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A comparative study on the TiO_2 mediated photo-oxidation of uracil, thymine and 6-methyluracil

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Abstract

The semiconductor TiO_2 assisted photo-oxidation of uracil, thymine and 6-methyluracil has been carried out in aqueous suspension with an excitation wavelength of 365 nm. The rate and quantum yield ($\varnothing$) of this heterogeneous photoprocess were measured based on the disappearance of the pyrimidine bases spectrophotometrically (265 nm) and hence the quantum yield ($\varnothing$) has been evaluated as a function of concentration of the substrate (pyrimidine bases), weight of TiO_2 and pH. The reaction rates are found to conform to the Langmuir–Hinshelwood isotherm and the k and K values thus determined are reported. The influence of pH on the $\varnothing$ values reveals a varying proportion of contribution of h^+_{vb} and $^{\bullet}OH$ on the reactivity of the substrate biomolecules, and the effect of $[Ag^+]_0$ on $\varnothing$ points to a decreased h^+–e^- recombination with a concomitant increase in h^+ capture by the substrate biomolecules, leading to an enhancement of the reaction rate. A mechanism consistent with the observed data is proposed. © 1997 Elsevier Science S.A.

Keywords: Heterogeneous photocatalysis; Titania; Pyrimidine bases

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1. Introduction

Photocatalytic investigations on the degradation of a number of organic compounds have been extensively carried out [1–4]. The utility of the photocatalytic methods in waste water treatment processes [5,6] and solar energy research [7] has been well explored. Hence increasing interest in semiconductor mediated photocatalysis continues to grow due to the versatile possibility in the utilisation of semiconductor photoproduced efficient redox equivalents, h^+_{vb} and e^-_{cb}, for various reactions. The role of surface modification of various semiconductor materials (TiO_2, CdS, ZnS, ZnO) has been studied and improvement in photocatalytic efficiency reported [8–12]. Of the various available semiconductors, TiO_2 appears to be the most widely employed due to its photostability (against corrosion), non-toxicity and insolubility in water [13].

Photoreactions of certain inorganic compounds [14] and transition metal complexes [15–17] sensitised by TiO_2 have also been carried out. There have been only a few studies on the TiO_2 assisted photoreactions of biomolecules. The present work plays a vital role in understanding the photo-oxidation ability of certain biomolecules (uracil, thymine and 6-methyluracil) in a heterogeneous environment similar to biological interfaces. A study of this nature may be extended to provide information on the electrostatic and electronic interactions with the metal. Different photosensitisers, e.g. porphyrins, acridines and metal polypyridyl complexes were used to enhance the cleavage of DNA. One drawback in the use of such photosensitisers to initiate cleavage is that they remain present and may subsequently react with the DNA base or sugar radicals in the secondary steps [18]. In respect of this, a semiconductor photocatalyst approach may prove to be a simpler and neater method of photogenerating the potential oxidising intermediates ($^{\bullet}OH$, h^+_{vb}) [19]. As a part of our investigations, we report the TiO_2 mediated photo-oxidation of uracil, thymine and, 6-methyluracil. It may be noted that a part of our proposed work involving the TiO_2 mediated photo-oxidation of thymine carried out under different experimental conditions from those in the present work has been reported by us [19].

2. Experimental details

The pyrimidines, namely uracil, thymine, and 6-methyluracil, 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 preparations. The titanium dioxide photo-

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catalyst was Degussa P-25. This material is mainly anatase, and has a Brunauer-Emmett-Teller (BET) surface area of 50 m^2 g^{-1} and a mean particle size of 30 nm.

Irradiations were performed with a medium pressure mercury pencil lamp (Spectronics Corporation, USA) emitting nearly 100% at 365 nm. Aqueous suspensions of TiO_2 containing the pyrimidine base in a polymerization tube, with an inlet for O_2 and with constant magnetic stirring, were irradiated for different intervals of time. All the experiments were carried out in the presence of O_2 as a scavenger for e^-_{cb}. The pH of the solutions was 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 the pyrimidine base decomposed with respect to time was calculated. The rate constants k (s^{-1}) were evaluated from plots of log(*absorbance*) vs. irradiation time, and the initial rates of decomposition of the pyrimidines were calculated by multiplying the rate constants with the appropriate initial pyrimidine concentrations, $[\text{pyrimidine}]_0$. Quantum yield (∅) was calculated based on ferrioxalate actinometry [20].

2.1. *Product analysis*

The product, pyrimidine glycol, was identified as follows: The irradiated solution was centrifuged and extracted with dichloromethane. It was then evaporated. The resulting solid was recrystallised from ethanol. The Fourier transform infrared (FTIR) spectrum of the product obtained in the case of uracil/TiO_2 after centrifugation, as a typical example, run in KBr pellet on a Bruker IFS 66v FTIR Spectrophotometer, showed a broad absorption peak centred around 3470 cm^{-1}, corresponding to OH-stretching vibration. The spectrum also showed strong absorption bands in the region between 1550–1740 cm^{-1} which corresponds to the carbonyl and amide region. It was found to be in good agreement with that of the 5,6-dihydroxyuracilglycol. The UV spectrum of the product isolated from uracil/TiO_2, run in doubly distilled water on a Hitachi U-3410 Spectrophotometer, was also very similar to that of the authentic sample of 5,6-dihydroxyuracilglycol. It was also found that there was no overlapping interference from the FTIR and UV spectra of the reactant with the product. These facts thus lend support to the formation of the corresponding pyrimidine glycol as a product in our studies.

3. Results and discussion

Results pertaining to the effects of (i) concentration of pyrimidine base, (ii) weight of TiO_2, (iii) pH and (iv) $[Ag^+]$ on the photocatalytic degradation (oxidation) rate are presented and discussed. It must be pointed out that the degradation of the pyrimidines, under the conditions used here, is a light induced reaction mediated by illuminated TiO_2, as no change was observed under direct irradiation (no TiO_2) or with TiO_2 in the dark. Moreover, the possible formation of one or more photointermediates, which could in principle thermally participate in the degradation of the pyrimidines in a secondary path, is also excluded as no postirradiation effects were observed.

3.1. *Effect of* $[\textit{pyrimidine base}]_0$

The effect of various initial [pyrimidine base] on the photodegradation rate was studied at a fixed weight of TiO_2 and pH. A plot of log(*absorbance*) vs. irradiation time from these experiments yielded straight lines (Fig. 1), and from the slopes, the rate constants k (s^{-1}) were evaluated. The above figure is a typical example for the case of uracil/TiO_2 and it is to be noted that a similar behaviour was exhibited by the other two systems studied (thymine and 6-methyluracil). The corresponding $[\text{pyrimidine base}]_0$ vs. rate data are given in Table 1. The rates were computed as: $rate = k\ (s^{-1}) \times [\text{pyrimidine base}]_0$. Experiments performed with various initial concentrations of the pyrimidine bases (0.5×10^{-4} mol dm^{-3} to 3.5×10^{-4} mol dm^{-3}) at the natural pH of the solution indicate that the rate and hence the quantum yield (∅) of degradation (Table 1) initially increases with an increase in $[\text{pyrimidine base}]_0$ and then levels off beyond a certain point (Fig. 2), indicative of Langmuir kinetics [21]. This is confirmed by the linear plot of $rate^{-1}$ vs. $[\text{pyrimidine base}]_0^{-1}$, with an intercept on the ordinate (Fig. 3), in conformity with the equation:

$$rate = \frac{kK[\text{pyrimidine}]_0}{1 + K[\text{pyrimidine}]_0}$$

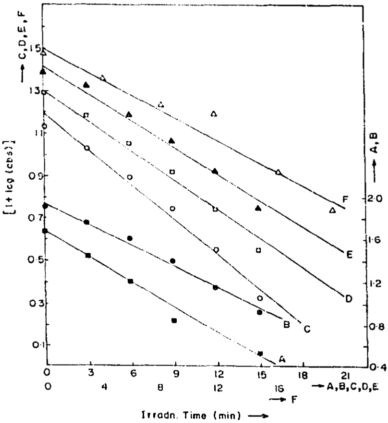


Fig. 1. Typical plot: influence of $[\text{uracil}]_0$ on photocatalytic degradation rate; 0.005 g TiO_2/40 ml, pH: 6.5. A: [uracil]: 0.52×10^{-4} mol dm^{-3}; B: [uracil]: 1.0×10^{-4} mol dm^{-3}; C: [uracil]: 1.5×10^{-4} mol dm^{-3}; D: [uracil]: 2.0×10^{-4} mol dm^{-3}; E: [uracil]: 2.5×10^{-4} mol dm^{-3}; F: [uracil]: 3.0×10^{-4} mol dm^{-3}.

Table 1
Influence of [pyrimidine base]$_0$ on the photocatalytic degradation rate and ∅

(i) Uracil[a]			(ii) 6-methyluracil[b]			(iii) Thymine[b]		
[uracil] × 10^4, mol dm^{-3}	*Rate* × 10^7, mol dm^{-3} s^{-1}	∅ × 10^2	[6-methyl uracil] × 10^4, mol dm^{-3}	*Rate* × 10^7, mol dm^{-3} s^{-1}	∅ × 10^2	[Thymine] × 10^4, mol dm^{-3}	*Rate* × 10^7, mol dm^{-3} s^{-1}	∅ × 10^2
0.5	1.72	0.85	0.5	1.35	0.68	1.0	2.23	1.10
1.0	2.49	1.20	1.0	1.72	0.85	1.5	2.53	1.25
1.5	3.07	1.60	1.5	2.47	1.22	2.0	3.18	1.57
2.0	3.45	1.70	2.0	2.87	1.42	2.5	3.58	1.77
2.5	4.15	2.10	2.5	3.66	1.81	3.0	3.89	1.92
3.0	4.19	2.10	3.0	3.82	1.89	3.5	4.12	2.04
3.5	3.81	1.89	4.0	4.16	2.06			

[a] TiO_2: 0.005 g; pH: 6.5; vol.: 40 ml; I_a: 12.04 × 10^{18} photons s^{-1}.
[b] TiO_2: 0.01 g; pH: 6.0; vol.: 50 ml; I_a: 12.04 × 10^{18} photons s^{-1}.

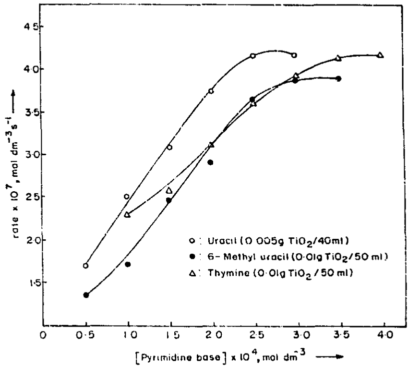


Fig. 2. Degradation rate vs. [pyrimidine base]$_0$: ○ uracil (0.005 g TiO_2/40 ml); ● 6-methyl uracil (0.01 g TiO_2/50 ml); △ thymine (0.01 g TiO_2/50 ml).

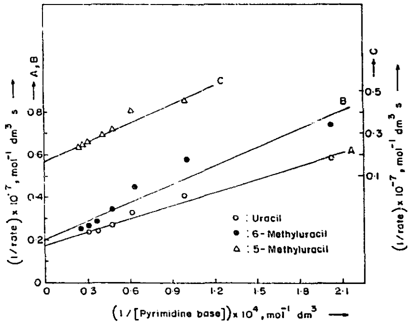


Fig. 3. Langmuir adsorption isotherm: ○ uracil (0.005 g TiO_2/40 ml); ● 6-methyluracil (0.01 g TiO_2/50 ml); △ thymine (0.01 g TiO_2/50 ml).

hence,

$$\frac{1}{rate}=\frac{1}{kK[\text{pyrimidine}]_0}+\frac{1}{k}$$

where *k* is a proportionality constant and *K* is the equilibrium adsorption coefficient. The values of *k* (mol dm^{-3} s^{-1}) and *K* (mol^{-1} dm^3) obtained from the intercept and slope of these plots for all the pyrimidines studied are depicted in Table 2. The Langmuir–Hinshelwood (L–H) kinetic model as proposed in this work has often been used to describe semiconductor photocatalysis [22,23]. The higher values of *k* and *K* obtained for 6-methyluracil (than for uracil and thymine) indicate that it adsorbs relatively more onto TiO_2 leading to an enhanced photodegradation.

Band gap irradiation of the semiconductor TiO_2 leads to the generation of valence band holes and conduction band electrons [24]. Due to the presence of O_2 in the reaction solution, scavenging of the conduction band electrons is envisaged as [25]:

$$TiO_2 \rightarrow h^+_{vb} + e^-_{cb}$$

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

Hence it is clear that the recombination of $h^+{}_{vb}$ and $e^-{}_{cb}$ is prevented, enabling $h^+{}_{vb}$ to oxidise the pyrimidine base. Furthermore, importantly the $^{\cdot}OH$ produced (step 2) is a powerful oxidant [26] and hence can oxidatively degrade the pyrimidines.

The $^{\cdot}OH$ induced oxidation of thymine by pulse radiolysis in homogeneous solution has been reported [27]. In the present work, the corresponding pyrimidine glycols were found

Table 2
Langmuir isotherm

	k (mol dm^{-3} s^{-1})	*K* (mol^{-1} dm^3)
Uracil	0.171	0.209
6-methyluracil	0.196	0.295
Thymine	0.164	0.200

Table 3
Dependence of photocatalytic degradation rate on the amount of TiO_2 and Ø

(i) Uracil[a]			(ii) 6-methyluracil[b]			(iii) Thymine[c]		
Wt. of TiO_2, g	Rate $\times 10^7$, mol dm^{-3} s^{-1}	Ø $\times 10^2$	Wt. of TiO_2, g	Rate $\times 10^7$, mol dm^{-3} s^{-1}	Ø $\times 10^2$	Wt. of TiO_2, g	Rate $\times 10^7$, mol dm^{-3} s^{-1}	Ø $\times 10^2$
0.005	2.49	1.2	0.010	1.72	0.85	0.010	2.23	1.10
0.010	3.58	1.8	0.015	2.45	1.21	0.015	2.46	1.22
0.015	3.95	2.0	0.020	2.96	1.46	0.020	2.71	1.34
0.020	4.72	2.3	0.025	3.10	1.53	0.025	3.02	1.49
0.025	4.57	2.3	0.030	3.07	1.51	0.030	3.10	1.53
0.030	4.75	2.3				0.035	3.10	1.53

[a] [uracil]: 1×10^{-4} mol dm^{-3}; pH: 6.5; vol.: 40 ml; I_a: 12.04×10^{18} photons s^{-1}.
[b] [6-methyluracil]: 1×10^{-4} mol dm^{-3}; pH: 6.0; vol.: 50 ml; I_a: 12.04×10^{18} photons s^{-1}.
[c] [Thymine]: 1×10^{-4} mol dm^{-3}; pH: 6.0 vol.: 50 ml; I_a: 12.04×10^{18} photons s^{-1}.

to be the products formed. Thymine glycol was also identified as a product in the $^{\bullet}OH$ induced oxidation of thymine [27], indicating that a similar mechanism occurs in both cases.

The mechanistic scheme in the present work can be described as follows [9]:

1. $TiO_2 \rightarrow h^+ + e^-$
2. $h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+$
3. $O_2 + e^- \rightarrow O_2^{\bullet -}$
4. $O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet}$
5. $HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$
6. $H_2O_2 + O_2^{\bullet -} \rightarrow OH^{\bullet} + OH^- + O_2$
7. $h^+ + OH^- \rightarrow OH^{\bullet}$
8. $H_2O_2 + e^- \rightarrow OH^{\bullet} + OH^-$

Pyrimidine glycol can originate from the attack on the C_5-C_6 double bond by $^{\bullet}OH$ (step 2). This has been well established by electron spin resonance (ESR) studies [28]. Indeed, it has been reported that $^{\bullet}OH$ is the main active species causing damage to the pyrimidine base [29]. Two isomeric radicals, namely 5-hydroxy-6-yl, A, and 6-hydroxy-5-yl, B, of thymine are the expected intermediates. These radicals differ in their redox properties [30]. In an earlier study using pulse radiolysis, it was observed that the 5-yl radical is oxidising and the 6-yl radical is reducing in nature [30]. Hence, in the present work, of the primary redox equivalents generated, namely h_{vb}^+ and e_{cb}^-, it is reasonable to foresee the oxidation of the 6-yl thymine radical by the powerful oxidant h^+. This is in accord with the enhanced reducing power of the 5-hydroxy-6-methyluracil-6-yl radical (towards h^+) due to the presence of an electron releasing methyl group at C_6. It is also possible that, based on the comparable oxidative ability of h^+ and $SO_4^{\bullet -}$, the oxidation of the pyrimidine bases by the loss of an electron from the C_5-C_6 double bond to give the corresponding radical cation intermediates, leading finally to the pyrimidine glycols (by subsequent reaction of the radical cation with water), may occur [31]. Indeed, the involvement of such radical cations in the reaction of thymine with $SO_4^{\bullet -}$ has been documented [31]. Finally, it may be interesting here to make a comparison of the K (adsorption coefficient) values of the present work with the K value for the degradation of methylene blue on TiO_2 [4]. The very high K value (1.79×10^4 dm^3 mol^{-1}) with the methylene blue system indicates that the photoadsorption of it on TiO_2 involves a hydrophilic controlling factor [4]. The very low value of K (0.2 dm^3 mol^{-1}) observed in this present work shows that for the TiO_2 powder, the hydrophilic surface (bound with hydroxy groups) makes it difficult for the pyrimidines to be adsorbed, i.e. the pyrimidines favour hydrophobic adsorption. Such a similar behaviour has also been reported with the adsorption of dichlorophenol onto TiO_2 [12].

3.2. Effect of oxygen

In the present work, the photocatalytic experiments were also carried out in the absence of oxygen (i.e. using deaerated water by purging with nitrogen) and the results thus obtained were compared with those in presence of oxygen, other conditions being the same. It was noticed that initially the rate of photocatalytic oxidations was the same, irrespective of the presence or absence of oxygen in the aqueous solution, while at higher conversion the rate decreased in the absence of oxygen. This is indicative of the participation of lattice oxygen in the reaction. In view of the observed fact that the oxidation of the organic substrate occurs at a higher rate even in absence of oxygen in the initial stages of the reaction, it is envisaged that the surface bound OH^- participating in reaction step 7 may be available from the following reaction involving lattice oxygen (oxide ion) as

$$O_L^{2-} + l + H_2O \rightarrow O_LH^- + l - OH^-$$

where l is an adsorption site on the catalyst.

3.3. Effect of catalyst

The effect of the amount of catalyst TiO_2 on the photodegradation rate was investigated. At a fixed pH and initial concentration of the pyrimidines, experiments were performed with varying amounts of TiO_2 (0.001 to 0.035 g per 50 ml). The rate and the corresponding Ø values of the photodegradation obtained from such experiments are depicted in Table 3. It is clear from this table that for all the

Table 4
Effect of pH on the photocatalytic degradation rate and ∅

(i) Uracil[a]			(ii) 6-methyl uracil[b]			(iii) Thymine[c]		
pH	*Rate* × 10^7, mol dm^{-3} s^{-1}	∅ × 10^2	pH	*Rate* × 10^7, mol dm^{-3} s^{-1}	∅ × 10^2	pH	*Rate* × 10^7, mol dm^{-3} s^{-1}	∅ × 10^2
4	2.57	1.3	4.5	2.30	1.13	4.5	1.91	0.94
7	2.49	1.2	6.0	1.72	0.85	6.0	2.23	1.10
9	2.91	1.4	8.0	1.88	0.93	8.0	2.18	1.08

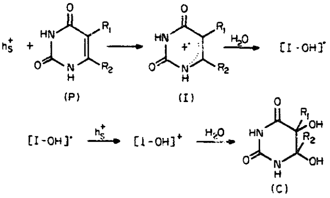
[a] [Uracil]: 1×10^{-4} mol dm^{-3}; TiO_2: 0.005 g; vol.: 40 ml; I_a: 12.04×10^{18} photons s^{-1}.
[b] [6-methyluracil]: 1×10^{-4} mol dm^{-3}; TiO_2: 0.01 g; vol.: 50 ml; I_a: 12.04×10^{18} photons s^{-1}.
[c] [Thymine]: 1×10^{-4} mol dm^{-3}; TiO_2: 0.01 g; vol.: 50 ml; I_a: 12.04×10^{18} photons s^{-1}.

pyrimidine bases, the rate initially increases with an increase in the amount of catalyst and then attains a plateau (levelling off) above a certain point (Table 3). This is attributed to the contribution of two main factors. It is envisaged that the decrease of catalytic effect at relatively higher proportions (Table 3) is due to inner filter effect and scattering.

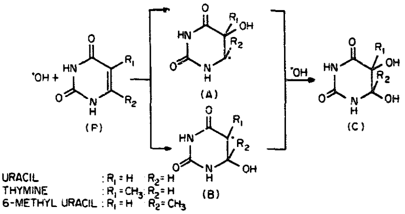
As the amount of catalyst is increased, the number of photons absorbed and the number of pyrimidine molecules adsorbed are increased due to an increase in the number of catalyst particles. The density of particles in the area of illumination also increases and so the degradation rate is enhanced. At a certain level, the number of available substrate molecules is insufficient for adsorption by the increased number of TiO_2 particles, that is, although more area is available, for constant $[\text{pyrimidine}]_0$, the number of substrate molecules present in the solution remains the same. Hence, above a certain level, additional catalyst amount is not involved in catalysis and thus the rate levels off.

3.4. *Effect of pH*

The influence of pH on the photocatalytic degradation rate was studied at pH values acidic (4–4.5), neutral (7), and slightly alkaline (8–9) for the pyrimidines used. This study was carried out at constant $[\text{pyrimidine base}]_0$ (1×10^{-4} mol dm^{-3}) and weight of TiO_2 (0.01 g) (Table 4). In the case of uracil the initial rate was almost constant at all pH values. With 6-methyluracil, the initial rate showed a decreasing trend from the acidic pH with increase in pH. It has been mentioned above that the photodegradation of the pyrimidine bases is mainly initiated by the attack of $^{\bullet}OH$ and h_{vb}^+. This type of pH dependent behaviour indicates a varying degree of contribution by $^{\bullet}OH$ and h_{vb}^+ on the pyrimidines studied. It is already known that the 5-hydroxy radical adduct of 6-methyluracil is a better reducing agent than are those of uracil and thymine [30]. The maximum degradation rate at acidic pH region for 6-methyluracil is due to the preponderance of the oxidation of 6-methyluracil-6-yl radical by h_s^+ (Scheme 1) compared to the $^{\bullet}OH$ mediated attack (Scheme 2) on 6-methyluracil. The slower initial rate observed at acidic pH for thymine is attributable to the predominance of $^{\bullet}OH$ mediated attack (against the h_s^+ induced oxidation of the corresponding 6-yl radicals in conformity with the better reducing ability of 6-methyluracil-6-yl radical over those of thymine) on this pyrimidine base [30]. The increase of initial photodegradation rate for uracil and thymine with pH from 4 to 7 is due to a great extent to surface coverage by OH^- ions, which in turn can be converted into $^{\bullet}OH$ and ultimately lead to the degradation of the substrate molecules. However, the increased reactivity of uracil over thymine at all pH values may be attributed to the enhanced probability of $^{\bullet}OH$ attack at C_5 (Scheme 2) of uracil due to the absence of any steric hindrance unlike the C_5 of thymine.



Scheme 1.



Scheme 2.

The decrease in initial degradation rate observed with increase in pH for all the three pyrimidine bases suggests that the pH_{zpc} of TiO_2 plays an important role. Hence, as the pyrimidine bases become negatively charged (due to N(1)H and N(3)H deprotonation), there is a decrease in the extent of adsorbability leading to a decrease in the rate. Further, it is also possible that a fraction of the 5-hydroxy-pyrimidine-6-yl radicals (reducing) are converted into oxidising radicals at alkaline pH [32,33]. Such a redox inversion phenomenon has already been documented in a study of the properties of these radicals using pulse radiolysis. Moreover, the reaction of O_2 with the pyrimidine-5-hydroxy radicals forming the corresponding peroxy radicals followed by their OH^- catalysed decomposition [34] could also account for the observed rate decrease at higher pH. As a consequence of this competition for O_2 by the organic radicals, the efficient scavenging of e^- by O_2 decreases, resulting in enhanced e^-–h^+ recombination, which also accounts for the observed initial rate decrease. The decrease in initial rate at higher pH is also due to Nernstian shift of the band edges of the semiconductor to more negative values with increasing pH [35], leading to a decreasing oxidation potential of h^+_{vb} at high pH.

3.5. *Effect of* $[Ag^+]$

The role of Ag^+ as an additional electron acceptor (in addition to O_2) in semiconductor mediated photoreactions of certain organic compounds has been reported. In the TiO_2 assisted photodecomposition of monochlorophenol, a detailed report concerning the effect of Ag^+ on the initial degradation rate has been made [36]. In the present work, the influence of Ag^+ has been studied and the results are indicated in Table 5. For uracil and 6-methyluracil, it is observed from this table that the initial rate increases with increase in $[Ag^+]$ up to a point and then decreases with further increase in $[Ag^+]$. The results on the effect of $[Ag^+]$ on thymine are not included in this work due to some discrepancy observed in the behaviour of this system. The rate enhancement is due to the increased capacity for electron capture at the illuminated microinterfaces [37] which leads, by virtue of reduced electron–hole recombination, to a corresponding increase in the possibility for hole capture by the pyrimidines. The rate enhancing effect of $[Ag^+]$ is reported to be dependent on the photon flux [37]. At low photon flux the electron–hole recombination is expected to be less [37]. Hence, the effect of added $[Ag^+]$ on initial rate will be marginal. In the TiO_2 mediated photodecomposition of monochlorophenol the effect of $[Ag^+]$ on initial rate was studied at high ($I_0 = 2.1 \times 10^{18}$ photons min^{-1}) and low ($I_0 = 1.7 \times 10^{16}$ photons min^{-1}) photon fluxes. It was found that the role of $[Ag^+]$ in enhancing the reaction rate was only marginal at low photon flux and was attributed to decreased electron–hole recombination at low photon flux [37]. From the high photon flux used in this study ($I_0 = 12 \times 10^{18}$ photons s^{-1}), the effect of $[Ag^+]$ on the initial degradation rate is expected to be appreciable. However only a marginal influence is noticed (Table 5). This could be due to the lower concentration of the pyrimidines (1×10^{-4} mol dm^{-3}) employed in these experiments as it is natural to expect a need for appreciable concentrations of the substrate molecules to take full advantage of the added possibility for hole capture. A possible alternative origin of increased rate in presence of added Ag^+ could probably involve synergistic effects between dioxygen and Ag^+ at UV-illuminated aqueous solution TiO_2 interfaces, whereby blockage of photoactive sites by peroxy species derived from O_2 may be removed by autocatalytic interaction with Ag^+, as has been hypothesized in the literature [38]. Photoelectrochemical evidence exists for peroxy species at such interfaces [39]. The decrease in initial rate observed at higher $[Ag^+]$ (Table 5) may be attributed to a possible scattering of the incident light by the silver precipitate formed (due to reduction of Ag^+ by e^-) progressively in the suspension.

Table 5
Influence of $[Ag^+]_0$ on photocatalytic degradation rate and ∅

(i) Uranil $[Ag^+]_0 \times 10^4$, mol dm^{-3}	Rate × 10^7, mol dm^{-3} s^{-1}	∅ × 10^2
1	1.83	0.9
2	2.66	1.3
3	3.14	1.6
4	2.15	1.1
6	1.70	0.8
8	1.87	0.9
(ii) 6-Methyluracil $[Ag^+]_0 \times 10^4$, mol dm^{-3}	Rate × 10^7 mol dm^{-3} s^{-1}	∅ × 10^2
1.0	1.7	0.85
1.5	1.8	0.89
2.0	2.0	0.99
3.0	2.2	1.08
4.0	1.9	0.94

[a] [Uracil]: 1×10^{-4} mol dm^{-3} TiO_2: 0.005 g vol.: 40 ml pH: 6.5 I_a: 12.04×10^{18} photons s^{-1}.

[b] [6-Meuracil]: 1×10^{-4} mol dm^{-3} TiO_2: 0.01 g vol.: 50 ml pH: 6.0 I_a: 12.04×10^{18} photons s^{-1}.

4. Conclusion

The semiconductor TiO_2 promoted photo-oxidation of three pyrimidine bases, uracil, 6-methyluracil, and thymine carried out in aqueous suspension reveals certain characteristic features:

1. The photoprocess conforms to a Langmuir–Hinshelwood isotherm.
2. The dependence of initial photocatalytic degradation rate and ∅ depend on the weight of TiO_2 exhibiting a saturation type behaviour.
3. The dependence on pH of the photocatalytic degradation rate and ∅ is contributed by a varying magnitude of $^{\bullet}OH$ and h^+_{vb} attack according to the nature of the pyrimidine bases studied. The rate of two isomeric hydroxy adduct radicals of the pyrimidine bases with differing redox properties is discussed. The redox inversion phenomenon of the radicals at alkaline pH (8), followed by their reaction with O_2 yielding the corresponding peroxy radicals, thus leading to an increased e^-–h^+ recombination and hence

resulting in a decrease of the rate and ∅ of the photoprocess, has been observed.

4. The role of the additional electron acceptor, Ag^+, on the degradation rate and ∅ has been studied. The rate and hence ∅ enhancing effect of $[Ag^+]_0$ is attributed to the increased possibility of h^+ capture by the substrate molecules. Despite the pronounced effect of $[Ag^+]_0$ on rate and ∅ at the high photon flux employed in this work, the only marginal influence observed is attributed to a lower range of [pyrimidine base] used, which thus results in an inefficient h^+ capture by the substrate molecules.
5. A comparison of the K (adsorption coefficient) values of the present work with that of TiO_2/methylene blue in aqueous suspension indicates a sort of hydrophobic adsorption in the former versus the hydrophilic one in the latter, based on the surface charge of TiO_2 and the substrate molecules.

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