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An investigation on ZnO photocatalysed oxidation of uracil

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Abstract

The semiconductor ZnO mediated photo-oxidation (λ_{irr} = 365 nm) of a biologically important compound, uracil, carried out in aqueous suspension reveals certain features: (i) initial rate dependence on [uracil]$_0$, (ii) Langmuir adsorption behavior, (iii) initial linear dependence of rate on the amount of ZnO followed by saturation behavior at higher values, and (iv) influence of pH and [Cu^{2+}] on rate. The involvement of some radical intermediates in the reaction was hinted at by the rate retarding influence of [acrylamide]. A mechanism involving the oxidation of uracil induced by $\dot{O}H$ and h_{vb}^+ leading to the formation of uracil glycol is proposed.

Keywords: ZnO; Photo-oxidation; Uracil

1. Introduction

The subject of semiconductor mediated photocatalysis has gained much attention in recent years [1]. The degradation of toxic pollutants like phenols [2], surfactants [3] and certain dyes [4] has been observed to be efficiently catalysed by irradiated semiconductors. The use of semiconductor photocatalysis in water splitting is also worthy of mention [5]. Recent research works involving metal ions doped and immobilised semiconductors as efficient promoters of catalysis have been described [6]. Very recently, the use of TiO_2 in synthesis has also been mentioned [7]. Previously we have reported the TiO_2 assisted photo-oxidation of thymine [8]. The intention of such studies is to understand the role of the semiconductor in effecting the photo-oxidation of the biomolecules in a heterogeneous environment. Studies on ZnO assisted photoreactions of biomolecules are scanty. Such model investigations possess significant relevance to the (direct) effect of ionising radiation on DNA involving radical cation intermediates. Further, the advantages associated with such studies over the homogeneous ones have already been outlined [8]. As part of our goal on various semiconductors promoting photo-oxidation of the biomolecules (the pyrimidine bases), herein we report one such study on the ZnO mediated photoreaction of uracil. In order to understand the nature of heterogeneous kinetic behavior and the mechanism of this photoprocess, the influences of various parameters such as [uracil]$_0$, weight of ZnO, pH and acrylamide on the rate have been investigated.

2. Experimental details

Uracil, ZnO, NaOH, $HClO_4$ and all other chemicals used were of AnalaR grade. Water, distilled from a Kilburn still, was redistilled over alkaline permanganate in an all-glass vessel and used for solution preparation. The surface area of ZnO was 8 ± 2 m^2 g^{-1} [9].

Irradiations were performed with a medium pressure mercury pencil lamp emitting at 365 nm (Spectronics Corporation, USA). Aqueous suspensions of ZnO containing uracil in a polymerisation tube, with an inlet for O_2 and with constant stirring, were irradiated for different intervals of time. All the experiments were carried out in the presence of O_2 as scavenger for e_{cb}^-. The pH of the solutions were measured with a Toshniwal CL-46 pH meter. The progress of the reaction was followed by monitoring the disappearance of the pyrimidine base at 265 nm. The amount of uracil decomposed with respect to time was calculated. The rate constants k (s^{-1}) were evaluated from plots of log(Absorbance)$_{265}$ vs. irradiation time, and the initial rates of decomposition of uracil were calculated by multiplying the rate constants with the appropriate initial uracil concentrations [uracil]$_0$. The intensity of the light absorbed (I) was evaluated based on ferrioxalate actinometry [10]. The quantum yields (ϕ) were calculated using the equation

$$\phi = \frac{\text{Number of moles decomposed per unit time}}{\text{Number of einsteins absorbed per unit time}}$$

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It must be pointed out that the degradation of the pyrimidines, under the conditions used here, is a light-induced reaction mediated by illuminated ZnO, as no change was observed under direct irradiation (no ZnO) or with ZnO in the dark. Moreover, the possible formation of a photo intermediate(s), which could in principle thermally participate in the degradation of the pyrimidines in a secondary path, is also excluded as no post irradiation effects were observed.

3. Product analysis

The product uracil glycol was determined as follows. The irradiated solution was centrifuged and extracted with dichloromethane. It was then evaporated. The resulting solid was recrystallized from ethanol. The melting point and R_f value (paper chromatography) were determined; these were in close agreement with literature values [11] confirming the formation of uracil glycol. Based on earlier works involving pulse radiolytic investigations on the mode of reactivity of $\dot{O}H$ with uracil, it is beyond doubt that the major product that could be formed is uracil glycol. This is also clear from our previous studies [8].

4. Results and discussion

In this work, the influences of varying the initial concentration of uracil, the weight of ZnO, pH, addition of Cu^{2+}, effect of acrylamide and effect of Ag^+ on the initial photocatalytic rate of oxidation of uracil have been investigated.

4.1. *Effect of [uracil]*

It was observed that the plot of log(Absorbance) vs. time at different initial $[Uracil]_0$ values yielded a straight line (Fig. 1); the slope gave the rate constant k (s^{-1}). Rate vs. $[Uracil]_0$ values are reported in Table 1. Experiments conducted with various initial concentrations of uracil (1×10^{-4} to 4.5×10^{-4} mol dm^{-3}) at the natural pH (7.5) of the solution showed that the rate and the corresponding ϕ values of the photo-oxidation of uracil (rate $= k(s^{-1}) \times [Uracil]_0$) increased with an increase in $[Uracil]_0$ initially and remained almost constant beyond a certain level (Fig. 2), indicative of Langmuir kinetics [12]. This is confirmed by the linear plots of 1/rate vs. $1/[Uracil]_0$ with an intercept on the ordinate (Fig. 3), in agreement with the equation:

$$\text{rate} = \frac{k'K[\text{Uracil}]_0}{1 + K[\text{Uracil}]_0}$$

Hence,

$$\frac{1}{\text{rate}} = \frac{1}{k'K[\text{Uracil}]_0} + \frac{1}{k'}$$

where k' is a proportionality constant and K is the equilibrium constant (adsorption coefficient). The values of k' and K obtained from the intercept and slope of this plot are 0.215 mol dm^{-3} s^{-1} and 0.64 mol^{-1} dm^3 respectively. It may be interesting here to compare these values with those obtained from TiO_2 promoted photo-oxidation of uracil. The values in the latter system are considerably smaller in magnitude than in the present work. This is attributable to the formation of surface adsorbed peroxides with TiO_2 which effectively results in a short-circuiting of the photochemistry of this semiconductor [9]. It may be noted that the surface of ZnO is not poisoned by peroxides in the same way as that of TiO_2. In fact, such a similar difference in the behavior of the TiO_2 and ZnO mediated photo-oxidation of methyl orange was observed [9]. Bandgap excitation of ZnO (with 365 nm

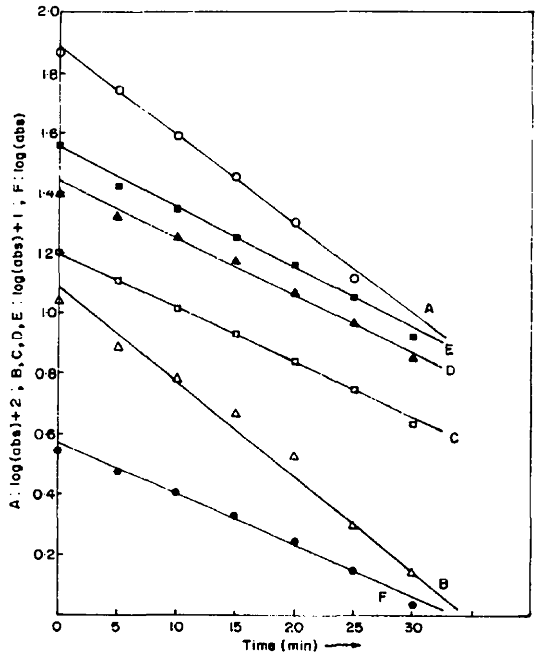


Fig. 1. Influence of $[Uracil]_0$ on photocatalytic degradation rate 0.02 g ZnO/70 ml, pH 7.5. $[Uracil]_0$ ($\times 10^4$ mol^{-1} dm^{-3}): A, 1.0; B, 1.5; C, 2.0; D, 3.0; E, 4.0; F, 4.5.

Table 1
Dependence of the photocatalytic degradation rate and ϕ on $[uracil]_0$

$[Uracil]_0 \times 10^4$ (mol dm^{-3})	Rate $\times 10^7$ (mol dm^{-3} s^{-1})	$\phi \times 10^2$ (ein s^{-1})
1.0	1.30	1.01
1.5	1.69	1.31
2.0	1.43	1.10
3.0	2.09	1.61
4.0	3.11	2.40
4.5	2.91	2.25

pH 7.5; weight of ZnO 0.02 g per 70 ml.
$I_a = 12.94 \times 10^{18}$ photons s^{-1}.

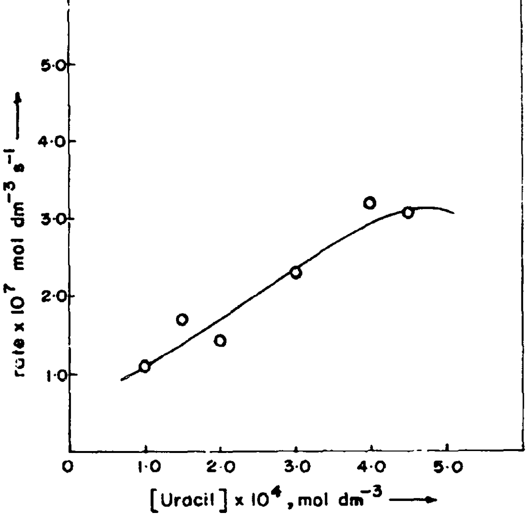


Fig. 2. Rate vs. [Uracil]. 0.02 g ZnO/70 ml, pH 7.5.

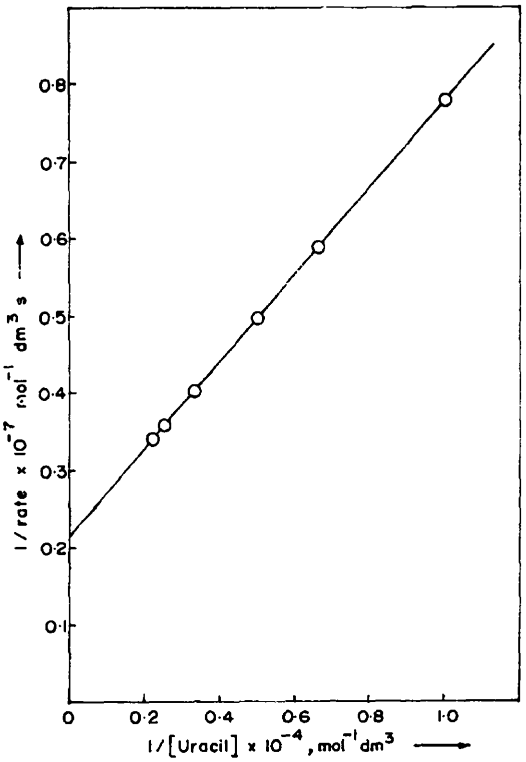


Fig. 3. Langmuir adsorption isotherm. 0.02 g ZnO/70 ml, pH 7.5.

light) results in the generation of valence band holes and conduction band electrons [13]. Due to the presence of O_2 in the solution, the scavenging of e_{cb}^- is envisaged as [14]:

$$ZnO \xrightarrow{h\nu/365\ nm} h_{vb}^+ + e_{cb}^- \qquad (i)$$

$$O_2 + e_{cb}^- \rightarrow O_2^{\cdot -} \qquad (ii)$$

Hence, it is seen that the recombination of h_{vb}^+ and e_{cb}^- is rendered less effective, enabling h_{vb}^+ to oxidise the pyrimidine molecule (uracil). Further, the $\dot{O}H$ produced (step iii) being a powerful oxidant [15] can also oxidatively degrade the uracil molecule.

The mechanistic scheme leading to the photo-oxidation is shown to be

$$h_s^+ + H_2O \rightarrow \dot{O}H_s + H_{aq}^+ \qquad (iii)$$

$$h_s^+ + Uracil \rightarrow Product(s) \qquad (iv)$$

$$\dot{O}H_s + Uracil \rightarrow Product(s) \qquad (v)$$

On comparing the IR spectrum of the product (Fig. 4) with that of the authentic sample (Fig. 5), it is found that the frequency (3200–3500 cm^{-1}) corresponding to the –OH groups found in the authentic sample (Fig. 5) also appear in the IR spectrum of the product (Fig. 4). This confirms the formation of the above-mentioned uracil glycol as a product. It may also be noted that this IR frequency peak is absent in the IR spectrum of the starting material (Fig. 6), namely uracil which again supports that glycol is a product in the reaction.

4.2. *Effect of amount of catalyst*

Experiments performed with various amounts of catalyst powder (0.005 g to 0.03 g per 70 ml) at constant $[Uracil]_0$ (1×10^{-4} mol dm^{-3}) showed the following behavior: the rate and the corresponding ϕ values increased with an increase in the amount of catalyst and remained almost constant above a certain level (Fig. 7, Table 2). This can be explained as: as the amount of catalyst is increased, the number of photons absorbed and the number of uracil molecules adsorbed are increased owing to an increase in the number of ZnO particles. The density of particles in the area of illumination also increases and so the rate is enhanced. Above a certain level, the substrate molecules (uracil) available are not sufficient for adsorption by the increased number of ZnO particles, i.e. although more area is available, for a constant $[uracil]_0$, the number of substrate molecules present in the solution remain the same. Hence, the additional catalyst employed is not involved in the catalyst activity and so the rate and ϕ values do not increase with an increase in the amount of catalyst beyond a certain limit.

4.3. *Effect of pH*

The influence of pH on the photocatalytic degradation rate and ϕ was studied in the pH range: 5.5 to 10.5. This study was performed at constant $[uracil]_0$ (1×10^{-4} mol dm^{-3}) and weight of ZnO (0.02 g per 70 ml). It is noticed from

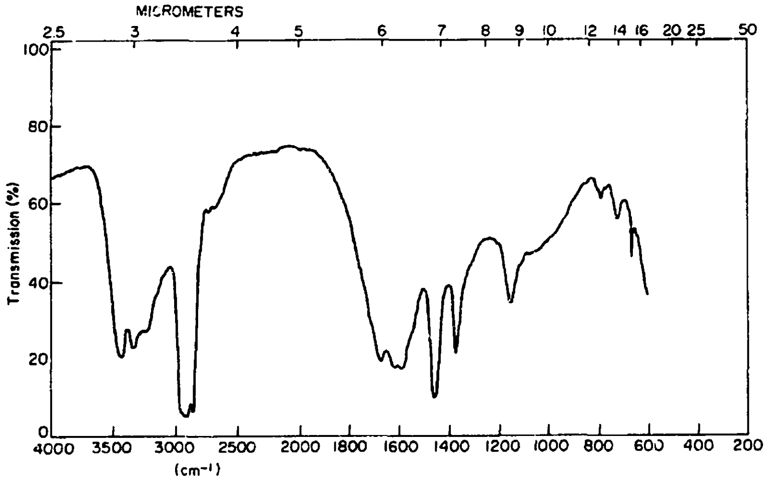


Fig. 4. IR spectrum of product.

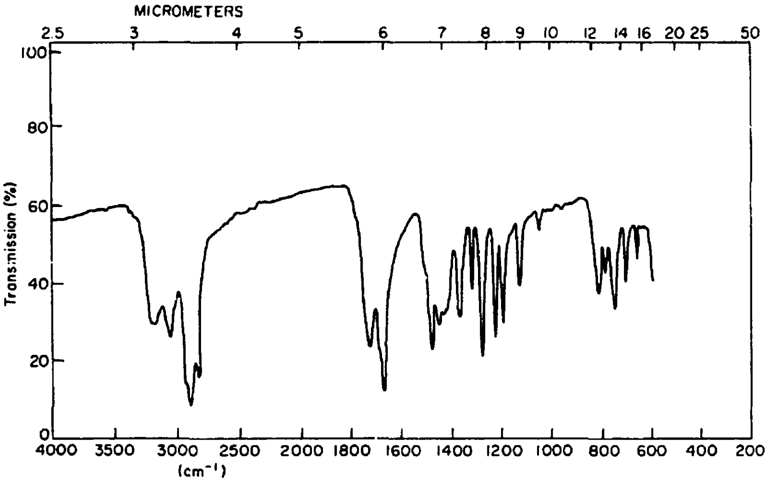


Fig. 5. IR spectrum of authentic sample.

Table 3 that the photocatalytic rate and the respective ϕ values increase from pH 5.5 to 9.0 and then decrease. The rate is maximum at pH 9.0, the pH_{zpc} of ZnO. The decrease in the rate beyond pH 9.0 is due to the repulsion between the negatively charged surface of ZnO [16] and to the N–H deprotonated form of the uracil ($pK_a \approx 9.0$) [17], bearing a negative charge. The decrease in the initial rate at higher pH values is also attributable to nernstian shift of the band edges of the semiconductor to more negative values with increasing pH [18], leading to a decreasing oxidation potential of h_{vb}^{+} at high pH. It is also possible that the increase in pH, i.e. an increase in the number of hydroxyl groups on the surface, caused a decrease in the conduction band electrons due to electron–hole recombination at $\dot{O}H$ sites [19]:

$$Zn-OH+h^{+} \rightarrow \overset{+}{Zn}-OH$$

$$\overset{+}{Zn}-OH+e_{cb}^{-} \rightarrow ZnOH$$

which may be also a reason for a decrease in the rate as the pH increases. Faster hole–electron recombination at pH 9.5 than at lower pH has been already postulated by a model based on the greater surface concentration of hydroxyls at pH 9.5. [19]. An additional factor possibly contributing to the observed lower steady-state concentration of unpaired electrons at pH 9.5 is that the capacitative effects associated with surface charge should then be lowest [19].

It has been shown by Weisz, based on the boundary layer theory [20], that most of the electron–hole pairs photogenerated at pH < 9.5 are born in a potential gradient tending to separate them by moving electrons towards the interface and holes toward the interior of the particles [20]. Thus capacitative effects of the positive surface potential existing at

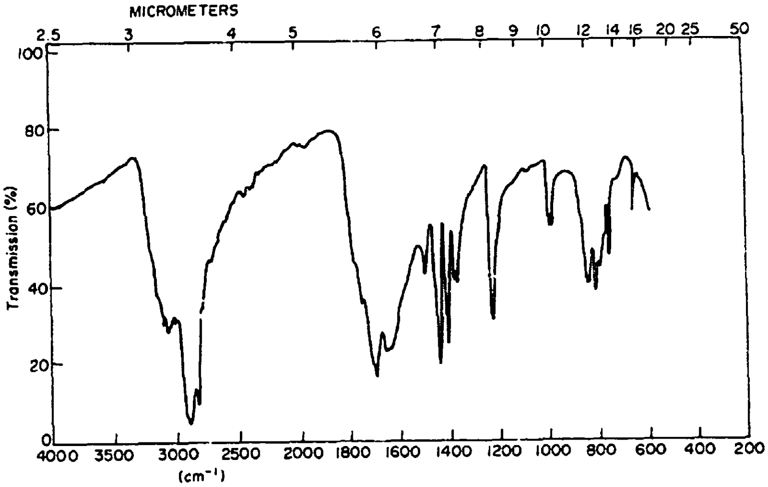


Fig. 6. IR spectrum of Uracil.

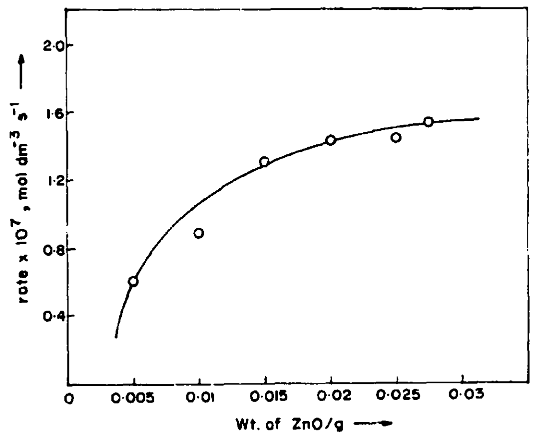


Fig. 7. Dependence of Photocatalytic degradation rate on the amount of ZnO. [Uracil] = 1×10^4 mol dm^{-3}, pH 7.5.

Table 2
Dependence of the photocatalytic degradation rate and ϕ on the amount of ZnO

Weight of ZnO (g) per 70 ml	Rate × 10^7 (mol dm^{-3} s^{-1})	$\phi\times10^2$ (ein s^{-1})
0.005	0.59	0.45
0.010	0.88	0.68
0.015	1.30	1.00
0.020	1.43	1.10
0.025	1.44	1.16
0.030	1.54	1.19

pH 7.5; [uracil]$_0$ = 1×10^{-4} mol dm^{-3}.
I_a = 12.94×10^{18} photons s^{-1}.

7 tend to maintain a separation between photogenerated electrons and holes and thus to reduce recombination by opposing their diffusion toward one another [19]. Thus, the observed higher rate at pH 7 than at 9.5 in this study is in keeping with the foregoing arguments.

Table 3
Effect of pH on the photocatalytic degradation rate and ϕ weight of ZnO, 0.02 g per 70 ml; [uracil]$_0$ = 1×10^{-4} mol dm^{-3}

pH	Rate × 10^7 (mol dm^{-3} s^{-1})	$\phi\times10^2$ (ein s^{-1})
5.5	0.15	0.12
6.5	2.06	0.15
7.0	2.32	1.79
9.0	2.19	1.70
9.5	1.66	1.28
10.5	1.63	1.26

I_a = 12.94×10^{18} photons s^{-1}.

Table 4
Effect of [Cu^{2+}] on the photocatalytic degradation rate and ϕ weight of ZnO, 0.02 g per 70 ml; [uracil]$_0$ = 1×10^{-4} mol dm^{-3}

[Cu^{2+}] × 10^4 (mol dm^{-3})	Rate × 10^7 (mol dm^{-3} s^{-1})	$\phi\times10^2$ (ein s^{-1})
1.0	1.94	1.50
2.0	0.92	0.71
3.0	0.64	0.50
4.0	0.54	0.42
5.0	0.40	0.31

I_a = 12.94×10^{18} photons s^{-1}.

4.4. Effect of Cu^{2+}

The effect of Cu^{2+} as a co-catalyst has been studied. The results are depicted in Table 4 and Fig. 8. It is noticed that the reaction rate and the ϕ decrease with increasing [Cu^{2+}]. That is, an induction period in the photo-oxidation process is

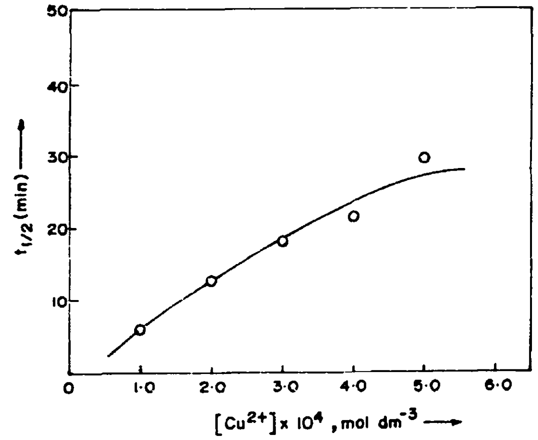


Fig. 8. Effect of $[Cu^{2+}]$ on the photocatalytic degradation rate at $t_{1/2}$. 2 g ZnO/70 ml. [Uracil] = 1×10^{-4} mol dm^{-3}. pH 6.5.

inferred in the presence of Cu^{2+} ions. It is possible that the Cu^{2+} ion can be adsorbed on the surface of the ZnO particle. The Cu^{2+} ion adsorbed on the ZnO particle can trap an electron. This is understandable considering the high redox potential of $E^0(Cu^{2+}/Cu^+) = 0.17$ V [21] compared with the potential of the electrons in the particle (-0.15 V), which is more negative than the former [22]. This fact predicts that the reduction of Cu(II) ions by photogenerated electrons is thermodynamically feasible. In fact, such an observation has been made already by Domenech and Prieto [22]. In the photodegradation of 2,4-dichlorophenol by TiO_2, a very similar effect of Cu^{2+} has been suggested invoking the reduction of adsorbed Cu^{2+} by photogenerated electrons [23]. The reduction of Cu^{2+} to Cu via Cu^+ on TiO_2 was indicated based on the high redox potential of $E^0(Cu^{2+}/Cu^+) = 0.17$ V as opposed to the more negative conduction band potential of TiO_2 [23]. Thus, it is clear from these arguments that an induction period exists in the photoprocess in presence of Cu^{2+}. The higher the concentration of Cu^{2+} ions added, the longer the induction period. During this period, the photo-oxidation rate is lower. In such cases, it is no longer reasonable to use the initial reaction rate. For the overall reaction, the half-life of the reaction can be used for this purpose. If the degradation rate at $t_{1/2}$ is considered, it is clear that increases in Cu^{2+} concentration always increase the reaction rate at $t_{1/2}$ as is evident from Table 5. This can be explained by the more efficient trapping of the photogenerated electron owing to the higher adsorption coverage of Cu^{2+} and the resulting more efficient transfer of the electron from the ZnO particles to the oxygen molecule. This oxygen captures an electron from Cu^{2+} coadsorbed on ZnO to prevent the electron from recombining with the surface-trapped hole. The superoxide ion ($O_2^{\cdot -}$) thus formed can then react with H^+ to produce $H\dot{O}_2$ and other oxidising species as:

$$O_2 + e^- \rightarrow O_2^{\cdot -}$$

Table 5
Dependence of rate at $t_{1/2}$ on $[Cu^{2+}]$

$[Cu^{2+}] \times 10^4$ (mol dm^{-3})	Rate at $t_{1/2}$ (M s^{-1})
1.0	5.96
2.0	12.60
3.0	17.95
4.0	21.36
5.0	28.83

$$O_2^{\cdot -} + H^+ \rightarrow H\dot{O}_2$$

$$H\dot{O}_2 + H\dot{O}_2 \rightarrow H_2O_2 + O_2$$

$$O_2 + H\dot{O}_2 \rightarrow O_2 + HO_2$$

$$HO_2^- + H^+ \rightarrow H_2O_2$$

$$H_2O_2 \xrightarrow{h\nu} 2\dot{O}H$$

$$H_2O_2 + O_2^{\cdot -} \rightarrow \dot{O}H + OH^- + O_2$$

$$H_2O_2 + e^- \rightarrow \dot{O}H + OH^-$$

Hence, the rate of photo-oxidation is enhanced. In fact, such a scheme of reactions has been suggested [23] in the TiO_2 assisted photodegradation of 2,4-dichlorophenol in the presence of Cu^{2+}. The Cu^{2+} involved in such a process can be regarded as an electron-transfer relay which facilitates the migration of the electron from the TiO_2 particle to the O_2 molecule [23].

4.5. Role of acrylamide

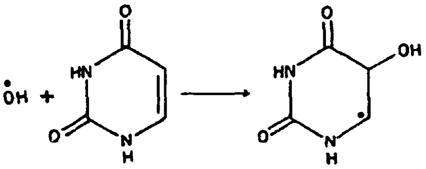
It is clear from the foregoing discussions that the mechanism of the photo-oxidation involves free radicals. A check for this possibility was made by studying the effect of added acrylamide on the photodegradation rate and ϕ. From Table 6, it is observed that an increase in [acrylamide] results in a decrease of the reaction rate and the quantum yield. Hence, it is clear that some radical intermediates are involved in the reaction. This is attributable to the scavenging of the radical intermediates by acrylamide resulting in the termination of

Table 6
Effect of acrylamide on the photocatalytic degradation rate and ϕ weight of ZnO (0.02 g). $[uracil]_0 = 1 \times 10^{-4}$ mol dm^{-3}

Acrylamide $\times 10^4$ (mol dm^{-3})	Rate $\times 10^8$ (mol dm^{-3} s^{-1})	$\phi \times 10^3$ (ein s^{-1})
1.0	8.30	6.41
2.0	6.80	5.26
3.0	6.30	4.87
4.0	5.78	4.47
5.0	5.57	4.30
8.0	5.51	4.25

$I_a = 12.94 \times 10^{18}$ photons s^{-1}.

the propagation of the free radical forming steps involved in the mechanism. For example, it is possible that the reaction of $\dot{O}H$ with the pyrimidine base, uracil forms a hydroxyl radical adduct of uracil, the $\dot{O}H$ adding at C_5 of uracil thus creating the 5-hydroxyuracil-6-yl radical as:



The formation of such radical adduct intermediates has been well proved by pulse radiolysis study [24]. The isomer radical, 6-hydroxyuracil-5-yl could also be formed. However, in view of the differences in the redox properties of these isomeric radical intermediates [24] (5-yl radical as an oxidant and 6-yl one as a reductant), it is possible that the 6-yl can be oxidised by the powerful oxidant h^+, forming the corresponding radical cation which subsequently reacts with H_2O finally giving the respective glycol as the product.

4.6. Effect of [Ag^+]

It was observed that the addition of Ag^+ in the present experiments led to a drastic increase in the rate of the reaction making it difficult to measure the same. Such a rate enhancing effect of Ag^+ was noticed in the TiO_2 mediated photodecomposition of monochlorophenols [25] and attributed to the increased capacity for electron capture by Ag^+ at the illuminated microinterfaces thus leading to a reduced electron–hole recombination [25] resulting in a corresponding increase in the possibility for the hole capture by the substrate (uracil) molecule. It is interesting to note that the immeasurability of the reaction rate with ZnO (this work) unlike that of TiO_2 could probably be due to the non-existence of surface adsorbed peroxides on ZnO [9] than on TiO_2.

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