

Photocatalytic decolorisation of methylene blue (MB) over titania pillared zirconium phosphate (ZrP) and titanium phosphate (TiP) under solar radiation

D.P. Das, N. Baliarsingh, K.M. Parida *

Colloids and Materials Chemistry Cell, Regional Research Laboratory (CSIR), Bhubaneswar 751013, Orissa, India

Received 18 July 2006; received in revised form 7 August 2006; accepted 8 August 2006

Available online 15 August 2006

Abstract

The photodegradation of methylene blue (MB) was studied in aqueous solution over titania pillared ZrP and TiP under solar radiation. The reaction was studied by varying different parameters such as pH, titania load, catalyst concentration, initial MB concentration, irradiation time, effect of hydrogen peroxide (H_2O_2), effect of inorganic salts such as potassium persulphate ($K_2S_2O_8$) and sodium chloride (NaCl). The initial rate of photodegradation of methylene blue is favoured in neutral pH (pH 7.0). Potassium persulphate and hydrogen peroxide were found to impose the enhancing effect on the rate of photodegradation of MB where as sodium chloride exhibits an inhibiting effect.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Titania pillared; Methylene blue; Hydrogen peroxide; Potassium persulphate ($K_2S_2O_8$); Sodium chloride (NaCl)

1. Introduction

Dye source from the textile industries are an important source of environmental contamination. It is estimated that from 1 to 15% of the dye is lost during dyeing process and is released in wastewaters [1]. The release of these colored wastewaters in ecosystem is a dramatic source of aesthetic pollution, eutrophication and perturbations in aquatic life [2]. As international environmental standards are becoming more stringent (ISO 14001, October 1996), technological systems for the removal of organic pollutants, such as dyes have been recently developed. Among them, physical methods such as adsorption [3], biological methods (biodegradation) [4,5] and chemical methods (chlorination, ozonation) [6] are the most frequently used. Biological treatment is a proven technology and cost effective. However, it has been also reported that most of the dyes are only adsorbed on the sludge and are not degraded [7]. Physical methods are also ineffective for the pollutants which are not readily adsorbable or volatile and have further disadvantages that they simply transfer the pollutants to another phase rather than destroying them. Due

to the above mentioned disadvantages, there is a active search for highly effective method to degrade the dyes into environmentally compatible products. It has been revealed from the literature that photocatalysis can be used to destroy the dyes using semiconductor catalyst under light irradiation [8,9]. Among the new oxidation methods or advanced oxidation processes (AOP), heterogeneous photocatalysis appears to be the most emerging destructive technology leading to the total mineralisation of most of organic pollutants [10–12]. Among the semiconducting materials used in AOP, titania is one of the well known efficient photocatalysts. The capability of TiO_2 -based photocatalyst to degrade gaseous and aqueous contaminants makes it a good candidate for use in air clean up and water purification [13].

The present work deals with the catalytic evaluation of titania pillared zirconium phosphate and titanium phosphate towards the photodegradation of cationic dye, methylene blue (MB) (Fig. 1) under solar radiation.

2. Experimental

2.1. Material preparation

Titania intercalated ZrP and TiP were prepared by the procedure reported by Yamanaka et al. [14] using Na-form of the

* Corresponding author. Tel.: +91 674 2581636/425; fax: +91 674 2581637.
E-mail addresses: das_diptiprakashini@rediffmail.com (D.P. Das),
kmparida@yahoo.com (K.M. Parida).

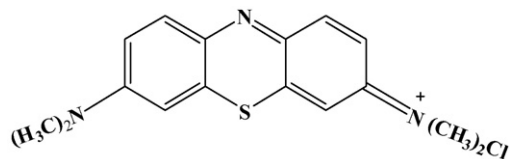


Fig. 1. Structure of methylene blue.

respective metal phosphates. First titania sol was prepared by drop wise addition of titanium(IV) isopropoxide to a vigorously stirred 1 M HCl solution to give a molar ratio of 0.25, between alkoxide and HCl solution. The resulting slurry was stirred for 3 h to get a clear titania sol. Then the aqueous suspension of sodium exchanged metal phosphate was added slowly to the sol. The resultant suspension was further stirred for 3 h at 50 °C. Then it was filtered, washed thoroughly with deionised water and dried at different temperatures for further studies. The best performing catalysts (2 wt.% TiO₂ pillared ZrP and 4 wt.% TiO₂ pillared TiP) were calcined at 500 °C for 5 h.

2.2. Physico-chemical characterisation

The X-ray powder diffraction pattern was taken in the Philips PW 1710 diffractometer fitted with an automatic control. The patterns were run with a monochromatic Cu K α radiation, with a scan rate of 2°/min.

The BET-surface area, pore size distribution, pore volume and pore radius analysis were done using Sorptomatic 1990 series by nitrogen adsorption–desorption at liquid nitrogen temperature (–196 °C). Prior to adsorption–desorption measurements, samples were degassed at 110 °C for 5 h in vacuum.

UV–vis DRS was taken in the Varian UV–vis Spectrophotometer in the range of 200–800 nm. The spectra were recorded against boric acid reflectance standard as base line. The computer processing of spectra with CARY 1E software consisted calculation of Kubelka–munk function $F(R_{\infty})$ from the absorbance. This diffused reflectance spectroscopy has been utilised to characterise the bulk structure. This is used to probe the band structure or molecular energy levels in the materials since UV–vis light excitation creates photo-generated electrons and holes. The UV–vis absorption band edge is strong function of cluster size diameter less than 10 nm, which can be attributed to quantum size effect for these semiconductors.

The FTIR spectra were taken using JASCO FTIR-5300 in KBr matrix in the range 400–4000 cm⁻¹.

2.3. Experimental procedure

The photo-oxidation of methylene blue was performed in batch reactors by taking 20 mg/L of the substrate (methylene blue in water) and 1 gm/L of the catalyst. The solution was exposed to sunlight (the average solar intensity = 0.80 kW/m²) in closed pyrex flasks at room temperature with constant stirring during the month of February–April, 2006. The solar experiments were compared with those which were carried out in dark. The methylene blue analysis was done by the Spectrophotometric method at 660 nm [15].

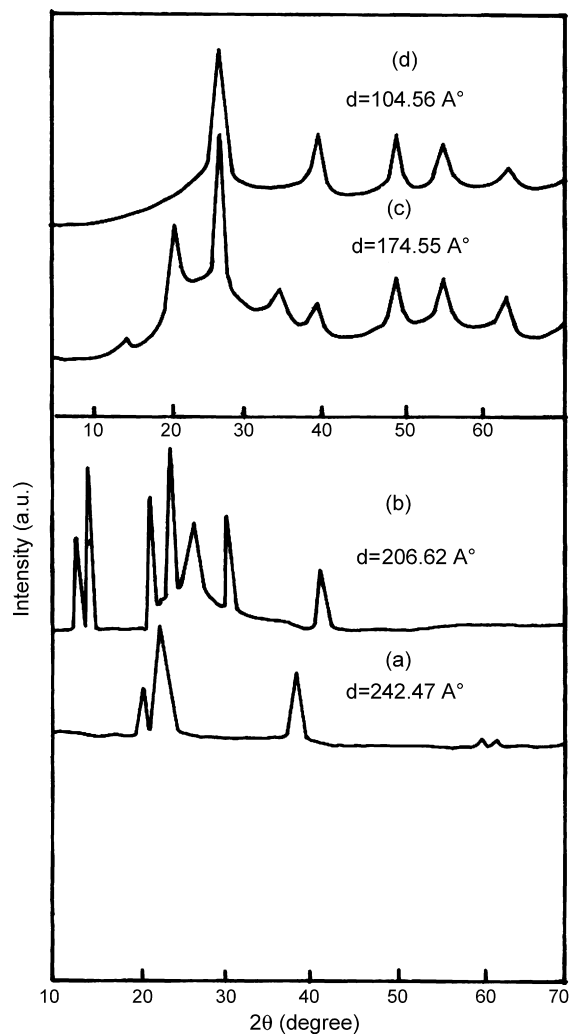


Fig. 2. The XRD pattern of 500 °C calcined: (a) ZrP, (b) TiP, (c) ZrP/TiO₂ 2 wt.%, and (d) TiP/TiO₂ 4 wt.% (d is the crystallite size (Å)).

3. Results and discussion

3.1. Physico-chemical characterisation

The XRD patterns (Fig. 2, the values of crystallite size was pointed out in the figure) show that the crystallite size was found to be less in case of 4 wt.% of titania loaded TiP (104.56 Å) support than that of neat TiP (206.62 Å) calcined at 500 °C and similar case was observed in case of 2 wt.% titania loaded ZrP (174.55 Å) and neat ZrP (242.47 Å) calcined at 500 °C. The decrease in the crystallite size in presence of titania species could possibly due to the interaction of titania species with ZrP and TiP.

From BET-surface area, it has been found that the specific surface area of titania pillared ZrP and TiP is higher than that of sodium exchanged metal phosphates calcined at 500 °C, which also confirms the effective pillaring of the metal phosphates (Table 1). ZrP and TiP loaded with 2 and 4 wt.% TiO₂, respectively, possessed higher surface area compared to other samples. This shows that pillaring is most effective in these cases, i.e. the titania species are well oriented inside the layers of ZrP and

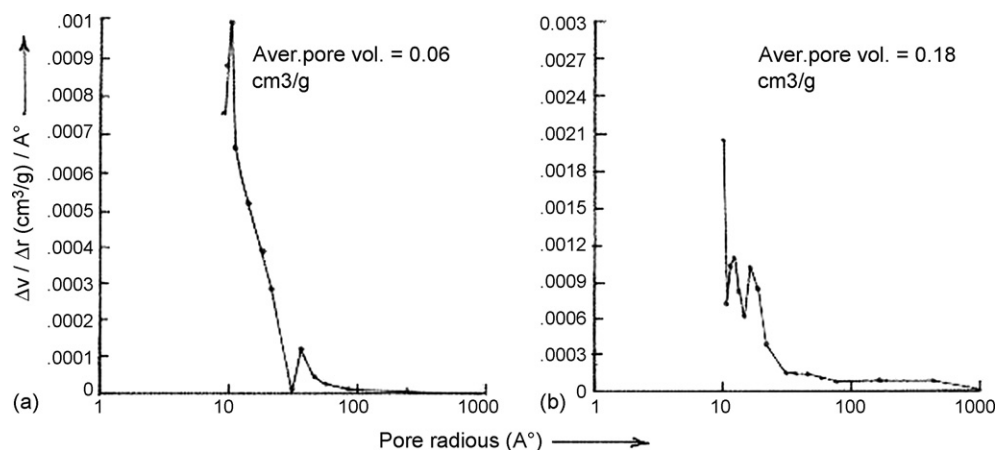


Fig. 3. Pore size distribution of 500 °C calcined: (a) ZrP/TiO₂ 2 wt.% and (b) TiP/TiO₂ 4 wt.%.

TiP. In addition to this, small size of ZrP/TiP supported titania particle increases the surface area, increasing the chance for the electrons and holes to reach the surface and react with the organic substrate. The presence of the support, transparent to visible radiation, allows higher catalyst concentration with no loss of effectiveness of irradiation as in case of bulk titania [16,17].

Fig. 3 depicts the pore size distribution of 2 and 4 wt.% titania pillared ZrP and TiP, respectively. The distribution indicates the mesoporous structure of titania pillared metal phosphates. It was also clearly observed from the figure that the average pore volume of 4 wt.% titania loaded TiP is more than that of 2 wt.% titania loaded ZrP.

From UV–vis diffused reflectance spectrum of TiO₂ pillared ZrP and TiP, it has been found that there is an increase in the peak height, i.e. the absorbance increases from 0.5 to 1.2 due to pillaring. The spectrum shows a sharp peak at 220 nm which correspond to Ti⁴⁺ [18] (Fig. 4c and d). From the individual DRS spectrum of ZrP and TiP, it has been observed that for ZrP a peak at 240 nm and for TiP a peak at 205 nm were found (Fig. 4a and b). The broad peak in the range of 200–300 nm shows that dif-

ferent environment of titania present in the material. A band at 220–230 nm is considered as characteristic of the incorporation of titanium in the lattice of ZrP or TiP. Due to this energy difference between the two phases, photoexcitation takes place and as a result of which the photodegradation occurred.

FTIR spectra of materials heated at 110 °C show strong IR bands in the region of 1300–900 cm⁻¹ for ZrP and for TiP, a broad absorption containing a poorly resolved (PO₃)_{asym} and (PO₃)_{sym} is observed in the region 1300–1000 cm⁻¹ and several (PO₃) deformation modes are in the region below 650 cm⁻¹. The typical symmetrical mode characterising the P–O–P bridge

Table 1
BET-surface area and basal spacing of different wt.% of titania loaded ZrP and TiP

Sample code	Sp. surface area (m ² /g)	Basal spacing (Å)	Initial rate of photodecolorisation of MB (ppm/min)
ZrP	60.83	7.56	–
ZrP/TiO ₂ 1	70.1	15.5	0.042
ZrP/TiO ₂ 2	116.95	19.3	0.058
ZrP/TiO ₂ 4	105.66	17.2	0.051
ZrP/TiO ₂ 8	50.02	16.4	0.046
ZrP/TiO ₂ 10	30.92	14.3	0.0353
TiP	63.83	7.6	–
TiP/TiO ₂ 2	100.56	17.3	0.052
TiP/TiO ₂ 4	172.33	25.9	0.0653
TiP/TiO ₂ 8	66.58	18.2	0.055
TiP/TiO ₂ 10	40.92	15.5	0.0454

ZrP/TiO₂: titania pillared zirconium phosphate, TiP/TiO₂: titania pillared titanium phosphate, ZrP/TiO₂ 2: 2 wt.% titania pillared zirconium phosphate and TiP/TiO₂ 2: 2 wt.% titania pillared titanium phosphate.

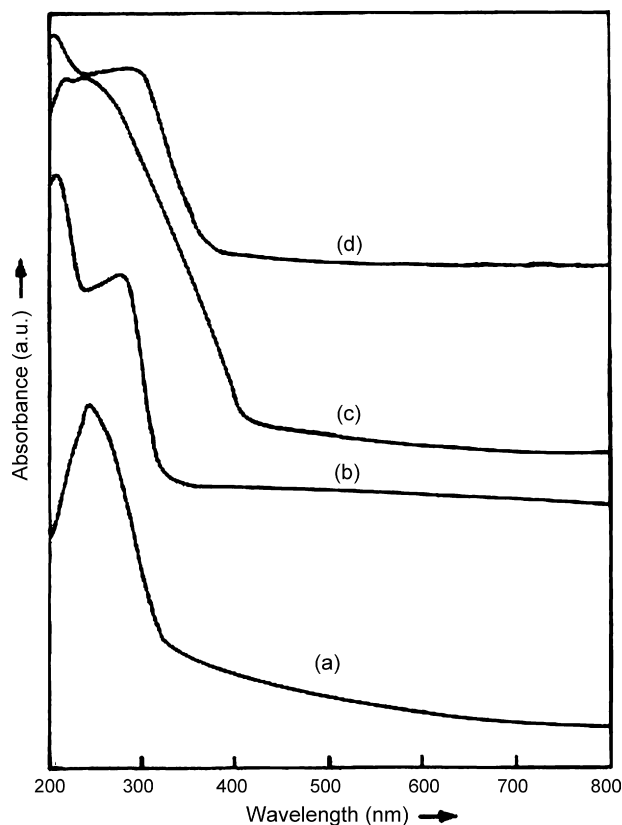


Fig. 4. UV–vis DRS of (a) ZrP and (b) TiP calcined at 110 °C and (c) ZrP/TiO₂ 2 wt.% and (d) TiP/TiO₂ 4 wt.% calcined at 500 °C.

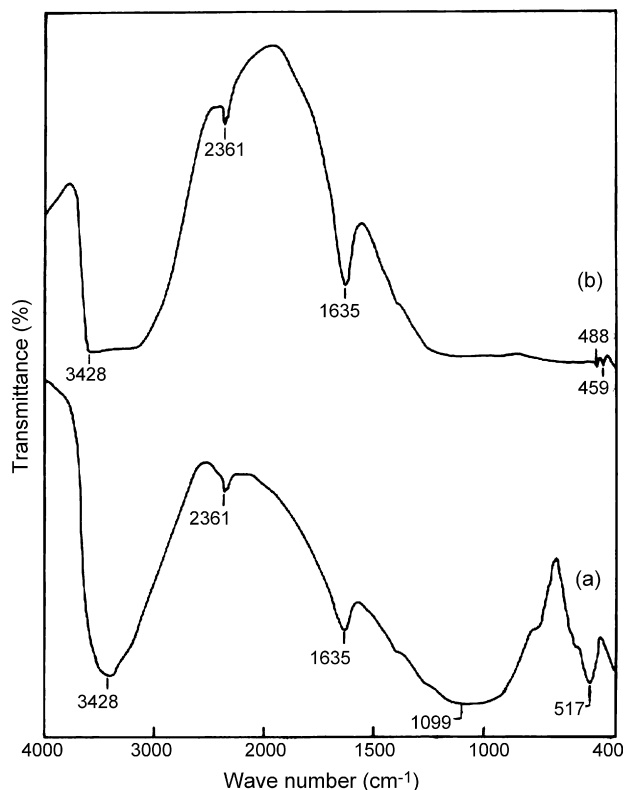


Fig. 5. FTIR spectra of 500 °C calcined: (a) ZrP and (b) ZrP/TiO₂ 2 wt.%.

is observed around 970 cm⁻¹. The band at 1619 cm⁻¹ (ZrP), 1617 cm⁻¹ (TiP) is due to the bending vibrations of -OH of water associated PO₄³⁻ group which supports the presence of water of crystallisation in the lamellar solid. A strong absorption band around 3148 cm⁻¹ (ZrP) and 3406 cm⁻¹ (TiP) is probably due to stretching vibration of -OH group and of physically adsorbed water and the broadness is due to the existence of hydrogen bond [19]. The appearance of two prominent bands at 3509, 3539 cm⁻¹ for ZrP and 3478, 3555 cm⁻¹ for TiP may be due to the stretching vibration of P-OH and Zr/Ti-OH, respectively. A broad peak at 1099 cm⁻¹ for ZrP (Fig. 5a) and 1082 cm⁻¹ for TiP (Fig. 6a) was noticed at 500 °C calcination instead of splitted peaks for phosphate. After the pillaring and monolayer formation with TiO₂, the PO₄³⁻ peak has been broadened and two new peaks in the lower wave number region around at 480–450 cm⁻¹ were found which is due to TiO₂ for ZrP (Fig. 5b). For TiP the PO₄³⁻ peak has been shifted to the lower wave number region from 1082 to 1049 cm⁻¹ and a new peak at 455 cm⁻¹ was found which is due to TiO₂ (Fig. 6b) [20]. Due to pillaring of TiO₂, all other peaks due to (PO₃)_{deformation} overlaps with the peaks due to TiO₂. This also confirms pillaring is effective.

3.2. Photodegradation of methylene blue

3.2.1. Effect of pH

The influence of pH on the decolorisation of MB over titania pillared ZrP and TiP was shown in Fig. 7. The effect of pH on the photodegradation of methylene blue can be well explained on the basis of surface charge of titania pillared ZrP or TiP. The surface

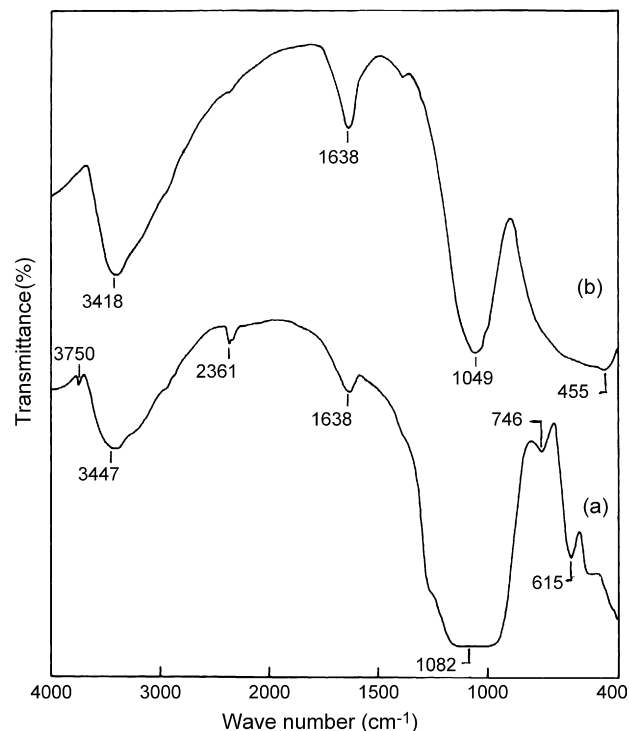


Fig. 6. FTIR spectra of 500 °C calcined: (a) TiP and (b) TiP/TiO₂ 4 wt.%.

charge of the catalyst under study is around five to six. Since methylene blue is a cationic dye, in solution it exists as a positive charged species. At pH < p*H*_{pzc}, the surface of the catalyst is positively charged. So in the acidic pH, there is an electrostatic repulsion between the dye species and the surface of the catalyst

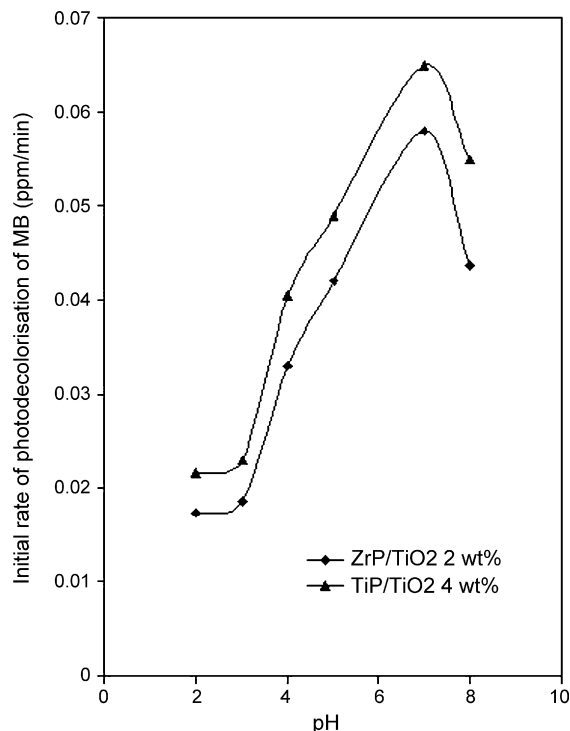


Fig. 7. Effect of pH on the initial rate of photodecolorisation of methylene blue. [Catalyst] = 1.0 g/L; [MB] = 20 mg/L; time = 240 min.

as a result of which the initial rate of photodegradation was found to be minimum, i.e. 0.0216 and 0.0174 ppm/min for titania pillared TiP and ZrP, respectively, at pH 2.0. With increase in the pH, the initial rate of photodegradation increases and reaches maximum, i.e. 0.065 and 0.058 ppm/min for titania pillared TiP and ZrP, respectively, at pH 7.0. With further increase in the pH, the initial rate of photodecolorisation decreases. This is mainly due to the fact that at pH 7.0, the surface of TiO_2/TiP or ZrP is negatively charged which can attract more number of dye species. As a result of which photodegradation was found to be more at pH 7.0. With further increase in the pH the rate decreases which could possible due to formation of methylene blue hydroxide species.

3.2.2. Effect of titania loading

The effect of titania loading was investigated on the supports ZrP and TiP (Table 1). It has been observed that, with increase in the titania loading up to 2 wt.% for ZrP, the initial rate of photodecolorisation increases to 0.058 ppm/min and for TiP up to 4 wt.%, the value increases to 0.0653 ppm/min. Thereafter these values decrease to 0.0454 and 0.0353 ppm/min for titania pillared TiP and ZrP, respectively. The promoting effect of titania can be understood by considering the following aspects:

- (1) Pillaring of titania resulted in higher surface area (Table 1), which allows more methylene blue to be adsorbed on the surface there by facilitating the photodegradation/decolorisation of methylene blue.
- (2) Pillaring of titania decreases the crystallite size (Fig. 2) which in turn increases the surface area and adsorption of methylene blue. This ultimately helps in increasing the initial rate of photodegradation/decolorisation of the dye.

3.2.3. Effect of initial concentration of MB

We have studied the effect of initial concentration of MB on photodecolorisation process. MB was completely decolorised when it is present in 2–5 mg/L. In general with increase in concentration from 2 to 80 mg/L, the percentage of degradation of MB decreases from 100 to 30.9 and 25.53 for titania pillared TiP and ZrP, respectively. This could possibly be due to the fact that with increase in the concentration of MB, the light absorbed by the substrate is more as compared to the catalyst, which is ineffective in bringing about the photoprocess. So at higher concentration, the percentage of photodegradation decreases.

3.2.4. Effect of irradiation time

Fig. 8 shows the effect of irradiation time on the percentage of photodegradation/decolorisation of methylene blue. With increase in the irradiation time from 30 to 240 min, the percentage of photodecolorisation increases from 30.9 to 78.36 and 23.5 to 69.56 for titania pillared TiP and ZrP, respectively. Thereafter the values remain almost constant. This is because of the fact that with increase in the irradiation time, there is an increase in the number of photons which in turn increases the percentage of photodecolorisation up to 240 min. Thereafter with further increase in the time the percentage of photodecolorisation remains constant.

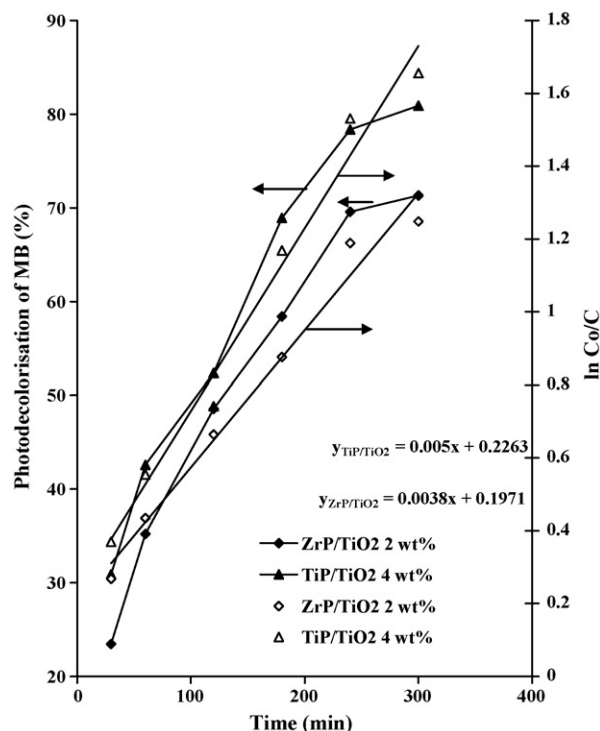


Fig. 8. Methylene blue decolorisation as a function of time of irradiation. [MB] = 20 mg/L; pH 7.0.

Fig. 8 shows a linear relationship between $\ln C_0/C$ and irradiation time, t . This shows that the photodecolorisation of methylene blue (20 mg/L) follows first-order kinetics over titania pillared ZrP (2 wt.%) and TiP (4 wt.%) which is in agreement with Senthilkumaar et al. [21]. The data calculated for first-order rate constants “ k ” for titania pillared ZrP (2 wt.%) and TiP (4 wt.%) were shown in the Table 2.

3.2.5. Effect of catalyst concentration

Experiments were carried out with different concentrations of catalyst (0.25–1.25 g/L) at fixed MB concentration (20 mg/L). It has been observed that the initial rate increases from 0.034 to 0.0653 and 0.029 to 0.058 ppm/min with an increase in the amount of catalyst from 0.25 to 1 g/L for titania pillared TiP (4 wt.%) and ZrP (2 wt.%), respectively, and thereafter the values remain almost constant (Fig. 9). This could possibly be due

Table 2
Rate constant values for photodecolorisation^a of methylene blue (MB)

Time (min)	$\ln C_0/C$	
	ZrP/TiO ₂ (2 wt.%)	TiP/TiO ₂ (4 wt.%)
30	0.268	0.3696
60	0.4343	0.5548
120	0.6647	0.7413
180	0.8761	1.168
240	1.189	1.531
300	1.248	1.655
Apparent rate constants, k (min ⁻¹)		
	0.00595	0.00769

^a [MB] = 20 mg/L, pH 7.0, and [catalyst] = 1 g/L.

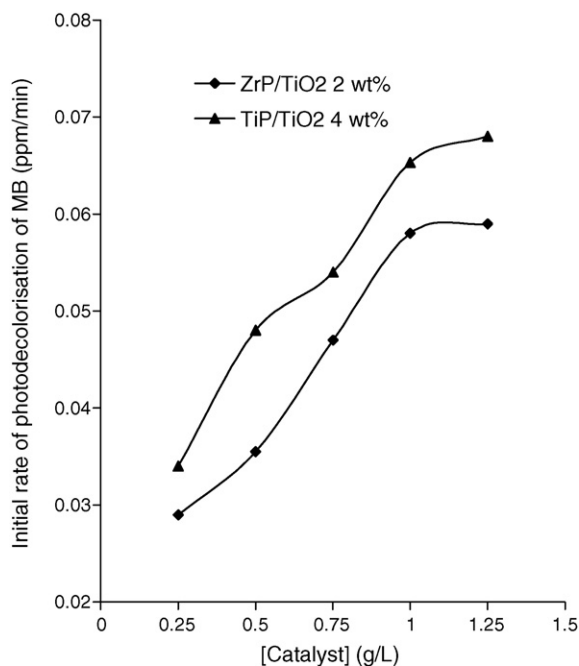


Fig. 9. Effect of catalyst concentration on the rate of photodecolorisation of methylene blue under solar irradiation. [MB] = 20 mg/L; time = 240 min; pH 7.0.

to the fact that with increase in the concentration of catalysts, the number of photons absorbed and the number of dye molecules adsorbed increase with respect to an increase in the number of active sites of the catalyst molecules. The density of the molecule in the area of illumination increases and thus the rate gets enhanced. After certain level the dye molecules available are not sufficient for adsorption by increased number of catalyst molecules. Hence, the additional catalyst is not involved in photocatalytic activity and the rate does not increase with increase in the catalyst concentration beyond certain limits. It is also expected that the aggregation of catalyst molecules at high concentration must also be considered, which causes a decrease the number of exposed active sites. Some authors reported [22] the negative effect on the percentage of degradation of reactive dyes at higher catalyst concentration. Our observation agrees with the observation reported by Sauer et al. [23] for degradation of Safira dye using Degussa P-25.

3.2.6. Effect of hydrogen peroxide (H₂O₂)

The effect of H₂O₂ concentration was studied by varying the concentration of H₂O₂. It was observed that, the initial rate of photodegradation/decolorisation (ppm/min) increases from 0.0653 to 0.082 and 0.0579 to 0.0755 ppm/min with increase in the H₂O₂ concentration from 0 to 20 mg/L for 2 and 4 wt.% titania pillared TiP and ZrP, respectively. This could possibly be due to the formation of more number of OH• radicals at higher hydrogen peroxide concentration, which inhibits the e⁻-h⁺ recombination process (Eq. (1)):

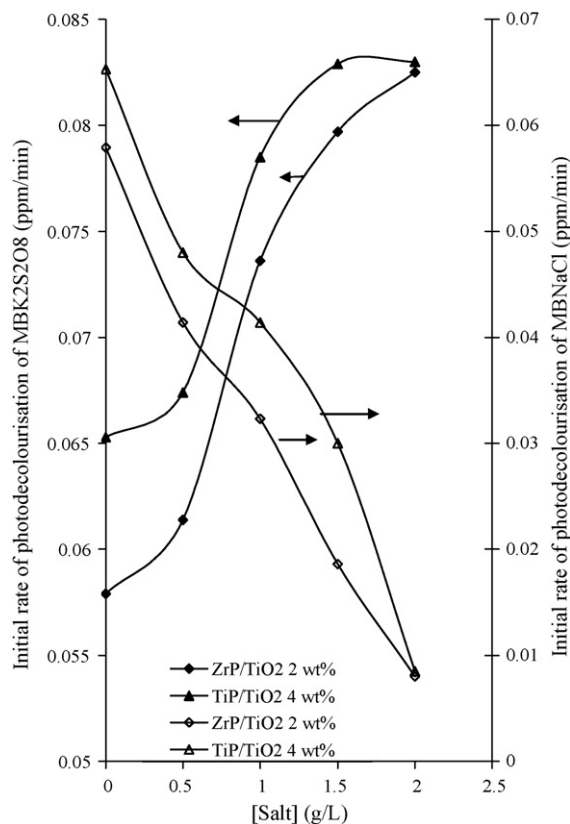
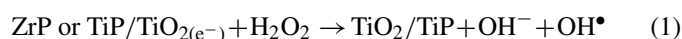
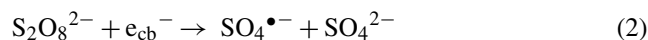


Fig. 10. Effect of inorganic salts on the initial rate of photodecolorisation of methylene blue. [MB] = 20 mg/L; pH 7.0; time = 240 min; [catalyst] = 1.0 g/L.

3.2.7. Effect of inorganic salts

In the present work we have investigated the effect of inorganic salts like potassium persulphate and sodium chloride. The effect of persulphate ion (electron scavenger) on photocatalytic degradation of MB over both the catalysts were investigated by varying its amount from 0.5 to 2 g/L of dye solution (Fig. 10). The initial rate of photodegradation of methylene blue increases with increasing the persulphate amount and attained 0.083 ppm/min (100% degradation) and 0.0825 ppm/min (99%) in 4 h for 2 g/L of K₂S₂O₈ amount in MB solution over 4 and 2 wt.% titania pillared TiP and ZrP, respectively. This enhanced degradation in presence of persulphate ion may be attributed due to the following reasons:

1. The sulphate radical anion (SO₄•⁻) formed from the oxidant (S₂O₈²⁻) by reaction (Eq. (2)) with the electron generated in the conduction band of ZrP or TiP/TiO₂ semiconductor:



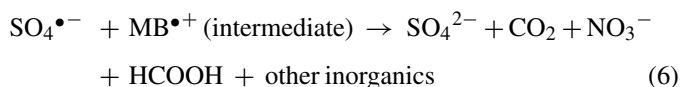
2. The sulphate radical anion (SO₄•⁻) is a strong oxidant and engages in three different processes with organic compounds: (i) by abstracting a hydrogen atom from saturated carbon (ii) by adding hydrogen to unsaturated or aromatic carbon (iii) by removing electron from certain neutral molecules [24–26]:



Table 3
Comparison of MB photodecolorisation over literature reported catalysts with that used in the present work

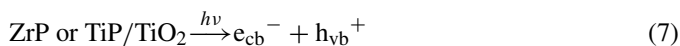
S. no.	Catalyst used	Conditions and removal	References
1.	Nanocrystalline TiO ₂	125 W (311 nm) medium pressure Hg lamp, [MB] = 10 mg/L, pH 6.8, time = 4 h, degr. (%) = 28%	[21]
2.	RuO ₂ loaded polycrystalline BiSbO ₄	500 W (365 nm) high pressure lamp, [MB] = 10 mg/L, catalyst = 2 g/L, 91.2% removal	[29]
3.	S-doped TiO ₂	1000 W Xe lamp (between 350 and 540 nm), [MB] = 50 mmol/dm ³ , rate of decomposition = 1.9 mmol/min	[31]
4.	Pure TiO ₂ Sulphated TiO ₂	Rate of decomposition > 2 mmol/min Solar radiation (aver. light intensity 0.80 kW/m ²), [MB] = 100 mg/L, catalyst = 1.6 g/L, removal = 99%	[32]
5.	Silica gel supported TiO ₂	20 W/220 V UV lamp (253.7 nm), [MB] = 20 mg/L, catalyst = 3 g/L, degr. (%) = 90.96%	[33]
6.	TiO ₂ pillared zirconium phosphate and titanium phosphate	Solar radiation (aver. light intensity 0.80 kW/m ²), [MB] = 20 mg/L, catalyst = 1 g/L, pH 7.0, 2 wt.% ZrP/TiO ₂ (degr. %) = 69.56% and 4 wt.% TiP/TiO ₂ (degr. %) = 78.36%	Present work

The sulphate radical anion and hydroxyl radical formed (Eqs. (2) and (4)) are powerful oxidants that can degrade the dye molecules at a very faster rate. The sulphate radical anion has a unique quality of attacking the dye at different positions forming fragmented dye molecules (Eq. (5) and (6)) [27,28]:



In the similar way effect of chloride (sodium chloride) ion was investigated on the photodegradation of MB (Fig. 10). The experiments were carried out by varying the chloride concentration, from 0.5 to 2.0 g/L of MB solution. From Fig. 10, it was observed that with increase in Cl⁻ amount the initial rate of photodegradation of MB decreases from 0.0653 to 0.0085 and 0.0579 to 0.008 ppm/min for 4 wt.% TiP/TiO₂ and 2 wt.% ZrP/TiO₂, respectively, which is in good agreement with Abdullah et al. [29] who observed a strong inhibiting effect of Cl⁻ ion on the photodegradation of salicylic acid, aniline and ethanol.

The decrease in initial rate of photodegradation of MB in presence of Cl⁻ is due to hole scavenging properties of Cl⁻ ion (Eq. (7) and (8)) [30]:



The radical Cl[•] formed (Eq. (8)) subsequently transformed to Cl₂^{•-} radical anion (Eq. (9)) which blocks the surface sites of ZrP or TiP/TiO₂ which are available for adsorption of MB and electron transfer from MB.

Table 3 emphasizes a comparative study of the catalysts studied by different researchers and that of the observations reported in the present work. From the table it can be clearly seen that the catalysts used in the present work, i.e. titania pillared ZrP and TiP are comparable to those reported in the literature.

Comparing the results reported in the present work, 4 wt.% titania pillared TiP is showing good results as compared to that of 2 wt.% titania pillared ZrP. This could possibly be due to higher surface area, basal spacing, pore volume and lower crystallite size as compared to that of 2 wt.% titania pillared ZrP.

4. Conclusions

1. By varying the wt.% of titania, it was observed that 2 and 4 wt.% titania pillared ZrP and TiP, respectively, possessed highest surface area, basal spacing and lowest crystallite size.
2. The photodecolorisation of methylene blue was favoured in neutral pH with 78.36 and 69.56% degradation over 4 and 2 wt.% titania pillared TiP and ZrP, respectively.
3. The initial rate of photodecolorisation of MB increases from 0.034 to 0.068 and 0.029 to 0.058 ppm/min with increase in the catalyst concentration from 0.25 to 1.25 g/L for 4 and 2 wt.% titania pillared TiP and ZrP, respectively.
4. The photodecolorisation of methylene blue was studied by using wide ranges of MB concentration 2–80 mg/L. With increase in the MB concentration, the percentage of photodecolorisation decreases from 100 to 30.9% and 25.53% for 4 wt.% TiP/TiO₂ and 2 wt.% ZrP/TiO₂, respectively. This photodecolorisation process follows first-order kinetics.
5. It was observed that with increase in the amount of hydrogen peroxide, the initial rate of photodecolorisation increases up to 0.082 and 0.0755 ppm/min over TiP/TiO₂ and ZrP/TiO₂, respectively, for 20 mg/L of H₂O₂ concentration due to formation of more number of hydroxyl radical.
6. Comparing the effects of inorganic salts like K₂S₂O₈ and NaCl in both the catalysts, K₂S₂O₈ was found to impose an enhancing effect on the photodegradation/decolorisation of MB where as NaCl was found to impose a negative effect.

Acknowledgements

The authors are thankful to Prof. B.K. Mishra, Director, Regional Research Laboratory (CSIR), Bhubaneswar for his keen interest and permission to publish this paper. One of the

authors (DPD) is obliged to CSIR, New Delhi for a Senior Research Fellowship.

References

- [1] C. Galindo, P. Jacques, A. Dalt, *Chemosphere* 45 (2001) 997.
- [2] J.M. Herrmann, M. Vautier, C. Guillard, *J. Catal.* 201 (2001) 46.
- [3] P.B. Dejohn, R.A. Hutchins, *Tex. Chem. Color.* 8 (1976) 69.
- [4] S.S. Patil, V.M. Shinde, *Environ. Sci. Technol.* 22 (1988) 1160.
- [5] A.T. More, A. Vira, S. Fogel, *Environ. Sci. Technol.* 23 (1989) 403.
- [6] Y.M. Slokar, A.M. Le Marechal, *Dyes Pigments* 37 (1998) 335.
- [7] U. Pagga, K. Taeger, *Water Res.* 28 (1994) 1051.
- [8] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.
- [9] B. Neppolian, S. Sakthivel, M. Palanichamy, B. Arabindoo, V. Murugesan, *Stud. Surf. Sci. Catal.* 113 (1998) 329.
- [10] J.M. Herrmann, in: F. Jansen, R.A. van Santen (Eds.), *Environmental Catalysis, Catalytic Science Series*, vol. 1, Imperial College Press, London, 1999, pp. 171–194 (Chapter 9).
- [11] M. Schiavello (Ed.), *Photocatalysis and Environment: Trends and Applications*, Kluwer Academic Publishers, Dordrecht, 1988.
- [12] N. Serpone, E. Pelizzetti (Eds.), *Photocatalysis, Fundamentals and Applications*, Wiley/Interscience, New York, 1989.
- [13] A. Fujishima, T.N. Rao, D.A. Tryk, *J. Photochem. Photobiol. C: Photochem. Rev.* 1 (2000) 1.
- [14] H. Yoneyama, S. Haga, S. Yamanaka, *J. Phys. Chem.* 93 (1989) 4833.
- [15] A. Mills, J. Wang, *J. Photochem. Photobiol. A: Chem.* 127 (1999) 123.
- [16] R.W. Matthews, *J. Catal.* 113 (1988) 549.
- [17] M. Trillas, J. Peral, X. Domenech, *Appl. Catal. B: Environ.* 3 (1993) 45.
- [18] H. Kochkar, F. Figueras, *J. Catal.* 171 (1997) 420.
- [19] H. Kim, S.W. Keller, T.E. Mallouk, *Chem. Mater.* 9 (1997) 1414.
- [20] Z. Mengyue, C. Shifu, T. Yaowu, *J. Chem. Technol. Biotechnol.* 64 (1995) 339.
- [21] S. Senthilkumar, K. Porkodi, R. Vidyalakshmi, *J. Photochem. Photobiol. A: Chem.* 170 (2005) 225.
- [22] B. Neppolian, S. Sakthivel, M. Palanichamy, B. Arabindoo, V. Murugesan, *J. Hazard. Mater. B* 89 (2002) 203.
- [23] T. Sauer, G. Cesconeto Neto, H.J. Jose, R.F.P.M. Mareira, *J. Photochem. Photobiol. A: Chem.* 149 (2002) 147.
- [24] E. Pelizzetti, V. Carlin, C. Minero, M. Gratzel, *N. J. Chem.* 15 (1991) 351.
- [25] C. Minero, E. Pelizzetti, S. Malato, J. Blanco, *Chemosphere* 26 (1993) 2103.
- [26] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, *Chemosphere* 46 (2002) 1173.
- [27] Y. Yang, Q. Wu, Y. Guo, C. Hu, E. Wang, *J. Mol. Catal. A: Chem.* 225 (2005) 203.
- [28] M. Abdullah, G.K.C. Low, R.W. Matthews, *J. Phys. Chem.* 94 (1990) 6820.
- [29] X.P. Lin, F.Q. Huang, W.D. Wang, K.L. Zhang, *Appl. Catal. A: Gen.* 307 (2006) 257.
- [30] V. Nadtochenko, J. Kiwi, *Inorg. Chem.* 37 (1998) 5233.
- [31] T. Ohno, M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui, M. Matsumura, *Appl. Catal. A: Gen.* 265 (2004) 115.
- [32] P. Mohapatra, K.M. Parida, *J. Mol. Catal. A: Chem.* 258 (2006) 118.
- [33] Y.M. Wang, S.W. Liu, Z. Xiu, X.B. Jiao, X.P. Cui, J. Pan, *Mater. Lett.* 60 (2006) 974.