Sunlight induced removal of Rhodamine B from water through Semiconductor Photocatalysis: Effects of Adsorption, Reaction Conditions and Additives

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Abstract

Application of Advanced Oxidation Processes (AOP) for the removal of toxic pollutants from water has been receiving increasing attention in recent times. Photocatalysis using semiconductor oxides is one such AOP which is being investigated extensively for the degradation of dyes in effluent water. This paper reports our findings on the sunlight induced photocatalytic removal of the hazardous xanthene dye Rhodamine B from water, mediated by TiO_2 and 'platinum deposited TiO_2' (Pt/TiO_2).Unlike in the case of photocatalytic degradation of many organic pollutants which are driven by UV light, Rhodamine B can be removed in presence of TiO_2 even by visible light. Pt/TiO_2 is ~5 times more active than TiO_2 alone for the solar photocatalytic degradation of the dye, which is attributed to extension of the absorption of light to the visible range and retardation of the recombination of photogenerated electrons and holes. The dye itself can absorb visible light and act as a photo sensitizer to activate TiO_2. The effects of various parameters such as catalyst loading, concentration of the dye, pH, Pt concentration in Pt/TiO_2, externallyadded H_2O_2 etc on the adsorption and /or degradation of the dye are evaluated. The degradation of the dye proceeds through intermediates and complete removal of Total Organic Carbon (TOC) is achieved many hours after the decolorisation of the dye. The rate of degradation decreases beyond a critical concentration of the dye, possibly due to reduction in the path length of photons in deeply colored solution. The higher degradation in alkaline pH is explained in terms of the ionization state of the catalyst surface and the enhanced adsorption facilitated by the electrostatic attraction between the negatively charged catalyst surface and the zwitter ionic form of the dye. H_2O_2, upto a critical concentration, accelerates the degradation. The observations are critically analysed and suitable mechanism for the photocatalytic mineralisation of RhB is proposed.

Keywords: Photocatalysis, platinum, titanium dioxide, Rhodamine B, hydrogen peroxide, sunlight.

Introduction

Semiconductor mediated photocatalysis is fast becoming an efficient Advanced Oxidation Process (AOP) for the removal of chemical and bacterial pollutants from water[1-6]. Generally, photocatalysis by semiconductors is the result of the interaction of photogenerated electrons and holes with the substrate. These electrons and holes can participate in reductive and oxidative reactions that lead to the decomposition of pollutants. The most widely studied catalyst in this respect is TiO_2 in view of its favorable physicochemical properties, low cost, easy availability, high stability and low toxicity. However, TiO_2 has a wide band gap (Anatase, E_{bg} = ca. 3.2 eV, rutile, E_{bg} = ca.3.0 eV) and can absorb light only below 400 nm, which is in the UV range that constitutes less than 5% of sunlight. In aqueous solution, the reactive OH radicals generated on the catalyst surface can promote the oxidation and eventual mineralization of organic compounds.

A number of studies have been reported on the modification of semiconductor oxides in order to extend the absorption of light to the visible range. These include dye sensitization, semiconductor coupling, impurity doping, use of coordination metal complexes andmetal deposition[7-13]. Composites such as TiO_2/carbon have also been reported[14]. Physical modification of TiO_2 with small amounts of transition metal cations such as V^+ and Cr^+ etc can extend the absorption upto 550 nm, making it efficient under UV as well as sunlight[15]. Deposition of noble metals such as Pt, Pd, Au, Ag etc on TiO_2enhances the catalytic oxidation of organic pollutants[16-20]. The enhancement is attributed to the increased light absorption and retarding of the photogenerated electron-hole recombination.

Water contaminated with dyes is a major threat to the environment. Even very low concentration of dyes in the effluents is highly visible and undesirable. It reduces the light penetration resulting in inhibition of photosynthesis and ultimate destruction of organisms living in water bodies. In the present paper the possibility of using TiO_2 and Pt deposited TiO_2 for the photocatalytic removal of Rhodamine B, a highly soluble basic dye of the xanthenes class is examined. The influence of various operational parameters such as concentration of the dye, pH, catalyst loading, added H_2O_2 etc. on the rate of removal of the dye is investigated and optimum reaction parameters are identified.

It is reported that nano particles of noble metals such as Au, Ag and Pt are capable of absorbing visible light due to the Surface Plasmon Resonance (SPR) in which their conducting electrons undergo a collective oscillation induced by the electric field of visible light[16,21,22]. Ag and Au nanoparticles supported on insulators such as ZrO_2 and SiO_2 yield visible light active photocatalysts capable of promoting both oxidative and reductive reactions[23,24]. Zheng etal[16] has recently reported a facile insitu synthesis of visible light plasmonic photocatalysts M@TiO_2 (M= Au, Pt, Ag) and their evaluation for the oxidation of benzene to phenol in aqueous system. Other efficient and stable plasmonic catalysts such as Ag/AgCland Ag/AgBr/WO_3.H_2O are also reported[25,26]. In the case of such catalysts, visible light is absorbed by nanoparticles of the noble metal and the photogenerated electrons and holes are separated by the metal-semiconductor interface. Thus the electron-hole recombination is prevented and the photocatalytic process is accelerated. In the case of Au/TiO_2 plasmonic photocatalysts, the mechanism of visible-light induced photocatalytic oxidation involves the absorption of light by Au nanoparticles which causes electron transfer from them to the conduction band of TiO_2. Consequently, the oxidation of the organics will take place at the electron deficient Au nanoparticles[16].

In the present study the comparative photocatalytic activity of TiO_2 and Pt/$TiO_2$is evaluated for the removal of a typical pollutant dye,ie Rhodamine B, from water.

Material and Methods

Degussa P-25 TiO_2 (99% pure) consisting of approx. 70% anatase and 30% rutile is used as such without further purification. The average particle size was around 15-20 μmand the BET surface area was ~15 m^2/g. Analytical grade chloroplatininc acid (H_2PtCl_6.6H_2O) and Rhodamine B {RhB, C.I. Basic violet, C.I number 45170, chemical class: xanthenes, molecular formula $C_{28}H_{31}N_2O_3Cl$, molecular weight: 479.01g/mole, IUPAC name: N-[9-(ortho-carboxyphenyl)-6-(diethylamino)-3H-xanthen-3-ylidine]diethylammonium chloride} were from Sigma Aldrich India. The molecular structure of RhB is shown in figure 1.
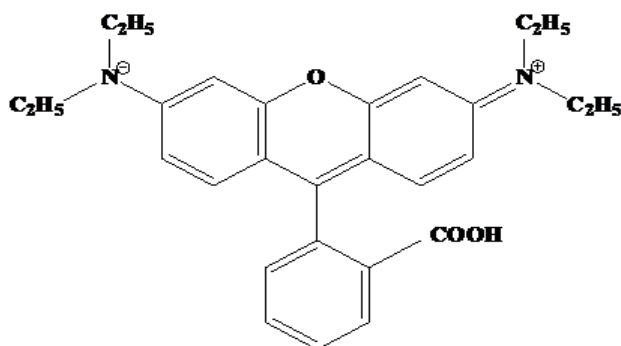

Figure-1
Structure of Rhodamine B

All other chemicals used were of AR grade. Doubly distilled water was used in all the experiments. The Pt/TiO_2 was prepared by standard techniques described earlier[18,27].

Aqueous suspension containing specific quantity of Degussa P-25 TiO_2 was taken in the photoreactor and purged with nitrogen to remove dissolved oxygen. Specified amounts of H_2PtCl_6.6H_2O dissolved in 20 ml methanol was then added to the aqueous suspension of TiO_2 and agitated with a magnetic stirrer. The suspension under nitrogen atmosphere is then irradiated with 400 W UV lamp for 8 hr. The milky white suspension turns grayish with the deposition of Pt. The suspension is then filtered and the residue, after repeated washings with doubly distilled water, is dried and powdered.

X-ray diffraction measurement was made by using Rigaku X-ray diffractometer with CuKα radiation. Scanning Electron Microscopy (SEM) measurements were performed with JEOL Model JSM-6390 LV. Diffuse Reflectance Spectra (DRS) were recorded with Varian Cary 5000 using $BaSO_4$ as the reference.

Photocatalytic experiments in presence of UV were performed in a jacketed pyrex reactor. The dye solution was taken in the inner compartment and cooling water from a thermostat (27± 1^0C) was circulated through the outer jacket. UV irradiation was done using a 400 W medium pressure mercury vapor lamp. Solar experiments were performed by placing the same system on the roof top of our laboratory at Kochi, Kerala, India (9^0 57' 51" N, 76^0 16' 59" E) during sunny days in February-May 2012. Thesuspension was stirredfrequently to ensure uniform mixing. Samples were drawn periodically and analyzed for the dye concentration by Spectrophotometry (555nm). Suspension kept under identical conditions in the dark was used as the reference in each case to eliminate the contribution from adsorption towards the reduction in the dye concentration.

Results and Discussions

Surface characterization of the photocatalyst: The catalysts $TiO_2$and Pt/TiO_2 were characterized by XRD analysis, Scanning Electron Microscopy (SEM) and Diffuse Reflectance Spectra. Photo deposition of platinum on the TiO_2 surface was indicated bycolor change of the particles from white to grey. However XRD analysis of the Pt deposited catalyst showed characteristic peaks of TiO_2 only with no indication of the presence of Pt (figure 2).

Since the deposition of Pt is confirmed by the visual color change, absence of Pt characteristics in the XRD may be because its concentration in the TiO_2 matrix is below detectable level.

Scanning Electron Microscopy (SEM) of the sample with 0.5 weight % of Pt on TiO_2 (figure 3) shows that the particles are approximately spherical in nature.
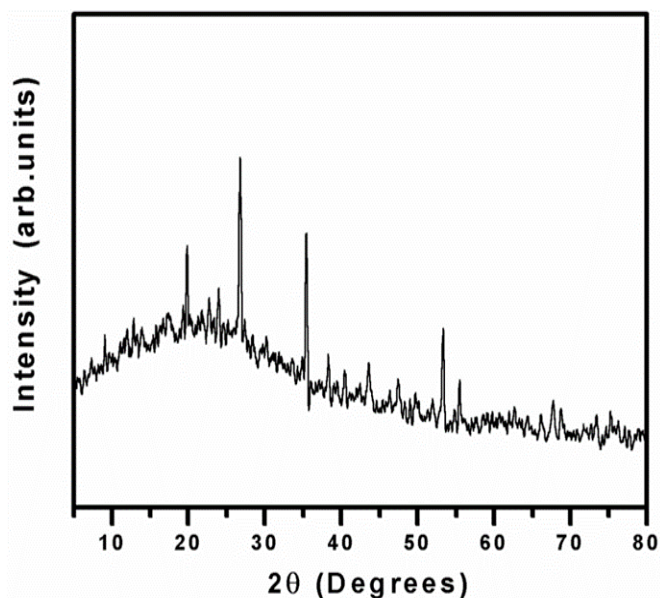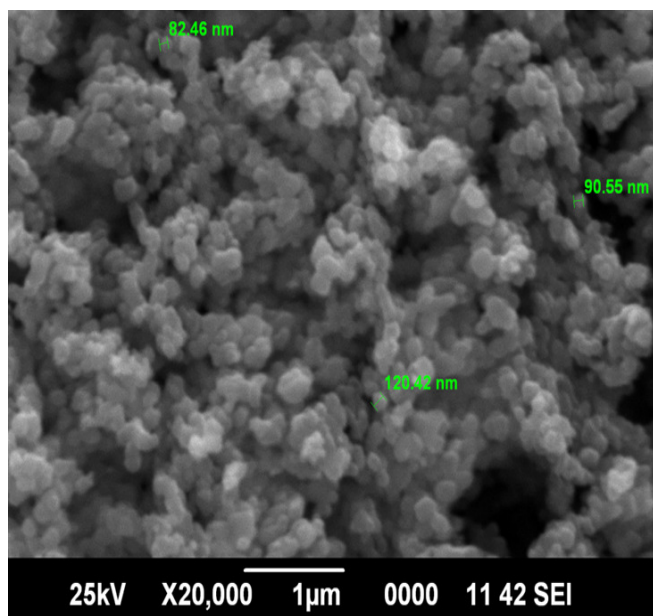
Figure-2
XRD pattern of Pt /TiO$_2$

Figure-3
SEM image of Pt (0.5%) deposited on TiO$_2$

Diffuse Reflectance spectrum (figure-4) shows that in the Pt-deposited TiO$_2$ optical absorption of the materialis enhanced significantly from 360 nm onwards.

This extension of absorption towards the visible region of the optical spectrum is consistent with the findings reported by earlier investigators[19,20]. This is further illustrated by the enhanced activity of the prepared catalyst for the degradation of the dye in visible light.
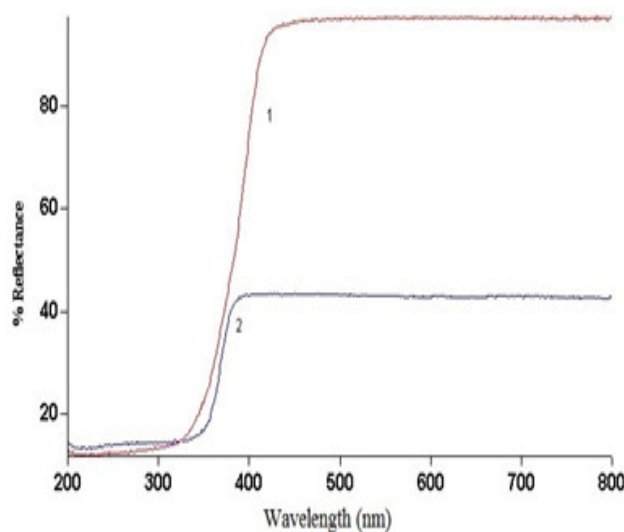

Figure-4
DRS spectra of (1) TiO$_2$ P-25 and (2) Pt- TiO$_2$

According to Li and Li[18] and Chen etal[19], deposition of Pt on TiO$_2$ results in the formation of Ti^{3+}, possibly due to the interaction between Pt and TiO$_2$ during photo reduction. The presence of Ti^{3+} sites in the lattice may form a defect energy level in the band gap of TiO$_2$ thereby absorbing visible light more efficiently and resulting in enhanced photocatalytic activity. The dispersion of Pt nanoparticles in the TiO$_2$ matrix can also produce some energy levels in the band gap of the latter[18]. Sakthivel etal[17] also concluded from similar studies that defect sites on the TiO$_2$ surface, identified as Ti^{3+} are necessary for adsorption and photoactivation of oxygen which are the primary steps in photocatalysis. In the present case, the deposition of Pt was made in the absence of air. Hence the insitu transformation of Ti^{3+} to Ti^{4+} by oxygen can be ruled out. However, in presence of the platinum salt, the photogenerated Ti^{3+} ions reduce the noble metal cations to neutral Pt atoms. These atoms can nucleate to grow into clusters, eventually forming nanoparticles of Pt on the TiO$_2$ surface. The Surface Plasmon Resonance (SPR) in Pt/TiO$_2$ under visible light irradiation enables the transfer of photogenerated electrons from the metal particles to TiO$_2$ conduction band by crossing the metal-semiconductor interface and surmounting the Schottky barrier[21]. This will reduce the recombination of the photogenerated electron-hole pair. The electronsare taken up by adsorbed oxygen forming reactive oxygen species which interact with the organic substrate, leading to eventual mineralisation. Presence of an organic substrate such as RhB in the present case compensates the depleted electron and the SPR is fully restored, thereby ensuring continued efficient photocatalytic activity.

Photocatalytic Degradation of Rhodamine B on TiO$_2$ and Pt/TiO$_2$: Photocatalytic degradation of Rhodamine B is evaluated using TiO$_2$ and Pt/TiO$_2$ insuspensions. Slow photodegradation of the dye takes place even in the absence of

catalyst. This may be due to the natural self-fading of the dye. The degradationis investigated in both UV light as well as in sunlight (SL). The pH of the system is maintained at 5.5 which is close to the natural pH of the dye solution under the reaction conditions used in the study. The results are plotted in figure 5.
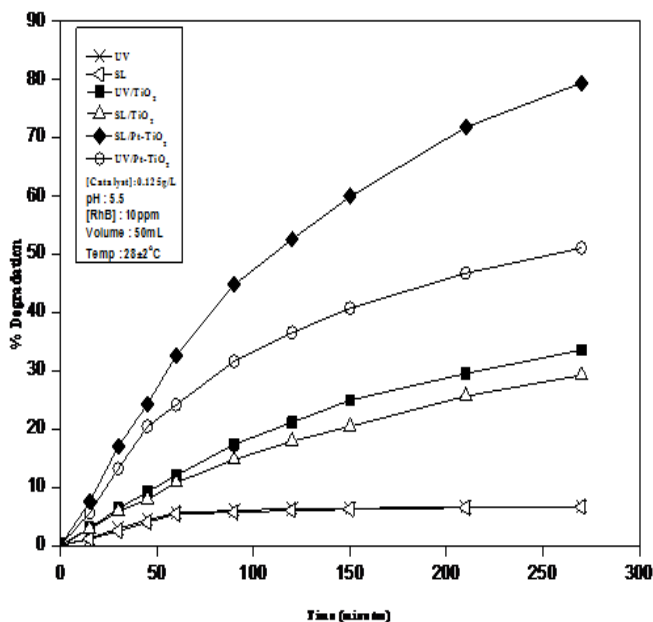

Figure-5
Degradation of Rhodamine B in UV and sunlight in presence of TiO_2 and Pt/TiO_2

As expected, Pt/TiO_2 is more active in the visible sunlight. In the UV region also, it is more active compared to TiO_2. Approximately 80% decolorisation of the dye is achieved in 4 hr time in presence of Pt/TiO_2 catalyst in sunlight.

The degradation in presence of $SL/Pt/TiO_2$ is about 60% more compared to UV/TiO_2. However $SL/Pt/TiO_2$ is approximately 2.5 times moreactive than Sunlight/TiO_2. The comparative enhancement in this case increases as the irradiation progresses. This is due to the inability of pure TiO_2 to get activated significantly in sunlight while Pt/TiO_2continues toabsorb visible light resulting in the formation of electron-hole pairs and subsequent activation of adsorbed oxygen. The comparative advantage of Pt/TiO_2 is not that significant in UV irradiation because TiO_2 itself is very active in this region. The photogenerated superoxide/hydroperoxide (O_2^-/$HO_2^·$) radicals initiate degradation of the dye. Repeated attacks by the O_2^- / $HO_2^·$ radicals on the pollutant nuclei can lead to the mineralization producing mainly CO_2 and water.

The effect of catalyst loading on the photocatalytic degradation of the dye is tested using pure TiO_2 and Pt/TiO_2 keeping all other reaction parameters constant (figure-6). The optimum loading is 0.100 and 0.125 g/L in the case of TiO_2 and Pt/TiO_2 respectively.
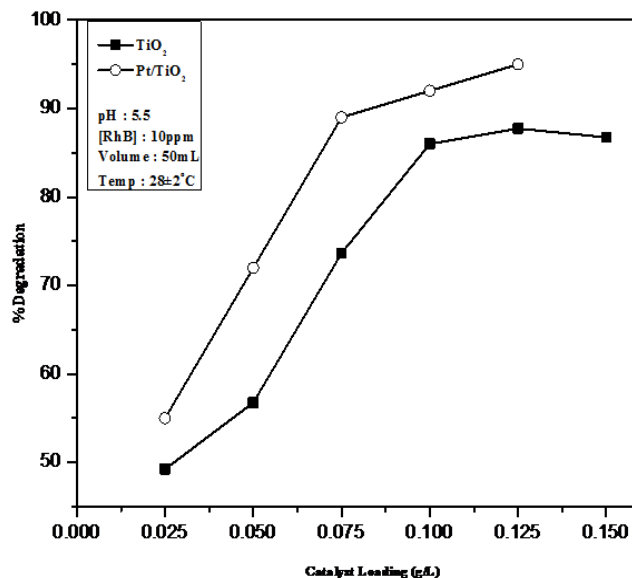

Figure-6
Effect of catalyst loading on the photod egradation of Rhodamine B

The effect of concentration of Pt in Pt/TiO_2 on the rate of degradation of the dye is tested by varying the loading of the former in TiO_2 from 0.2 to 1.0%. The initial rate constant of degradation in sunlight at various Pt concentrations is plotted in Figure 7. The rate increases with Pt loading initially. However, it levels off or even decreases slightly beyond the optimum level of 0.6%.
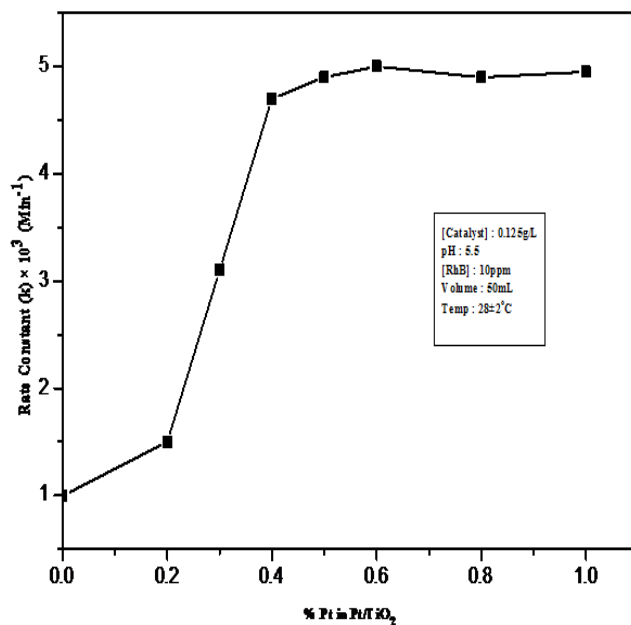

Figure-7
Effect of Pt concentration in Pt/TiO_2 on the photocatablytic degradation of Rhodamine B

All further studies were made using 0.1 g/L of TiO_2or 0.125 g/L of Pt (0.6%)-TiO_2unless mentioned otherwise. The detrimental effect of higher content of Pt in the Pt-semiconductor oxide catalyst on photocatalytic degradation has been reported earlier also[19]. During irradiation, photogenerated electrons are transferred from Pt metal to the TiO_2 conduction band. The metal-semiconductor interface separate the electron-hole pairs which prevents their recombination. However, at higher concentrations of Pt, the average distance of separation between the electrons and holes decreases and the Pt clusters themselves can act as recombination centers. Choi etal[28] also observed that there is an optimal metal dopant concentration above which the photocatalytic activity decreases.

Studies on the effect of concentration of Rhodamine in the range of 3-40 mg/L on the rate of photocatalytic degradation in presence of TiO_2 as well as Pt/TiO_2 in sunlight showed that the degradation remains steady or decreases with increasing initial concentration.. The results are plotted in figure 8.
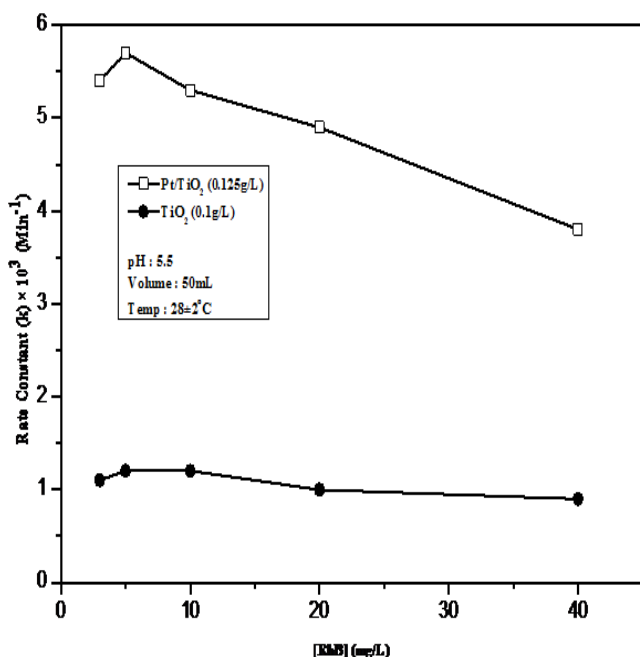

Figure-8'
Effect of initial concentration of Rhodamine B on its photocatalytic degradation

Since the degradation is accelerated by both catalyst and light, the negative effect of increasing concentration implies that at higher concentration, the dye is inhibiting the action of catalyst and/or light. At higher concentration there will be better adsorption of the dye on the surface of the catalyst. This will inhibit the direct absorption of light by the catalyst thereby affecting its ability to generate free radicals and reactive oxygen species. In the absence of continued significant degradation, the adsorbed dye will not leave the surface sites. This prevents the

adsorption of new molecules and continued degradation. Thus it is clear that light absorption and number of adsorption sites are the two factors affected by higher concentration of the dye. It is also known that the dye itself will be absorbing more solar light at higher concentration. The path length of light entering the system also decreases with increase in concentration[29].

The pH is an important factor in the case of wastewater and hence its effect on the photocatalytic degradation of the dye is investigated. The degradation increases with increase inpH, the rate of increase being more in the alkaline range. The results are shown in figure 9.
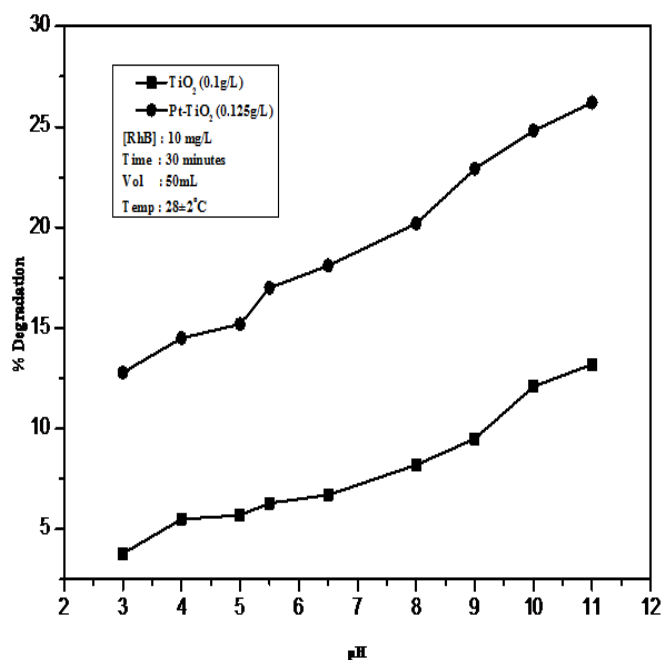

Figure-9
Effect of pH on the photocatalytic degradation of Rhodamine B

The variation is not due to any change in the absorption of light as the λ_{mx} for the dye changes very little (551-553 nm) in the pH range of 1-13 even though rhodamine exists in two principal forms in water, ie cationic (RhB^+) or zwitter ionic ($RhB^\pm$)[29]. At pH value less than the Point of Zero Charge (PZC) of TiO_2 (6.5), the surface will be positively charged. The effect of pH on the ionization state of the TiO_2surface is as follows:

$$TiOH + H^+ \rightarrow TiOH_2^+ \qquad (1)$$
$$TiOH + OH^- \rightarrow TiO^- + H_2O \qquad (2)$$
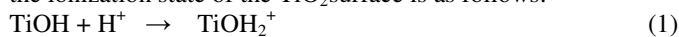
In the acidic range the dye will be in cationic form (RhB^+). Hence due to electrostatic repulsive forces, the adsorption of the dye on the catalyst is less. Thus the surface promoted degradation is less and the observed degradation is primarily taking place in the solution. At higher pH value, the RhB^+ gets deprotonated and its zwitter ion is formed (figure 10).
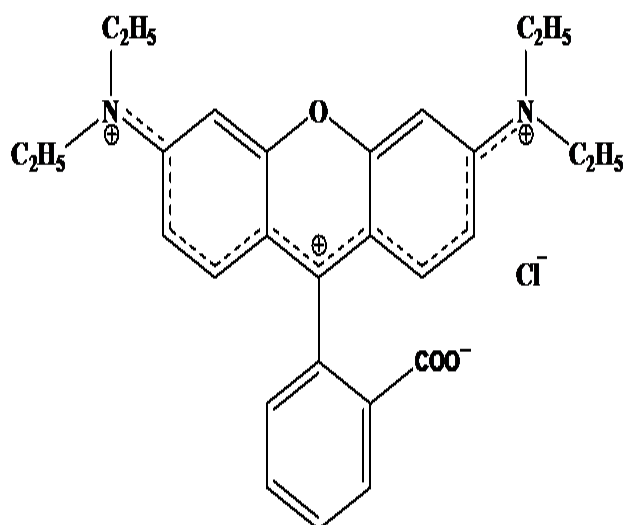
Figure-10
Zwitterion Structure of Rhodamine B

This can get adsorbed onto the negatively charged catalyst surface resulting in increaseddegradation of the dye. Further, under alkaline conditions, more OH radical formation is possible from the abundant hydroxide ions, which also enhances the degradation[29].

Adsorption vs Degradation: Since RhB is known to get adsorbed onto various solid surfaces, the comparative adsorption on some of the commonly used catalysts/adsorbents is measured and is shown in figue-11.
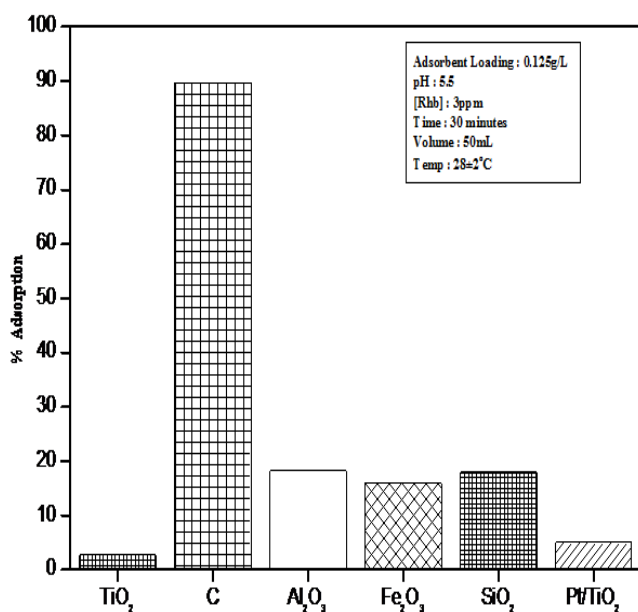

Figure-11
Adsorption of Rhodamine B on various surfaces

Activated carbon is a good adsorbent. But it does not degrade the dye. The adsorption is less on both TiO_2(3%) and Pt/TiO_2 (3.5%). However, both these can act as good photocatalysts for the removal of the dye in sunlight. Thus it is clear that the photocatalytic color removal is not due to simple adsorption. It happens by the degradation of the adsorbed molecule followed byliberation of the catalyst site, further adsorption of new dye molecules and reaction. Effective photocatalytic degradation is necessary to ensure continued adsorption of fresh molecules and their degradation. The more the degradation, the better will be the adsorption of new molecules. However, the net adsorption capability at any point of time is more or less the same.

Further, the color removal does not guarantee that the RhB is completely mineralized. As seen in figure 5 almost 80% of RhB is disappearing in two hr time. No other product detectable by UV-Vis spectroscopy is left in the reaction mixture. However, the TOC remained substantially higher after the first one hr showing that RhB is not fully mineralized and it is transformed to other organic compounds. In order to confirm the complete elimination of the pollutant the TOC concentration was determined. The results are plotted in figure-12.
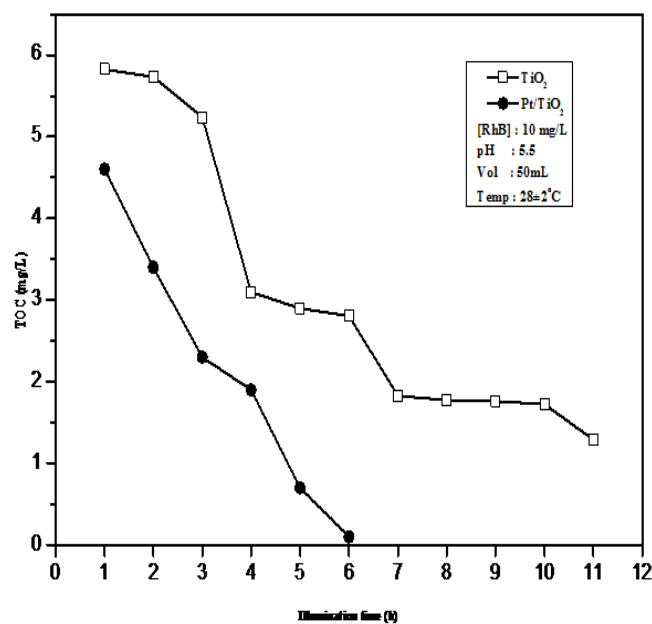

Figure-12
Decrease in TOC during the photocatalytic degradation of Rhodamine in presence of TiO_2 & Pt/TiO_2

As can be seen, the TOC remains high even when the dye is fully decolorized. In the case of Pt/TiO_2, the TOC is 3.4 mg/L after 2 hr. Continuation of the irradiation reduces the TOC and eventually brings it close to zero after about 11 hrand 6 hr in the case of TiO_2 and Pt/TiO_2 respectively. NMR studies of the products of photoelectrocatalytic degradation of RhB by Li etal[30] showed the presence of intermediates formed by deethylation and chromogen destruction.However, these

intermediates also get eventually mineralized resulting in CO_2 and H_2O.

Effect of added H_2O_2: One of the products of photocatalytic degradation of organic pollutants in water is H_2O_2 which itself can act as a source of active free radicals. In order to investigate the effect of H_2O_2, the photocatalytic degradation of RhB (10ppm) was performed with initially added H_2O_2 (3ppm). The results are shown in figure 13.
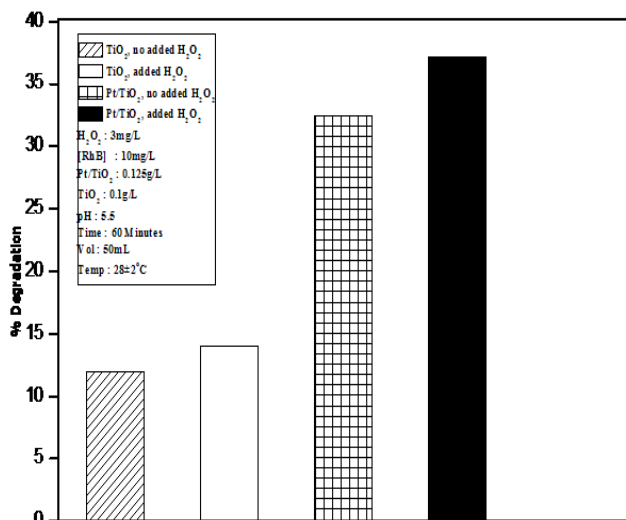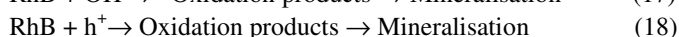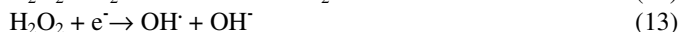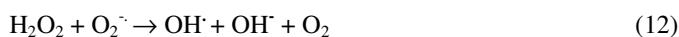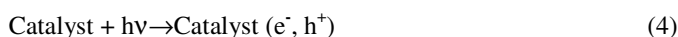

Figure-13
Effect of initially added H_2O_2 on the photocatalytic degradation of [RhB] in presence of TiO_2 and Pt/TiO_2

Control experiments with only H_2O_2 or H_2O_2 and catalyst, with no irradiation showed very little change in concentration of RhB. Irradiation after addition of H_2O_2 in the absence of the catalyst also showed very little degradation. Addition of H_2O_2 and irradiation by sunlight resulted in slight enhancement in the degradation of RhB in the case of TiO_2 as well as Pt/TiO_2.
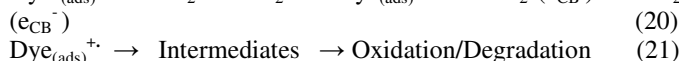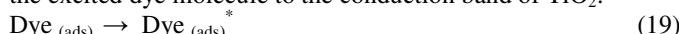
The enhancement is due to additional free radical generation[31]. However, the enhancement is not significantly highwhich may be due to ˙OH radical scavenging by H_2O_2 as follows:

$$H_2O_2 + \cdot OH \rightarrow \ H_2O + HO_2 \cdot \qquad (3)$$
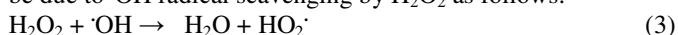
The overall mechanism of the photocatalytic degradation of RhB in presence of TiO_2 or Pt/TiO_2can be proposed as follows:

$$Catalyst + h\nu \rightarrow Catalyst\ (e^-, h^+) \qquad (4)$$
$$Catalyst\ (e^-, h^+) \rightarrow Catalyst \qquad (5)$$
$$O_2\ (ads) + e^- \rightarrow O_2^{\cdot-} \qquad (6)$$
$$H_2O \rightarrow OH^- + H^+ \qquad (7)$$
$$O_2^{\cdot-} + H^+ \rightarrow HO_2 \cdot \qquad (8)$$
$$2\ HO_2 \cdot \rightarrow H_2O_2 + O_2 \qquad (9)$$
$$HO_2 \cdot + e^- \rightarrow HO_2^{\cdot-} \qquad (10)$$
$$HO_2^{\cdot-} + H^+ \rightarrow H_2O_2 \qquad (11)$$

$$H_2O_2 + O_2^{\cdot-} \rightarrow OH^{\cdot} + OH^- + O_2 \qquad (12)$$
$$H_2O_2 + e^- \rightarrow OH^{\cdot} + OH^- \qquad (13)$$
$$H_2O_2 + 2\ h^+ \rightarrow O_2 + 2H^+ \qquad (14)$$
$$OH^- + h^+ \rightarrow OH^{\cdot} \qquad (15)$$
$$H_2O + h^+ \rightarrow H^+ + OH^{\cdot} \qquad (16)$$
$$RhB + OH^{\cdot} \rightarrow \ Oxidation\ products \rightarrow Mineralisation \qquad (17)$$
$$RhB + h^+ \rightarrow Oxidation\ products \rightarrow Mineralisation \qquad (18)$$

In the case of pure TiO_2 also, the degradation of the dye is significant in sunlight unlike in the case of substrates like phenol, alcohol, cresol etc where the degradation is much slower[32]. This may be because Rhodamine B can absorb visible light and act as a sensitizer thereby transferring electrons from the excited dye molecule to the conduction band of TiO_2.

$$Dye_{(ads)} \rightarrow \ Dye_{(ads)}^{*} \qquad (19)$$
$$Dye_{(ads)}^{*} + \ TiO_2/Pt\text{-}TiO_2 \rightarrow \ Dye_{(ads)}^{+\cdot} + \ TiO_2\ (e_{CB}^-)/Pt\text{-}TiO_2\ (e_{CB}^-) \qquad (20)$$
$$Dye_{(ads)}^{+\cdot} \rightarrow \ Intermediates \ \rightarrow Oxidation/Degradation \qquad (21)$$

The electrons are scavenged by the oxygen adsorbed on the surface of TiO_2 as in (6) above. The dye behaves like an electron donor at the excited state and injects electrons directly to the conduction band upon irradiation. Anandan etal[33] also suggested similar pathway for the degradation of dyes on Ag/TiO_2 catalysts.

The extent of degradation effected by dye sensitized TiO_2 is much less compared to that by Pt/TiO_2. Deposition of Pt enhances the photocatalytic activity in two ways, ie by the prevention of electron hole recombination and the extension of the light absorption range. Pt particles in the TiO_2 matrix produce extra defect energy levels in the band gap of TiO_2.This will reduce the effective band gap thus making visible light adequate to promote electrons from the defect energy level to CB[19]. Modification of the surface of TiO_2 by Pt can also result in enhancement of the number of active sites for the dye-catalyst interaction which in turn can increase the photodegradation rate. On the other hand, dye sensitization leads to only visible light absorption which is highly concentration dependent. At lower concentration, when there is only monolayer coverage of the dye, light absorption may not be adequate to acquire sufficient energy to be transferred to the semiconductor. At the same time multilayer adsorption of the dye does not enhance the light absorption or photocatalytic efficiency significantly because the inner layers will tend to act as insulators with respect to outer layers[4].

Conclusion

$TiO_2$and Pt deposited $TiO_2$are good photocatalysts capable of mineralizing the dye Rhodamine B in presence of UV as well as direct sunlight. Pt incorporated in the TiO_2 matrix extends the light absorption of TiO_2 from UV to the visible range which makes the composite a good photocatalyst for solar decontamination of polluted water. Pt/TiO_2 is more effective than TiO_2 alone for the removal of the pollutant. Higher pH

favours the removal of Rhodamine B while increasein concentration of the dye decreases the rate of removal. There is an optimum for the catalyst loading as well as concentration of Pt beyond which the rate of degradationstabilizes or decreases. H_2O_2 enhances the degradation slightly. Simple decolorisation of the dye solution does not result in mineralisation as seen by the measurement of TOC which takes longer time to disappear. The degradation is proceeding through many stable intermediates which also get degraded further and mineralized, though slowly. A tentative mechanism for the photocatalytic degradation of the dye is proposed and discussed.

Acknowledgement

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