

# A study on the photocatalytic reactions of $\text{TiO}_2$ with certain pyrimidine bases: effects of dopants ( $\text{Fe}^{3+}$ ) and calcination

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Received 5 March 1999; received in revised form 10 April 1999; accepted 25 May 1999

## Abstract

A steady-state photolytic investigation using  $\text{TiO}_2$  as the photocatalyst in its reaction with uracil, thymine, 6-methyluracil and cytosine in an aqueous suspension has been carried out. Influence of initial [cytosine], amount of  $\text{TiO}_2$  added and pH on the reaction rate and  $\Phi$  were evaluated. The photoprocess obeys the Langmuir–Hinshelwood isotherm.  $\text{Fe}^{3+}$ -doped  $\text{TiO}_2$  prepared by the impregnation method was found to have a modified photocatalytic activity in the photooxidation of all the above-mentioned pyrimidine bases. The effect of calcination (preheat treatment) of the  $\text{TiO}_2$  photocatalyst was a rate retardation. The role of these parameters on surface properties of  $\text{TiO}_2$  is suitably explained. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:*  $\text{TiO}_2$ ; Pyrimidine bases; Dopants

## 1. Introduction

Photocatalysis mediated by semiconductors has been an active research field [1,2]. Its utility in solar energy conversion [3] and waste water treatment processes [4–6] is well documented. Studies involving certain synthetic transformations by irradiated semiconductor are also known [5]. Reports on the modification of certain semiconductor surfaces by metal ion dopants [7] and dyes [8] have been made. The advantage of dye capping on semiconductor in extending their visible absorption as light harvesting antenna has been observed [9,10]. In some cases, time-resolved spectroscopic studies on the nature of

transients involved are reported [11]. Thus, it is clear that semiconductor photocatalysis has enjoyed wide popularity with respect to the possibility of both oxidative and reductive chemical conversions (reactions) effected by the semiconductor surface produced  $h_{\text{vb}}^+$  and  $e_{\text{cb}}^-$  under appropriate conditions. Recently, the promising potentiality of  $\text{TiO}_2$  incorporated certain molecular sieves (e.g., MCM41) in catalysis and some photochemical reactions has been realised [12]. Earlier, we have published some studies on  $\text{TiO}_2$  catalysed photooxidation of certain pyrimidine bases [13]. In this work, we report our findings on the modification of the photocatalytic activity of  $\text{TiO}_2$  in its reactions with the pyrimidine bases, namely uracil, thymine, 6-methyluracil and cytosine, brought out by  $\text{Fe}^{3+}$  as a metal ion dopant and calcination of  $\text{TiO}_2$ .

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## 2. Experimental details

The pyrimidines namely uracil, thymine, 6-methyluracil and cytosine, NaOH,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{HClO}_4$  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  $\text{TiO}_2$  photocatalyst was Degussa P-25. This material is mainly anatase, and has a BET surface area of  $50 \text{ m}^2 \text{ g}^{-1}$  and a mean particle size of 30 nm.

Irradiations were performed with a medium pressure mercury pencil lamp (Spectronics, USA) emitting nearly 100% at 365 nm. Aqueous suspensions of  $\text{TiO}_2$  containing the pyrimidine base in a polymerization tube, with an inlet for  $\text{O}_2$  and with constant magnetic stirring, were irradiated for different intervals of time. All the experiments were carried out in presence of  $\text{O}_2$  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. After centrifugation, the amount of the pyrimidine base decomposed with respect to time was calculated. The rate constants  $k$  ( $\text{s}^{-1}$ ) were evaluated from slopes of plots of  $\log(\text{absorbance})$  vs. irradiation time, and the initial rates of decomposition of the pyrimidines were calculated by multiplying the rate constants with the appropriate initial  $[\text{pyrimidine}]_0$ . Quantum yield ( $\Phi$ ) was calculated based on ferrioxalate actinometry [14]. The product formed was the corresponding pyrimidine glycol as reported earlier [13].

### 2.1. Preparation of iron-doped titania

The doped catalyst was prepared by impregnation method. In this method [15], the iron salt,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , solution required for the doping was added to required weight of  $\text{TiO}_2$  in such a way that it wets the  $\text{TiO}_2$  completely. The slurry was stirred at ambient temperature overnight and dried in air oven at 393 K for 12

h. The dried powder was subjected to use for the reaction. The bare  $\text{TiO}_2$  was also treated as the same method of doped  $\text{TiO}_2$ .

## 3. Results and discussion

Results pertaining to the  $\text{TiO}_2$ -mediated photoreaction (photooxidation) of the pyrimidine base namely cytosine and the effects of  $\text{Fe}^{3+}$ -doped  $\text{TiO}_2$  and influence of calcinated Titania on the reaction of uracil, thymine, 6-methyluracil and cytosine are also presented and discussed.

### 3.1. Effects of [cytosine]

At a fixed weight of  $\text{TiO}_2$  and pH, variation of  $[\text{cytosine}]_0$  was studied. A plot of  $\log(\text{absorbance})$  vs. irradiation time yielded straight lines (Fig. 1), and from the slope the rate was

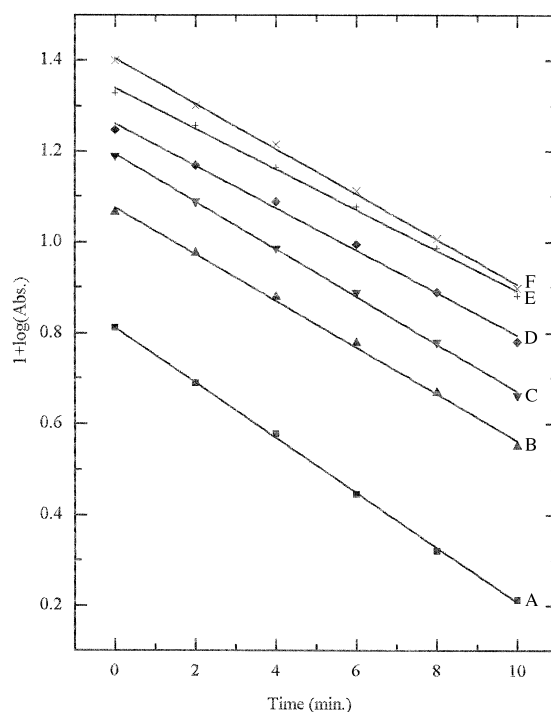


Fig. 1. Influence of [Cytosine] on the photocatalytic degradation rate (0.01 g  $\text{TiO}_2$  /50 ml; pH: 6.5) A, B, C, D, E, F are 1.0, 2.0, 2.5, 3.0, 3.5 and  $4.0 \times 10^{-4}$  M [cytosine] $_0$ , respectively.

evaluated. It exhibited a linear increase in rate followed by a levelling off (Fig. 2). This type of behavior is in accord with the Langmuir–Hinshelwood kinetics (Fig. 3) as per the equation [16]:

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

hence,

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

where  $k$  is a proportionality constant and  $K$  is the equilibrium adsorption coefficient.

In many of the  $\text{TiO}_2$ -promoted photodegradation of organic compounds, the Langmuir–Hinshelwood kinetics as observed in this work has been reported [17,18]. The values of  $k$  and  $K$  obtained from intercept and slope of the plot are  $0.205 \times 10^7 \text{ Ms}^{-1}$  and  $0.242 \times 10^{-3} \text{ M}$ .

A comparison of the values of  $k$  and  $K$  obtained from the Langmuir plot ( $1/\text{rate}$  vs.  $1/[\text{pyrimidine}]$ ) for uracil, thymine, 6-methyl-

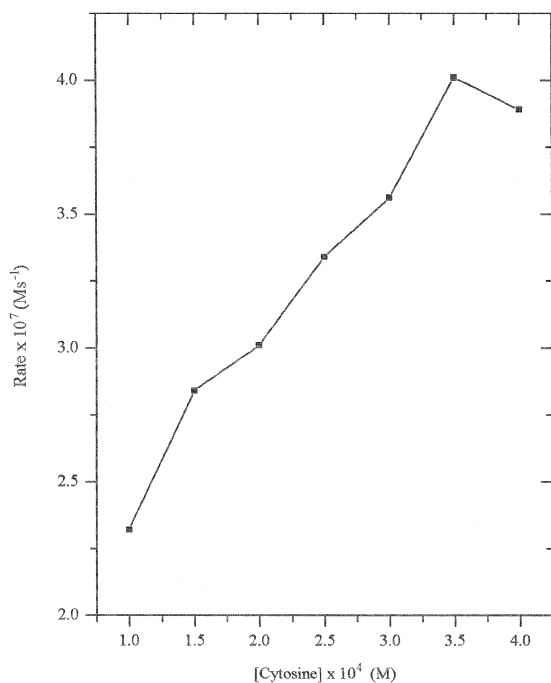


Fig. 2. Rate vs.  $[\text{Cytosine}]_0$  (0.01 g of  $\text{TiO}_2$  per 50 ml; pH: 6.5).

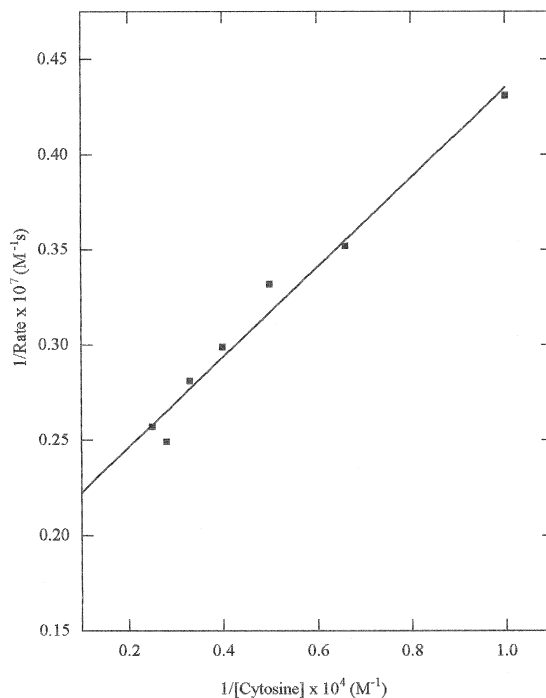


Fig. 3. Langmuir adsorption isotherm (0.01 g of  $\text{TiO}_2$  per 50 ml; pH: 6.5).

uracil and cytosine is indicated in Table 1. As inferred from this table, the almost constant values of  $k$  and  $K$  for all pyrimidines show that the same type of reaction (mechanism) operates in all the cases, namely  $\cdot\text{OH}$  and  $\text{h}^+$  induced sequence of steps leading finally to the oxidation of pyrimidines.

### 3.2. Effect of catalyst

The effect of the amount of catalyst  $\text{TiO}_2$  on the photodegradation rate was investigated. At a fixed pH and initial concentration of the cytosine, experiments were performed with varying

Table 1  
Langmuir isotherm

	$k \times 10^7 \text{ (Ms}^{-1}\text{)}$	$K \times 10^3 \text{ (M)}$
Uracil	0.171	0.209
Thymine	0.196	0.295
6-Methyluracil	0.194	0.200
Cytosine	0.205	0.242

amounts of  $\text{TiO}_2$  ( $0.5 \times 10^{-2}$  g to  $4.0 \times 10^{-2}$  g per 50 ml). The rate of the photodegradation obtained from such experiments are depicted in Table 2. It is clear from this table that for all the pyrimidine bases, as with cytosine, the rate initially increases with an increase in the amount of catalyst and then attains a plateau (leveling off) above a certain point (Fig. 4). This is attributed to the contribution of two main factors. It is envisaged that the decrease of catalytic effect at relatively higher proportions 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 rate is enhanced. At a certain level, the number of available substrate molecules is insufficient for adsorption by the increased number of  $\text{TiO}_2$  particles, that is, although more areas are 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.

### 3.3. Effect of pH

At fixed  $[\text{cytosine}]_0$  and weight of  $\text{TiO}_2$ , the rate of photooxidation was measured at three different pH values. The increase of rate with

Table 2

Effect of catalyst

$[\text{Cytosine}]_0$ :  $1.5 \times 10^{-4}$  M; pH: 6.5; Vol.: 50 ml; Ia:  $2.022 \times 10^{-5}$  Ein/s.

Weight of $\text{TiO}_2 \times 10^2$ (g)	Rate $\times 10^7$ ( $\text{Ms}^{-1}$ )	$\phi \times 10^2$
0.5	1.65	0.81
1.0	2.84	1.40
1.5	3.40	1.68
2.0	3.56	1.76
2.5	3.66	1.81
3.0	3.62	1.79
3.5	3.26	1.61
4.0	2.89	1.42

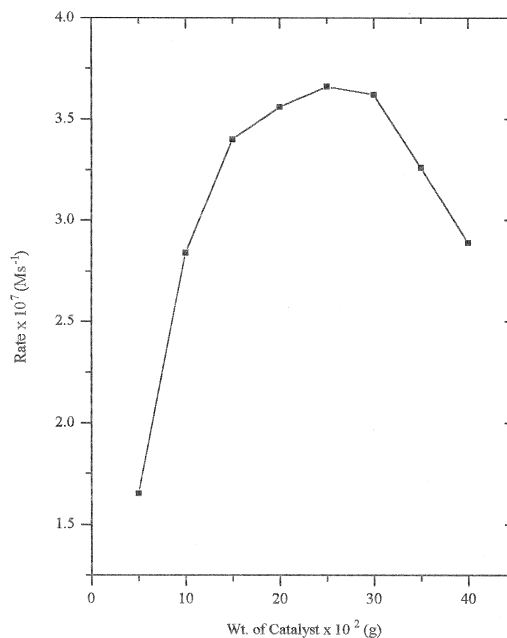


Fig. 4. Dependence of the photocatalytic rate on the amount of catalyst ( $[\text{cytosine}]_0$ :  $1 \times 10^{-4}$  M; pH: 6.5).

pH from 4.5 to 6.5 (Table 3) is in accordance with the increased formation of  $\text{h}^+$  and due to the more availability of the  $\text{OH}^-$  on the surface of  $\text{TiO}_2$ . However, the decrease in rate with increase of pH from 6.5 to 8.5 despite the enhanced availability of  $\text{OH}^-$  in  $\text{TiO}_2$  surface (to give more  $\text{h}^+$ ) shows the predominant role of the repelling electrostatic charge effect between the negatively charged pyrimidine and the negatively charged surface of  $\text{TiO}_2$ .

### 3.4. Effect of temperature pretreatment of $\text{TiO}_2$

From Table 4, it is seen that the rate of the photocatalytic process slows down with increase

Table 3

Effect of pH

$[\text{Cytosine}]_0$ :  $1 \times 10^{-4}$  M  $\text{TiO}_2$ : 0.01 g/50 ml; Ia:  $2.022 \times 10^{-5}$  Ein/s.

pH	Rate $\times 10^7$ ( $\text{Ms}^{-1}$ )	$\phi \times 10^2$
4.5	1.53	0.78
6.5	2.32	1.15
8.5	1.37	0.68

Table 4

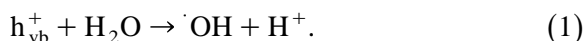
Influence of heat treatment of TiO<sub>2</sub> on the photocatalytic degradation rate

[Uracil] = [6-MethylUracil] = [Thymine] = [Cytosine] = 1 × 10<sup>-4</sup> M.

TiO<sub>2</sub>: 0.02 g/50 ml; pH: 6.5.

Temperature (°C)	Rate × 10 <sup>7</sup> (Ms <sup>-1</sup> )			
	Uracil	Thymine	6-Methyluracil	Cytosine
100	4.72	–	2.96	3.56
300	3.91	3.00	1.05	2.37
500	3.07	2.50	0.96	2.14
600	2.12	1.98	0.89	2.11

of TiO<sub>2</sub> pretreatment temperature. This shows a participation of the TiO<sub>2</sub> surface [19,20] in the degradation process, due to surface bound ·OH radicals and molecular oxygen [21]. It is already clear that the photocatalysis is mainly mediated by ·OH produced via the step involving the attack of h<sub>vb</sub><sup>+</sup> on surface bound water or OH<sup>-</sup>



The density of surface hydroxyls varies with the annealing temperature [22]. From earlier work involving temperature programmed desorption studies (TPD), it is known that the extent of rehydroxylation depends upon the temperature of annealing [22]. Thus the powders heat treated at 700°C are only partially rehydroxylated in comparison to the same powders heat treated at < 300°C. Chemisorbed water directly bound at Ti(IV) ion on the surface is higher at lower temperature [23]. Hence, the present observation in this work is in accord with this. That is, with increase in the temperature (heat) treatment of TiO<sub>2</sub> the density of surface bound hydroxyls (OH<sup>-</sup>) or chemisorbed H<sub>2</sub>O decreases which subsequently reduces the probability of ·OH production (Eq. (1)), thus retarding the photoreaction. It is also possible that the (photo) adsorptive activity of the TiO<sub>2</sub> surface towards the substrates (pyrimidines) depends on the amount of surface OH<sup>-</sup> groups. More the number of surface OH<sup>-</sup> groups, faster the photocatalytic reaction. In an earlier study involving the adsorption of certain amino acids on TiO<sub>2</sub> [24], an observation of decreased ad-

sorption with increase of calcination temperature was made and attributed to the availability of surface OH<sup>-</sup> groups. A direct correlation between the amount of adsorption and the amount of OH<sub>s</sub><sup>-</sup> groups was noticed. Since it is known that the Bronsted acid sites due to ·OH groups on the TiO<sub>2</sub> surface are able to interact with NH<sub>3</sub> and pyridine [25], the ·OH groups may interact also with the pyrimidines containing such functionalities through the interaction with lone-pair electrons of the nitrogen atom. Hence, the decreased adsorptive activity of TiO<sub>2</sub> surface at higher temperatures reflects a minimum availability of surface OH<sup>-</sup> groups.

### 3.5. Effect of Fe<sup>3+</sup> as a dopant

From Table 5, it is clear that the photooxidation rate increases with increase in the level of Fe<sup>3+</sup> doped (onto TiO<sub>2</sub>) up to approximately 0.75 at.% followed by a decrease in rate with further increase in Fe<sup>3+</sup> level. A similar effect of Fe<sup>3+</sup> doping on TiO<sub>2</sub> resulting in an increase of photodegradation rate with increase in the amount of Fe<sup>3+</sup> followed by a decrease in the rate beyond further addition of Fe<sup>3+</sup> was reported for CHCl<sub>3</sub> degradation [26].

The increase in photodegradation rate with increase in the amount of Fe<sup>3+</sup> is explained by the ability of the metal ion dopant to act as a charge carrier trap site for e<sup>-</sup> [27–29]. Moreover, the rate enhanced effect of Fe<sup>3+</sup> is also

Table 5

Fe<sup>3+</sup>-doped TiO<sub>2</sub> photocatalytic reactions

[Uracil] = [6-MethylUracil] = [Thymine] = [Cytosine] = 1 × 10<sup>-4</sup> M.

Fe<sup>3+</sup>/TiO<sub>2</sub>: 0.03 g/50 ml; pH: 7.

Fe <sup>3+</sup> in percentage	Rate × 10 <sup>7</sup> (Ms <sup>-1</sup> )			
	Uracil	Thymine	6-Methyluracil	Cytosine
0	0.70	0.83	0.89	0.65
0.25	1.32	1.25	1.25	1.16
0.50	1.42	1.50	1.33	1.33
0.75	1.86	1.47	1.35	1.51
1.00	1.00	1.26	0.95	0.95
1.50	0.56	0.58	0.51	0.84
2.00	0.66	-	0.58	0.65

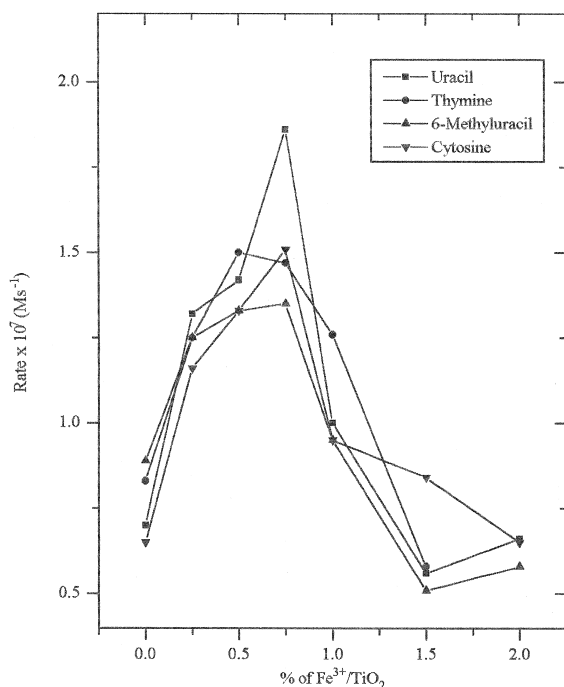
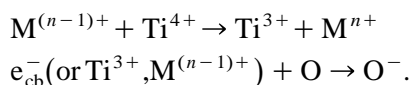


Fig. 5. Influence of doped titania. ([Uracil]=[6-Methyluracil]=[Thymine]=[Cytosine]= $1 \times 10^{-4}$  M.  $\text{Fe}^{3+}/\text{TiO}_2$ : 0.03 g/50 ml; pH: 7).

explainable due to the close proximity [30,31] of the energy levels of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Ti}^{3+}/\text{Ti}^{4+}$ . As a result of this proximity, it is expected that the trapped electron in the  $\text{Fe}^{2+}$  could easily be transferred to a neighbouring surficial  $\text{Ti}^{4+}$ , which then leads to interfacial electron transfer, thus resulting in decreased  $e^-/h^+$  recombination.



The existence of an optimal dopant concentration (Table 5 and Fig. 5) is interpretable in terms of a change in the space-charge layer thickness [32,33]. The decrease of photodegradation rate beyond a concentration of  $\text{Fe}^{3+}$  could be explained as per [34]:

$$k \propto \exp(-2R/a_0)$$

where  $R$  is the distance separating the  $e^-/h^+$  pair and  $a_0$  is the radones of the hydrogenic wave function of the trapped carriers. As a

consequence, the recombination rate increases exponentially with the dopant concentration because the average distance between the trap sites decreases with increasing the number of dopants within a particle.

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