate as due to the $\text{Cu}^{2+}/\text{Cu}^+$ acting as an additional recombination route).

1.3. Comparison of different isomers

Previous reports agree that the mononitrophenols are more reactive than the dinitrophenols [33] and that 2-NP and 4-NP are more reactive than the 3-NP [33, 44, 88, 99], but there is less agreement on the relative oxidation rates of 4-NP and 2-NP. Two studies [33, 88] suggest that the reactivities of the two isomers are similar. A third [44] reports that 2-NP is oxidized more rapidly than the 4-isomer. A fourth [99] reports the opposite. These discrepancies suggest that the measured rates are influenced by other experimental parameters, some of which are listed in Table 1.

Most authors consider different adsorption strengths, K_a , to be responsible for the differences in oxidation rate of the various isomers. However, Tanaka and co-workers [33] considered that degradation rate was controlled by the relative rates of electrophilic addition of the hydroxyl radical to the nitrophenol and demonstrate reasonable correlation between the activities of the nitrophenols and their respective Hammett constants.

1.4. The objectives of this study

UV attenuation caused by changes in the TiO_2 concentration is often invoked to explain changes in degradation rates with changes in catalyst loading [88, 1010–1212]. However, although the strong TN absorption of nitrophenol has been used to monitor its solution concentration [88, 1212], little attention has been paid to the effect of this absorption on the effective UV intensity at the surface TiO_2 particles in suspension.

UV attenuation is important because a reduction in the UV intensity incident on any one catalyst particle decreases the rate of hydroxyl radicals formation, their equilibrium concentration, $[\text{OH}^\bullet]_s$, and consequently the rate constant, k , in Equation (1). Therefore, kinetic analyses should allow for the reduction of $[\text{OH}^\bullet]_s$,

caused by increases in nitrophenol concentration. UV attenuation is expected to be especially significant for reactors using immobilized photocatalyst. It is recognized that photocatalyst immobilization may lead to increased mass transfer problems [1414, 1616], but less attention has been paid to the problems associated with UV penetration of the water to be treated. This paper reports measurements of adsorption on, and photocatalytic oxidation by, Degussa P25 TiO₂, of 2-NP and 4-NP over a range of concentration. The photo-oxidation measurements have been made at relatively low light intensities – as would be used in practical photo-reactors or photoelectrocatalytic reactors – and this has allowed the effect of UV attenuation by nitrophenol to be explicitly considered.

2. Experimental details

A commercial TiO₂ (Degussa P25, ~80% anatase; 20% rutile) was used for all the experiments. The surface area, determined by gravimetric adsorption of N₂ ($\sigma_{N_2} = 0.162 \text{ nm}^2$), after outgassing at 110 °C for 2 h, was $45 \pm 5 \text{ m}^2 \text{ g}^{-1}$ consistent with a primary particle size of 30 nm. Nitrophenol solutions were prepared by sonication of nitrophenol crystals (Aldrich; purity of 99+ % and used without further purification) in deionized water.

UV/visible spectra were recorded, on Shimadzu UV-160A single beam spectrometer, using a 1 mm far-UV quartz cell. Solution pH was altered by addition of 1 M HCl or 0.5 M NaOH. Nitrophenol concentration was followed by high-pressure liquid chromatography (Dionex model UVD170S HPLC fitted with a C₁₈ reverse phase column). Sample of 50 μl in a 40:60 v/v methanol/millipore water carrier solution were manually injected at a flow rate of 1 ml min⁻¹. Total carbon content was determined using a Dohrmann Phoenix, model 8000, UV persulphate TOC analyser. Organic carbon content was calculated by subtraction of the inorganic carbon from the total carbon content.

For measurements of nitrophenol adsorption on TiO₂, nitrophenol solutions, 50 ml, of concentrations 1, 2, 4, 5, 6, 8 and 10 mM were placed in 100 ml conical flasks, sealed and equilibrated for 18 h. A 5 ml sample of the nitrophenol was first taken for TOC analysis. 1.5 g P25 was then added to the solution. The flask was resealed and the stirred slurry was equilibrated in the dark for 18 h. After equilibration, samples (2 ml) were taken and centrifuged at 3200 rpm for an initial 30 min. The supernatant suspension was then decanted and centrifuged at 3200 rpm for a further 30 min. This removed the TiO₂ powder, 5 ml aliquots of the centrifugate were diluted with millipore water to 25 ml for injection into the TOC for analysis. This was taken to be the equilibrium concentration. The adsorption constant (K_{NP}) and the monolayer volume (V_m) were calculated using Langmuir analysis.

Nitrophenol oxidation was measured using 8 g dm⁻³ TiO₂ dispersions prepared by mixing 0.4 g P25 in 50 ml nitrophenol solution for 30 min prior to illumination. (Preliminary experiments had indicated that this was

sufficient equilibration time). During this period the vessel was equilibrated at 303 K and sparged with a constant flow of oxygen. Subsequently, irradiation was begun whilst a flow of oxygen was slowly bled across the top of the continuously stirred suspension. Measurements were made for initial concentrations from 0.5 to 8 mM, for 2-NP, and 0.25 to 4 mM, for 4-NP. When appropriate, pH alteration or sodium bicarbonate additions were made prior to equilibration.

The reaction was carried out in a cylindrical pyrex vessel [1717] illuminated, from the base, by two Philips PL-L 36W 09 lamps placed horizontally in a light box from which radiation was emitted through a circular port, whose aperture matched the reactor diameter, and heat filter. The relative wavelength distribution of the lamp immediately above the heat filters was measured at him intervals with a Spex 740A Radiometer and is shown in Figure 1b. Where appropriate, neutral density filters were fitted between the heat filter and the bottom of the reactor. Two sizes of reactor were used, one of 45 mm diameter and 130 mm height, and one (used if oxidation was to be followed by TOC measurement) of 60 mm diameter and 200 mm height. The reactor temperature was controlled at 303 K by a closely fitting cylindrical heater. Samples of the reaction mixture were withdrawn by a hypodermic syringe through a sampling port fitted with a septum cap both before illumination and typically at 30 min intervals. They were then centrifuged, to remove TiO₂, prior to analysis by HPLC or TOC as described above.

3. Results

3.1. UV absorption spectra

The absorption spectra of solutions of 2-NP (1 mM) and 4-NP (0.25 mM) are shown in Figure 1a and 1b. At their natural pH (~5.8), both compounds absorb to a similar extent at 36 nm the wavelength of maximum UV output. However, from 300 to 350 nm and at wavelength above 375 nm, the 4-NP absorbs more strongly than 2-NP. The figures also show the dependence of absorption on pH which results from the change in nitrophenol ionization with pH. For 2-NP a peak at 415 nm replaces the peak at 350 nm as pH increases. A similar effect is observed for 4-NP – a peak at 400 nm gradually replaces that at 317 nm. At 365 nm, the wavelength of maximum UV emission from the PL-L 09 lamps, the absorption of 2-NP gradually decreases, by ~20%, as pH is raised, but the absorption of 4-NP increases by a factor of 4 as the pH is raised from 5 to 9.

3.2. Adsorption of nitrophenols by TiO₂

Adsorption of nitrophenols on the TiO₂ at the natural pH (~5) of the nitrophenol/TiO₂ slurries is shown in Figure 2. It is immediately obvious that 2-NP adsorbs

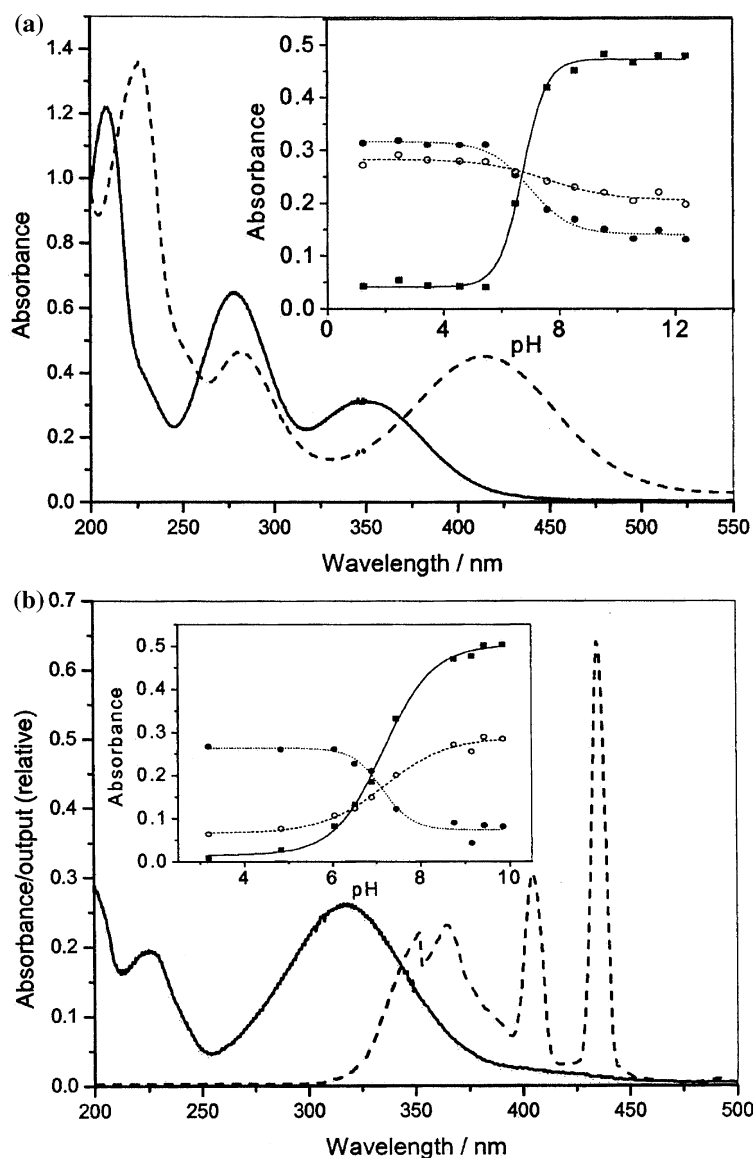


Fig. 1. (a) Absorption spectra of 2-Nitrophenol (1 mM) at the natural pH of 5.2 (solid line) and pH 8.5 (dotted line). The inset shows the absorbance at 415 nm (solid line), 365 (empty symbols, dotted line) and 350 nm (full symbols, dotted line) as a function of pH. (b) Absorption spectra of 4-Nitrophenol (0.25 mM) at the natural pH of 5.4 (solid line) and spectral output of the UV lamps (dotted line). The inset shows the absorbance at 400 nm (solid line), 365 nm (empty symbols, dotted line) and 317 nm (full symbols, dotted line) as a function of pH.

much more strongly than 4-NP. In the range 0 to 3.5 mM, adsorption of 2-NP can be fitted to a Langmuir model and leads to $K_{2\text{-NP}} \sim 0.4 \text{ mmol}^{-1} \text{ dm}^3$. The corresponding value for 4-NP is too small to measure but is less than 5% of 2-NP value. Andreozzi et al. [1010] inferred that $K_{4\text{-NP}} = 1.4 \times 10^{-3} \text{ mmol}^{-1} \text{ dm}^3$ at pH 3 but detected no measurable adsorption at pH 8.5

3.3. Oxidation of 2-nitrophenol

Most oxidations were monitored by HPLC to follow the decrease in nitrophenol concentration. During the reaction small changes in the form of the UV absorption spectrum suggested the presence of intermediate oxidation products. Correspondingly, the HPLC output indicated the presence of three possible intermedi-

ates. None corresponded to catechol and it is probable that the most important is nitrohydroquinone. The relative amounts of these intermediates were assessed from comparative analyses by TOC and HPLC. The result of such an experiment, Figure 3a, shows that, at any given time, the total organic carbon is close to, but slightly higher than the nitrophenol. The small difference represents the total amount of intermediate oxidation products. By contrast, Figure 3b shows the total amount of the intermediate products as a fraction of the total amount of organic carbon and demonstrates that for reaction times below 180 min, the intermediates were less than 5% of the total organic molecules in solution. Hence, most measurements of 2-NP oxidation were followed by HPLC only and, to minimize the effects of possible reaction intermediates,

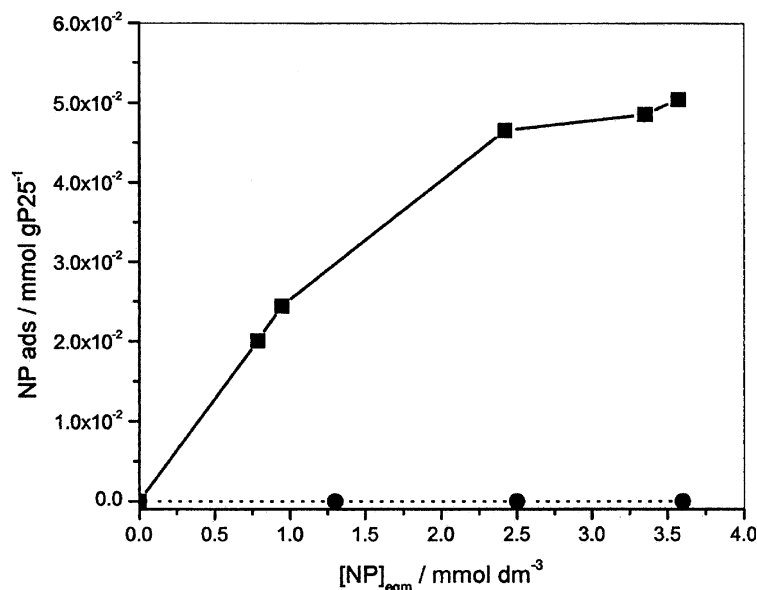


Fig. 2. Adsorption of 2-nitrophenol (■) and 4-nitrophenol (●) on TiO₂ (Degussa P25) from aqueous solution at natural pH.

kinetic analysis was restricted to times less than 180 min.

The results of a series of photo-oxidations of 2-NP are shown in Figures 4a. As adsorption on the TiO₂ led to significant reductions in (c_i) the nominal initial concentration of 0.5 to 8 mM, sufficient time was allowed, prior to starting a photocatalyzed degradation, for the solution concentration to reach an equilibrium value (c_0). It is this value that is plotted at $t=0$ used to derive rate constants. The corresponding first order plots, Figure 4b, are linear within experimental error (Triplicate measurements for selected runs indicated a reproducibility of $\pm 5\%$ in the derived slopes) and suggest that the system may be described by pseudo-first order kinetics. However, as shown in Table 2, increasing initial concentration of 2-NP results in decreasing rate constants and therefore the degradation rate of 2-NP does not increase proportionally to the concentration as would be expected for a true first order reaction. A 20-fold increase in 2-NP concentration leads to a 6 fold increase in the number of 2-NP molecules removed.

3.4. Oxidation of 4-nitrophenol

The results of an initial study to follow the 4-NP oxidation by both HPLC and TOC are shown in Figure 5a. From 30 to 150 min reaction the total amount of intermediate-products, shown as a fraction of the total amount of organic carbon were approximately constant at 15% of the total organic molecules in solution. This figure, though higher than the corresponding result for 2-NP oxidation still represents a relatively small fraction of the solution molecules. Hence, as for 2-NP, 4-NP oxidation was followed by HPLC only, with kinetic analysis based on results obtained within, the first 150 min.

Results of 4-NP photo-oxidation are shown in Figure 5b and in Table 3 showing similar trends to 2-NP oxidation. E.g. a 16 fold-increase in 4-NP concentration decreased the pseudo-first order rate constant but doubled the absolute amount of 4-NP degraded. These results were measured some time later than those for 2-NP, and, because of possible variations in the lamp output, are not strictly comparable with the, earlier, 2-NP results.

3.5. The effect of pH on nitrophenol oxidation

All the above results were measured on nitrophenol solutions at their natural pH. This was typically ~ 5 , but the precise value depended on the nitrophenol concentration and type, and on the reaction extent. Good first order plots were obtained despite the slight downward pH drift during oxidation (e.g. from 4.8 after equilibration to 4.2 during the first 1.50 min of oxidation of 1 mM 2-NP) and, to avoid possible effects of buffer adsorption, no attempt was made to use buffers to hold the pH constant. However, in order to investigate the dependence of oxidation rate on concentration of sodium bicarbonate, which increases the pH, the effect on oxidation rate of deliberately increasing pH with NaOH was measured. Figure 6 shows that a pH increase from 5.2 to 5.8 increases the degradation rate of 1 mM 2-NP by $\sim 70\%$ but from 5.84 to 7.7 any further increase was marginal ($\sim 10\%$). Correspondingly, results for 0.25 mM 4-NP showed a $\sim 10\%$ increase as the pH was increased from 5.0 to 5.8, a plateau until 8.0 and then a similar increase the pH was increased to 9.1. The results are reasonably consistent with the conclusion of Wang et al. [44], that pH 7 is the optimum for oxidation of both isomers, but contrary to the general decrease in

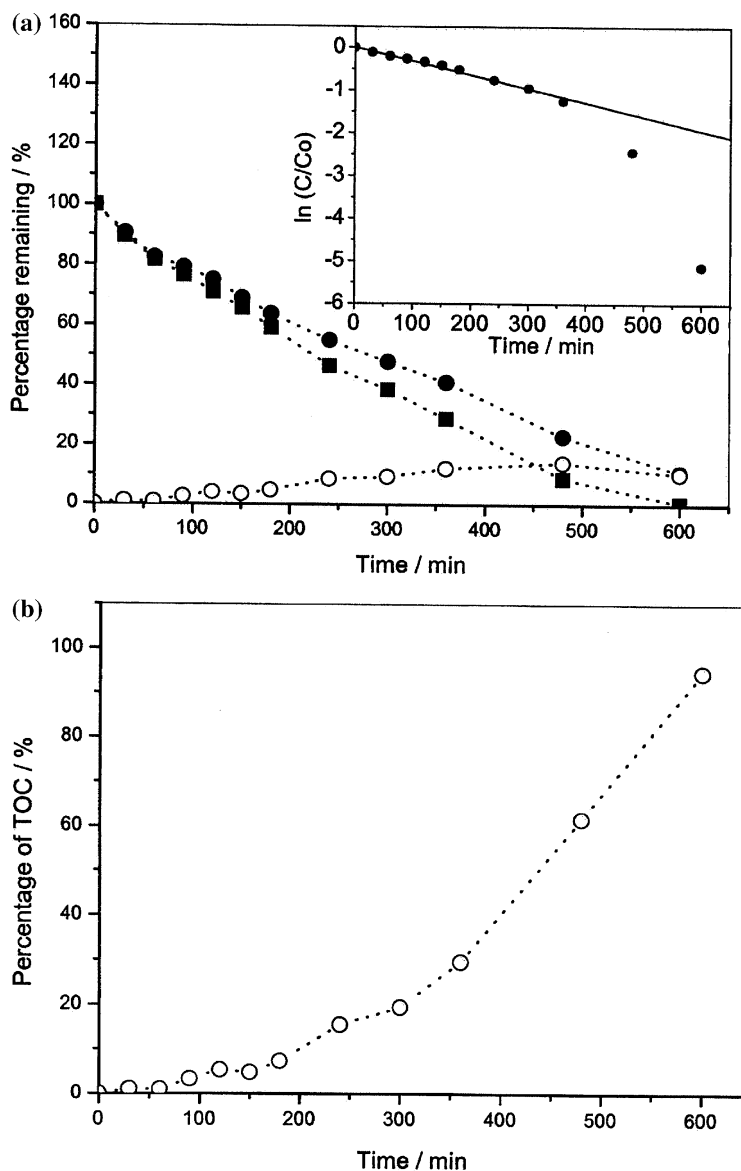


Fig. 3. (a) A comparison of the removal of 2-nitrophenol (initial concentration $c_i=1$ mM), measured by IPLC (■), and the removal of organic carbon, measured by TOC (●). The total amount of intermediate oxidation products (○) corresponds to the difference between the curves. The inset shows the first order kinetic rate plot as measured by HPLC. (b) The increase with time of the total amount of intermediate products, expressed as a fraction of the total organic carbon.

rate with increasing pH reported by Augugliarno et al. [99]. The differences may be due to the different TiO_2 used, Degussa P25, as here, and Merck Anatase, respectively.

Table 2. Rates, and derived rate constants, for photocatalytic removal of 2-nitrophenol in aqueous solution

C_0 , 2-NP Initial concentration/m mol dm^{-3}	$10^4 \times$ (Rate constant derived from the slope of Figure 4b)/ s^{-1}	$10^4 \times$ Rate/m mol $\text{dm}^{-3}\text{s}^{-1}$
0.25	1.35	0.34
0.57	0.98	0.56
1.27	0.72	0.91
2.3	0.47	1.1
5.4	0.34	1.9

3.6. The effect of sodium carbonate addition on nitrophenol oxidation

If oxidation of nitrophenol is via catalytically active hydroxyl radicals the addition of sodium bicarbonate, which trap hydroxyl radicals by



should decrease the rate of nitrophenol oxidation. The results in Table 4 show that, although increasing pH increased the nitrophenol degradation rate, bicarbonate addition decrease the rate *relative to solutions at the same pH* by an amount that is proportional to $\log[\text{NaHCO}_3]$, Figure 7. However a 35 mM solution of NaHCO_3 decreases the rate by only 40% and extraction of Figure 7 suggest that >10 M NaHCO_3 would be

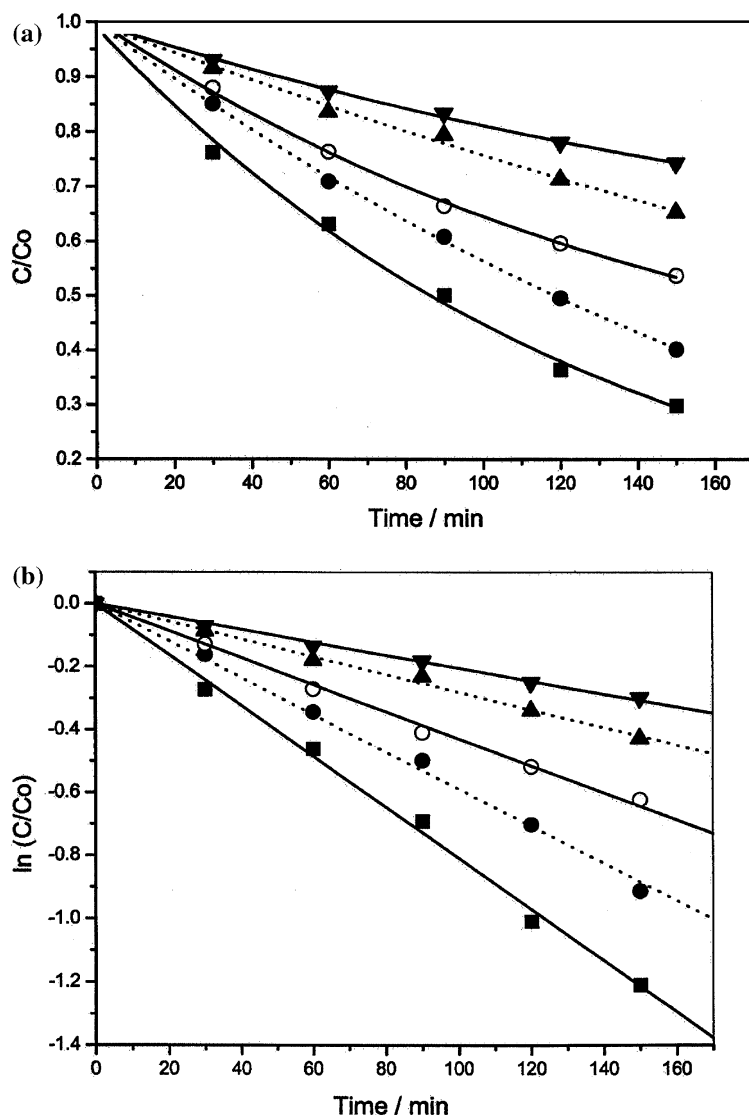


Fig. 4. (a) Photo oxidation of 2-nitrophenol expressed as C/C_0 $C_i=0.5$ mM (■), 1 mM (●), 2 mM (○), 4 mM (▲), 8 mM (▼). (b) Corresponding first order kinetic rate plots for photo-oxidation of 2-nitrophenol $C_i=0.5$ mM (■), 1 mM (●), 2 mM (○), 4 mM (▲), 8 mM (▼).

necessary to completely eliminate photocatalytic oxidation. Possibly, nitrophenol is oxidized not only by hydroxyl radicals but also by a direct hole transfer. In the accompanying paper [1818] methanol enhancement of photocurrent – attributed to direct hole transfer – is reported for sol gel electrodes which were more active for nitrophenol oxidation than were thermal electrodes for which methanol did not cause an increase in photocurrent.

3.7. Variation of oxidation rate with UV intensity

Photocatalytic oxidation rate varies with I , the incident UV intensity, according to I^n where the value of n depends on the details of the charge-carrier recombination [1919]. Figure 8 shows the effect of changes in light intensity on the degradation rate of 2-NP and 4-NP. For 1 mM 2-NP the rate is proportional to I^1 . For 0.25 mM 2-NP the dependence is more consistent with I^1 dependence at low intensities and $I^{0.5}$ at high light

intensity, For 0.25 mM 4-NP the rate is proportional to I^1 over the whole range of intensities.

4. Discussion

This study of nitrophenol oxidation has confirmed the decrease in the apparent first order rate constant with increasing nitrophenol concentration reported by others [33–55, 88–1212].

The simplest explanation is that, because the photon flux limits the number of molecules which react, the fraction of molecules which react necessarily decreases as nitrophenol concentration increases. This argument is too simple for three reasons. First, only a minority, < 5%, of incident photons lead to oxidation [11, 1919, 2020] – i.e., not all of the incident photons are used. Second, our results and those of others [99] show that the absolute amount of degradation increases despite the decrease of pseudo-first order rate constant. In our

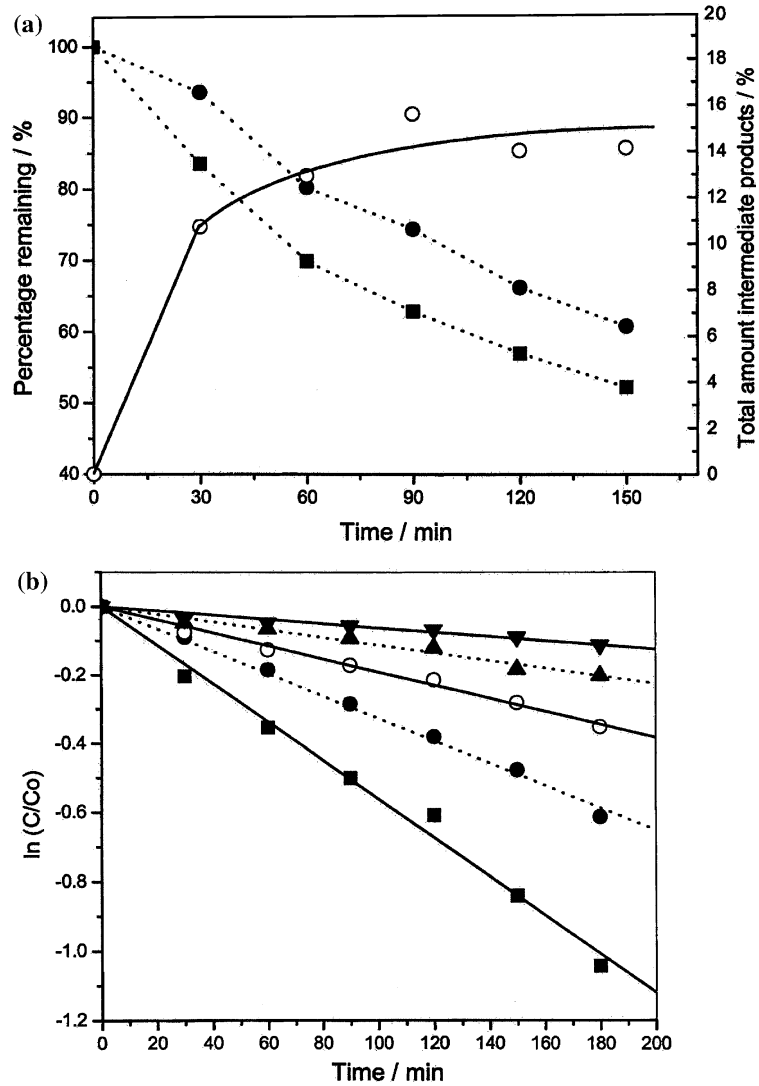


Fig. 5. (a) A comparison of the removal of 4-nitrophenol ($C_i=0.25$ mM), followed by HPLC (■), and by TOC (●), monitored over 2 h 30 min (left hand scale). The total amount of intermediate oxidation products (○) corresponds to the difference between the two curves (right hand scale). (b) First order kinetic rate plots for photo-oxidation of 4-nitrophenol. $C_{i0}=0.25$ mM (■), 0.5 mM (●), 1 mM (○), 2 mM (▲), 4 mM (▼).

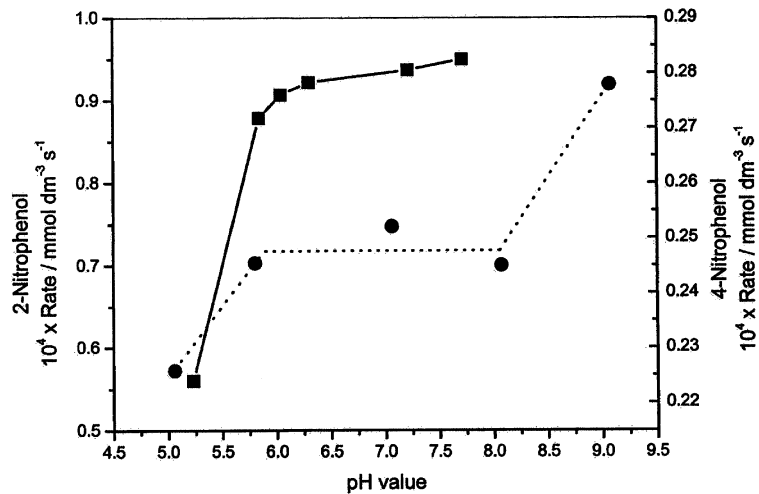


Fig. 6. The effect of pH on the initial degradation rate of 2-nitrophenol (■), left hand axis and 4-nitrophenol (●), right hand axis (1 mM initial concentration).

Table 3. Rates and derived rate constants, for photocatalytic removal of 4-nitrophenol in aqueous solution

C_0 4-NP Initial concentration/m mol dm^{-3}	$10^4 \times$ (Rate constant derived from the slope of Figure 5b)/ s^{-1}	$10^4 \times$ Rate/m mol $\text{dm}^{-3}\text{s}^{-1}$
0.25	0.935	0.234
0.5	0.545	0.273
1	0.318	0.318
2	0.188	0.377
4	0.105	0.418

system, a 16-fold increase in 4-NP concentration doubled the number of 4-NP molecules removed (Table 3) whilst a 20-fold increase in 2-NP concentration increased, by six, the number of 2-NP molecules removed (Table 2). This confirms that not all photons are being used. Thirdly, the variation in the apparent rate constant caused by fixed changes in concentration is not constant, but depends on other factors such as pH, see, e.g. [99].

Others have proposed that decreases in pseudo-first order rate constant with increased reactant concentration are caused by adsorption of intermediates or products. However, we emphasize the reduction of the effective UV flux at the surface of to catalyst particles.

4.1. Nitrophenol adsorption

The unexpected difference in adsorption of the two isomers mirrors a pattern in which the physical properties of 2-NP differ significantly from those of 3 and 4-NP. Thus 2-NP melts at a lower temperature, 45 °C, than 3-NP, 97 °C or 4-NP, 144 °C. These differences are attributed to the strong intramolecular

Table 4. Rates of degradation in the presence of bicarbonate relative to the rate at the same pH but in the absence of bicarbonate

$10^3 \times$ $[\text{HCO}_3^-]/\text{M}$	pH	$10^4 \times$ Rate/ mm s^{-1} in the presence of bicarbonate	$10^4 \times$ Rate/ mm s^{-1} at indicated pH, no bicarbonate	Bicarbonate induced Rate decrease%
0	5.2	0.560	0.560	0
2.2	5.8	0.785	0.878	11
4.4	6.0	0.743	0.907	18
8.8	6.3	0.693	0.922	25
17.6	7.2	0.645	0.937	31
35.2	7.7	0.578	0.950	39

hydrogen bonds between the nitro- and ON groups in 2-NP which suppress intermolecular hydrogen bonding. No intramolecular bonds occur in the other isomers and hence intermolecular association loads, e.g., to the increased melting points of 3-NP and 4-NP. We suggest that the hydrogen bonding between 4-NP molecules and H_2O and between and other 4-NP molecules reduces the adsorption of 4-NP at the solid surface. (The similar degree of adsorption of 2-NP and 2,6-dinitrophenol (DNP) [2121] on TiO_2 is consistent with this argument) 2-NP adsorption appears to reach an equilibrium value of $\sim 5 \times 10^{-2} \text{ mmol g}^{-1}$ of TiO_2 . If this corresponds to a monolayer, the calculated footprint of 0.98 nm^2 would agree reasonably well with 0.84 nm^2 estimated from bond lengths for a 2-NP flat on the surface. At higher solution concentrations of nitrophenol there is upturn in the isotherm (0.12 mmol g^{-1} at 7 mmol dm^{-3}) possibly caused by a change to a more vertical orientation of the adsorbed molecules.

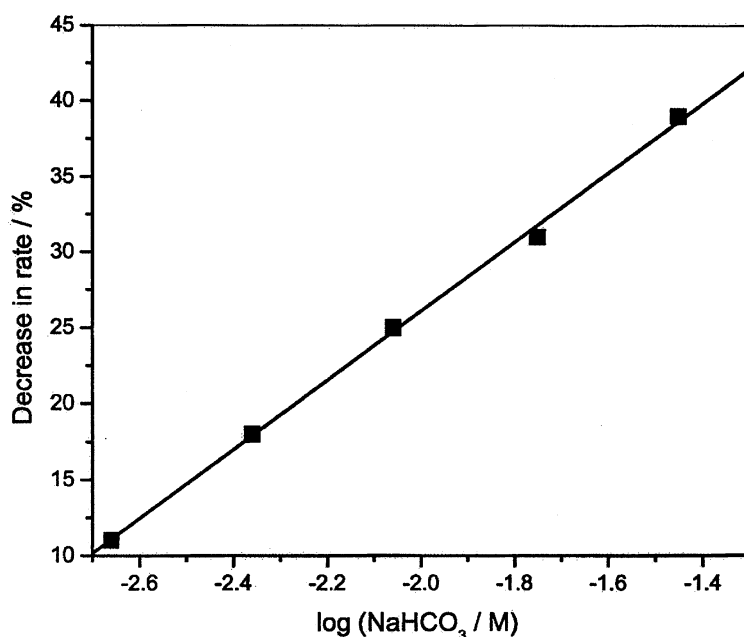


Fig. 7. The dependence of the % decrease in the rate of photocatalytic oxidation of 2-nitrophenol on the log of the concentration of sodium bicarbonate in solution.

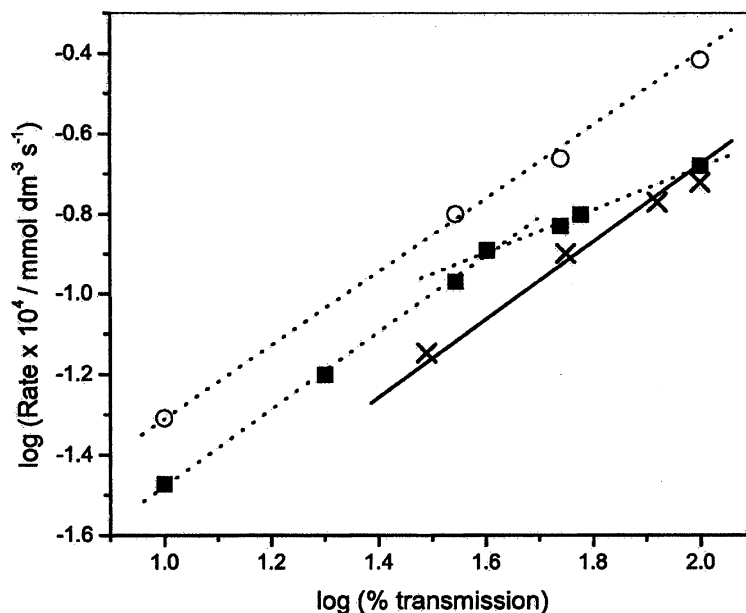


Fig. 8. Dependence of the rate of oxidation on the incident UV intensity for a (■) 0.25 mm; ○ 1 mm, 2-nitrophenol and × 0.25 mm 4-nitrophenol (solid line) solutions.

4.2. The effect of nitrophenol concentration on the measured rates of oxidation

The measured rates of 2-NP and 4-NP oxidation are shown in Figure 9. The measured first order rate constants, enumerated in Tables 2 and 3, decrease with increasing 2-NP or 4-NP concentration, as first reported by Augugliano et al. [88] and confirmed by others [55, 99, 1212]. This decrease is generally attributed to competitive adsorption by degradation-intermediates but this seems improbable, in our case, because our results were derived using conditions that minimized the

presence of reaction intermediates. The resulting simplified form of Equation (1)

$$\text{Oxidation Rate} = \frac{-dc}{dt} = -kc = \frac{-k_{\text{surf}}K_a c_s [\text{OH}^\bullet]_s}{1 + K_a c_s} \quad (2)$$

leads to a plateau value of the rate constant, k , but does not explain decrease.

Since the previous argument *assumes* that OH and adsorbed nitrophenol do not compete for the same sites, 1 mM 2-NP solution was oxidized for 10 h, to test the kinetics in an alternative way (To provide sufficient sample for analysis, this experiment was carried out in

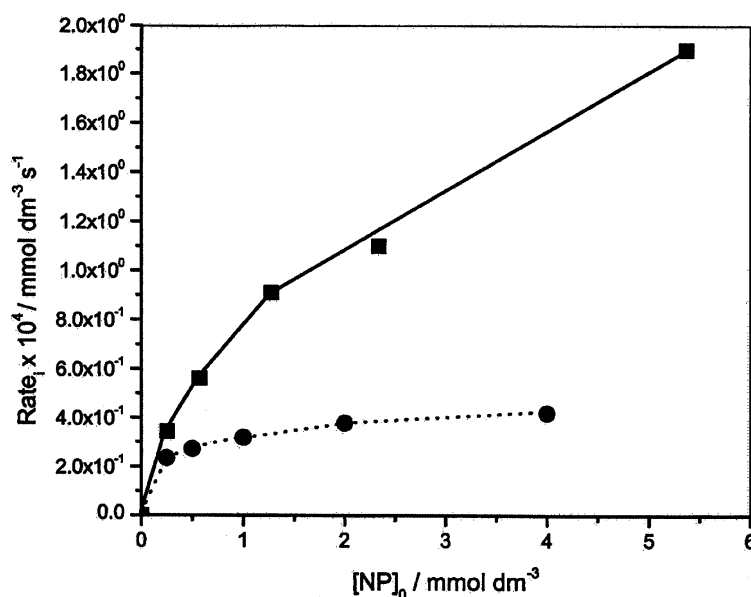


Fig. 9. Initial rate of disappearance of 2-nitrophenol and 4-nitrophenol and as a function of equilibrium concentration. (■) 2-nitrophenol; (●) 4-nitrophenol.

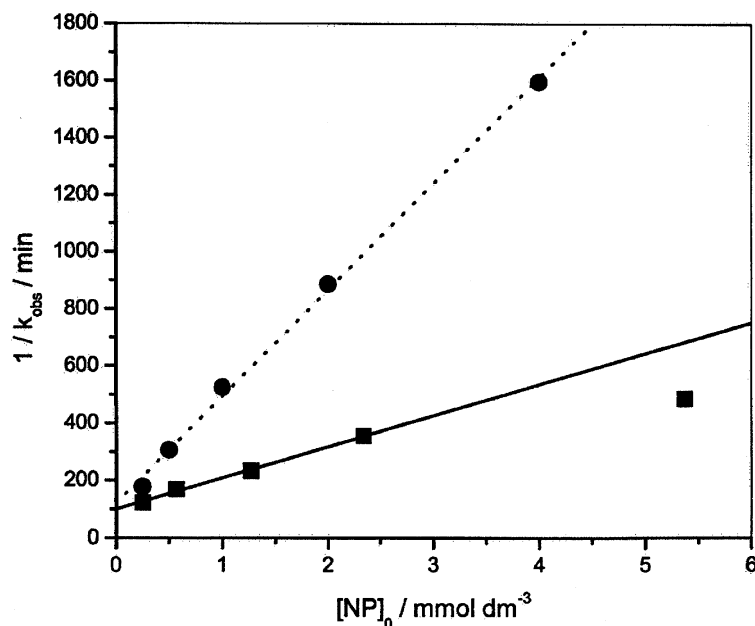


Fig. 10. Conventional test of Langmuir–Hinshelwood behaviour for 2-nitrophenol (■) and 4-nitrophenol (●).

the larger of the two reactors and because of slight differences in the optics the derived rate constants are not directly comparable with those in Table 2). At these long times the proportion of intermediates exceeds 20% of the total number of organic molecules, and could therefore be expected to affect the measured kinetics. The first order rate plot (see inset Figure 3a) showed no decrease in rate at reaction times greater than 360 min, as would have been expected if the surface was blocked by intermediates. Instead the deviation from the straight line is in the direction of *increased* degradation. Therefore, we again conclude that the decrease in measured rate constant with increased 2-NP concentration is unlikely to be caused by increasing competition by intermediate oxidation products.

The pattern of results found, for 2-NP is repeated for 4-NP. The adsorption results demonstrated that $K_{4\text{-NP}}$ ($0.02 \text{ m mol}^{-1} \text{ dm}^3$) \ll $K_{2\text{-NP}}$ ($0.4 \text{ m mol}^{-1} \text{ dm}^3$) and therefore a Langmuir–Hinshelwood model would predict that the plot of oxidation rate vs. nitrophenol concentration would saturate less rapidly for than for

Figure 9 shows that the reverse is the case. Although the conventional test of Langmuir–Hinshelwood behaviour – a plot (Figure 10) of $1/k_{\text{obs}}$ vs. c_0 gives acceptable straight lines – leading to values of $K_{2\text{-NP}} = 1.1 \text{ mmol}^{-1} \text{ dm}^3$ ($k_s_{2\text{-NP}} = 0.018 \times 10^{-3} \text{ s}^{-1}$) and $K_{4\text{-NP}} = 3.1 \text{ mmol}^{-1} \text{ dm}^3$ ($k_s_{4\text{-NP}} = 0.052 \times 10^{-3} \text{ s}^{-1}$) these values of K are inconsistent with those derived from direct measurements (Note also that the, often used, assumption that the adsorption constant K , for intermediate products equals the adsorption coefficient of nitrophenol [55,99] does not fit well with the large differences in K found for the two nitrophenol isomers). Quantitative analysis does not support the LH model.

Thus, all three different approaches to analysis of the measured rate constants have indicated the inadequacy of a simple Langmuir–Hinshelwood model. Similar analyses, comparing adsorption constants inferred from oxidation kinetics of benzoic acids with those derived from direct adsorption measurements, led Cunningham and Al-Sayyed [2222] to conclude that for substituted benzoic acids, as for nitrophenol, the Langmuir–Hinshelwood model cannot fully explain the experimental results. Mills and Wang [1414] found that the values of K derived from kinetic of chlorophenol oxidation by photocatalyst slurries are much larger than that previously measured [2323] in the dark – i.e. the variation of oxidation rate with concentration is larger than would be predicted from adsorption measurements made in the dark. Surprisingly, values of K derived from measurements on immobilized films were smaller than those found for dispersions of the same TiO_2 , even though the rate of oxidation was higher on the immobilized film.

Table 5. Average pathlength corresponding to 90% absorption of the incident intensity between 300 and 400 nm

Nitrophenol solution Concentration/mm	Path length/corresponding to 90% attenuation for 2-NP solution	Path length/mm corresponding to 90% attenuation for 4-NP solution
0.25	–	7.64
0.5	8.2	5.02
1	4.6	2.37
2	2.6	2.62
4	1.4	1.32
8	0.8	–

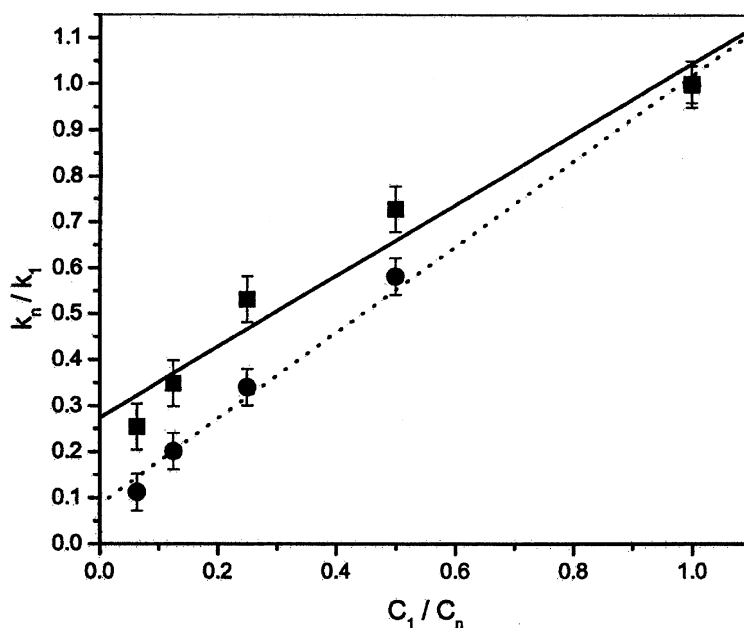


Fig. 11. Test for correlation of observed rate constants with proposed model for 2-nitrophenol (■) and 4-nitrophenol (●).

4.3. UV absorption

There is significant UV attenuation by nitrophenol solutions, even in the absence of TiO_2 . For 2-NP, the mean path-length corresponding to an absorbance of 1, i.e. to absorption of 90% of the incident UV, was estimated at 20 nm intervals from 300 to 400 nm. Mean pathlengths, Table 5, decrease from 2 to 0.8 mm as the concentration increases from 0.5 to 8 mM. Not only is all of the incident UV absorbed within the reactor, but, in addition, the UV flux experienced by most TiO_2 particles is significantly less than that at the reactor window. We therefore propose that the most probable cause of the inconsistencies in the LH analysis of nitrophenol oxidation is a failure to account for changes in the hydroxyl radical concentration that result from the strong absorption of 300–400 nm radiation in solutions of aromatic compounds such as nitrophenol.

4.4. The effect of UV absorption by nitrophenol on the measured oxidation rates

The rate of many simple photocatalytic oxidations has been demonstrated to be proportional to I^n , where the value of n depends on the details of the charge-carrier recombination. At very low light intensities $n=1$ but at higher light intensities, when charge carrier recombination dominates, n falls to 0.5 [1919, 2020, 2424, 2525]. If the same lamps, catalyst and reactor, as used for the nitrophenol oxidation, are used for isopropanol oxidation, $n=0.5$ [2626], demonstrating that the UV flux is sufficiently large for charge-carrier recombination to dominate. However the corresponding results

for nitrophenol oxidation show an I^1 dependence (except for 0.25 mM solutions of the more weakly absorbing 2-NP at high incident UV-intensity). The difference is attributed to strong UV attenuation, by the nitrophenol, which causes the effective UV flux at the catalyst particles to be much less than that in a corresponding propan-2-ol/ TiO_2 slurry. Consequently, the rate of charge carrier generation is lowered below the level at which recombination is rate-determining.

We consider the same UV attenuation by nitrophenol to be the main factor responsible for decreasing pseudo-first order rate constant with increasing nitrophenol concentrations; i.e. in Equation (1) the main cause of the decrease in k_{obs} , is the resultant decrease in $[\text{OH}]_s$ rather than the increase in the denominator suggested by the Langmuir–Hinshelwood model. A semi-quantitative analysis, ignoring UV attenuation by TiO_2 , assumes that the useful intensity, I , at a catalyst particle is the amount not absorbed by the nitrophenol. If I_0 is the UV intensity incident on the reactor, the pseudo-first order rate constant, k , at a catalyst particle at a distance x from the reactor window is,

$$k = \kappa I = \kappa I_0 e^{-\alpha x c} \quad (3)$$

where, α is the absorption coefficient of the nitrophenol of concentration c and κ is a constant. Integrating over all distances from 0 to ∞ leads to the expression

$$k = \frac{\kappa I_0}{\alpha c} \quad (4)$$

and for two different concentrations (A and B) of nitrophenol

$$\frac{k_A}{k_B} = \frac{c_B}{c_A}$$

A plot of k_A/k_B vs. c_B/c_A should therefore be a straight line. In Figure 11, the predicted behaviour is compared with the experimental results by normalising the results to $B = 1$ mM. The agreement is as good as can realistically be expected for a model which ignores scattering and absorption by the titania particles, and supports the conclusion of the 'rate vs. intensity study' that UV absorption by the nitrophenol is the major cause of the observed decrease in pseudo-first order rate constant with increasing concentration of nitrophenol.

4.5. The effect of pH on the rate of nitrophenol oxidation

Although the measurement of pH dependence of oxidation rate was carried out only to provide a reference for the bicarbonate addition, studies, we note that the increase in oxidation rate of 2-NP as pH is increased from 5 to 10 is qualitatively predicted by the corresponding decrease in both 350 and 365 nm absorption (Figure 1a inset). Quantitatively, this increase will depend not only on the nitrophenol concentration but also on the reactor geometry and wavelength distribution of the lamp. This may explain why different studies reported diverging conclusions with respect to the dependence of oxidation rate on pH.

4.6. The comparative oxidation rates of 2 and 4-nitrophenol

Light absorption would affect comparisons of the relative rates of photocatalytic oxidation of different nitrophenols. Our direct comparison gave relative rates for 1 mM 2-NP and 4-NP of 1:0.61. However, these relative rates depend on concentration and Figure 9 shows that the rates of 2N and 4-NP converge at low concentrations (though these 4-NP oxidations were measured some time after the 2-NP photo-oxidations.) Again, the comparative rates will also depend on the reactor geometry and wavelength distribution of the lamp. For example, measurements made with an immersed lamp reactor are likely to decrease the importance of 4-NP's greater absorption at 365 nm. Palmisano et al. [88] report that, using 50 ml flasks placed in a (Xe lamp) Solarbox the oxidation rate of 24 was 1.25 times that of 4 NP. However, when an immersed lamp (500 W Hg lamp) reactor was the two rates were similar.

5. Conclusions

We have analyzed nitrophenol oxidation kinetics under conditions which were demonstrated to give a low concentration of intermediates. We therefore consider that the decreases in the measured pseudo-first order

kinetic rate constants are not primarily controlled by adsorption of reaction intermediates. Further, the adsorption constants derived from a Langmuir–Hinshelwood analysis of the rates of degradation of 2 and 4-NP are not only quantitatively different from those determined by direct adsorption measurements but their relative magnitude is reversed. We propose that the major cause of the reduction in measured rate constants is UV absorption by nitrophenol. This absorption reduces the photon flux available at the surface of catalyst particles in suspension.

Although there is substantial agreement that first order rate constants decrease with increasing nitrophenol concentration, there is much less agreement concerning the relative rates of oxidation of the different isomers. We suggest that this is because changes in optical conditions affect the various isomers differently because they absorb differently. Similarly the practical effects of changed UV absorption associated with pH changes will depend on both the reactor geometry and the wavelength distribution of the UV.

The most general conclusion of this paper is that UV absorption by reactants must be taken into account when designing practical reactors for photocatalytic or photocatalytic degradation of strongly absorbing solutions. This is particularly important when designing either photocatalytic or photo-electrocatalytic reactors employing immobilized catalyst [1818].

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