

Research Article

Solar Photocatalytic Removal of Chemical and Bacterial Pollutants from Water Using Pt/TiO₂-Coated Ceramic Tiles

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Semiconductor photocatalysis has become an increasingly promising technology in environmental wastewater treatment. The present work reports a simple technique for the preparation of platinum-deposited TiO₂ catalysts and its immobilization on ordinary ceramic tiles. The Pt/TiO₂ is characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDAX), and diffuse reflectance spectroscopy (DRS). Deposition of Pt on TiO₂ extends the optical absorption of the latter to the visible region which makes it attractive for solar energy application. Optimum loading of Pt on TiO₂ was found to be 0.5%. The Pt/TiO₂ is coated on ceramic tiles and immobilized. This catalyst was found effective for the solar photocatalytic removal of chemical and bacterial pollutants from water. Once the parameters are optimized, the Pt/TiO₂/tile can find application in swimming pools, hospitals, water theme parks, and even industries for the decontamination of water.

1. Introduction

Semiconductor-mediated photocatalysis is fast becoming an efficient advanced oxidation process (AOP) for the removal of chemical and bacterial pollutants from water [1–5]. The most widely studied catalyst in this respect is TiO₂ in view of its favorable physicochemical properties, low cost, easy availability, high stability, and low toxicity. However, it is active only in the UV range which constitutes less than 5% of sunlight. Photocatalytic reactions take place when particles of the semiconductor absorb photon of energy equal to or greater than its band gap and the electrons get excited from the valence band to the conduction band. This results in the formation of an electron-hole pair which promotes oxidation/reduction of the adsorbed substrate. In aqueous solution, the reactive OH radicals 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, and metal deposition [6–18]. Composites such as TiO₂/carbon have also been

reported [19–21]. Deposition of noble metals such as Pt, Pd, Au, and Ag, on TiO₂ enhances the catalytic oxidation of organic pollutants [22–26].

Pt/TiO₂ nanocomposites have been shown to have high photocatalytic activity for the decomposition of organic compounds. In this case, the enhancement is attributed to the increased light absorption and retarding of the photogenerated electron-hole recombination [25–27]. However, since Pt is expensive, this type of catalysts will be unattractive from commercial application point of view unless they can be recycled. The problem can be overcome, at least partially by immobilizing the catalyst on suitable stable supports.

It is reported that nanoparticles 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 [28–30]. Ag and Au nanoparticles supported on insulators such as ZrO₂ and SiO₂ yield visible light active photocatalysts capable of promoting both oxidative and reductive reactions [31, 32]. Zheng et al. [28] have recently reported a facile in situ synthesis of visible light plasmonic photocatalysts M-TiO₂ (M = Au, Pt, Ag) and their evaluation for the oxidation of benzene to phenol in aqueous

phenol. Other efficient and stable plasmonic catalysts such as Ag/AgCl [33] and Ag/AgBr/WO₃·H₂O [34] are also reported. In 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/TiO₂ 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 TiO₂ particles. Consequently, the oxidation of the organics will take place at the electron-deficient Au nanoparticles [28].

In the present study, we have immobilized Pt/TiO₂ on a ceramic tile in order to enhance the commercial viability of the catalyst by recycling. The photocatalytic activity of this catalyst is tested for the removal of a typical chemical pollutant dye Rhodamine B and a bacterial pollutant *E. coli*.

2. Experimental

Degussa P-25 TiO₂ is used as such without further treatment. It is 99% pure and consisted of approximately 70% anatase and 30% rutile forms. The average particle size was around 200 nm, and the BET surface area was ~15 m²/g. Analytical grade chloroplatinic acid (H₂PtCl₆·6H₂O) and Rhodamine B were from Sigma-Aldrich, India. All other chemicals used were of AR grade. Doubly distilled water was used in all the experiments. The immobilized Pt/TiO₂ photocatalyst (Pt/TiO₂/tile) is prepared as follows [26].

Aqueous suspension containing specific quantity of Degussa P-25 TiO₂ was taken in the photoreactor and purged with nitrogen to remove dissolved oxygen. Specified amounts of H₂PtCl₆·6H₂O dissolved in 20 mL methanol were then added to the aqueous suspension of TiO₂ 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 after repeated washings with doubly distilled water, it is dried and powdered.

Common glazed tiles normally used for flooring are etched with dilute HF. The surface is then cleaned and coated uniformly with the paste of Pt/TiO₂ and polymethyl methacrylate in chloroform. The tile is then dried at 110°C and later heated at 350°C for 3 hr. A thin film of Pt/TiO₂ is formed on the surface of the tile. For control experiments, tiles were prepared exactly as above, one with TiO₂ only and another without any catalyst. The amount of catalyst coated was determined by measuring the weight difference of the tile before and after the coating.

X-ray diffraction pattern of the coated catalyst is determined by using Rigaku X-ray diffractometer with CuK α radiation. Scanning electron microscopy (SEM) measurements were performed with JEOL Model JSM-6390 LV. Energy dispersive X-ray spectroscopy (EDAX) measurements were made using JOEL model JED-2300 attached to SEM. Diffuse reflectance spectra (DRS) were recorded with Varian Cary 5000 using BaSO₄ as the reference.

Photocatalytic experiments with dye solution were performed as follows.

The coated tile (12 × 8 × 0.5 cm) is placed in a jacketed glass vessel of approximately 20 cm diameter and 3 cm height. The experimental dye solution of Rhodamine B (200 mL, 10 mg/L) is slowly added into the vessel. Water from a thermostat is circulated through the jacket to maintain the temperature at 27 ± 1°C. For UV experiments, the dye solution is irradiated with 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° 57' 51" N, 76° 16' 59" E) during sunny days in February–May 2010. Periodically, the dye solution is mixed gently. Samples were drawn periodically and analyzed for the dye concentration by spectrophotometry (555 nm). Solution kept under identical conditions in the dark is used as the reference in each case to eliminate the contribution from adsorption towards the reduction in the dye concentration.

For bacterial disinfection studies, *Escherichia coli* (ATCC 11775) was used as the test organism. Cells of *E. coli* were subcultured under sterile conditions at 37°C for 24 hr in 100 mL nutrient broth (pH ~ 7.2) containing 0.1 g of yeast extract, 0.5 g of peptone, and 0.5 g of NaCl. The cells were sedimented by centrifugation at 5000 rpm for 10 minutes, washed, and resuspended in sterile distilled water. Absorbance was measured using Shimadzu UV-1601 UV-VIS spectrophotometer. Cell cultures corresponding to ~10⁷ cells/mL were used to inoculate the reaction systems and controls. Control experiments run in parallel consisted of samples exposed to sunlight without catalyst and those in the dark with and without catalysts, all maintained under otherwise identical conditions. In catalytic experiments, the coated tiles were placed in aquarium jars containing 10 liters of the inoculated water. The jars were placed in a trough through which water at the required temperature is circulated and irradiated by sunlight. Sampling was done at predetermined intervals by pipetting out 1 mL of the experimental solution into 9 mL sterile saline which was serially diluted. After mixing, 0.1 mL aliquots of each dilution were spread onto McConkey agar plates. The cell inactivation was monitored by counting the colony forming units (CFU) after 24-hour incubation at 37°C.

3. Results and Discussions

3.1. Surface Characterization of the Photocatalyst. The photo deposition of Platinum on the TiO₂ surface was indicated by color change of the particles from white to grey. XRD analysis is done to study the phase structure of the catalyst. Figure 1 shows characteristic peaks of TiO₂ only with no indication of the presence of Pt. This may be because either Pt is not getting deposited on TiO₂ or the concentration of Pt in the TiO₂ matrix is too small to be detected by XRD. As the results presented later in this paper show, reflectance spectrum and enhanced photocatalytic activity of the prepared material reveal modification in the properties of TiO₂, which can be attributed to the presence of small amounts of highly dispersed Pt. Scanning electron microscopy (SEM) of

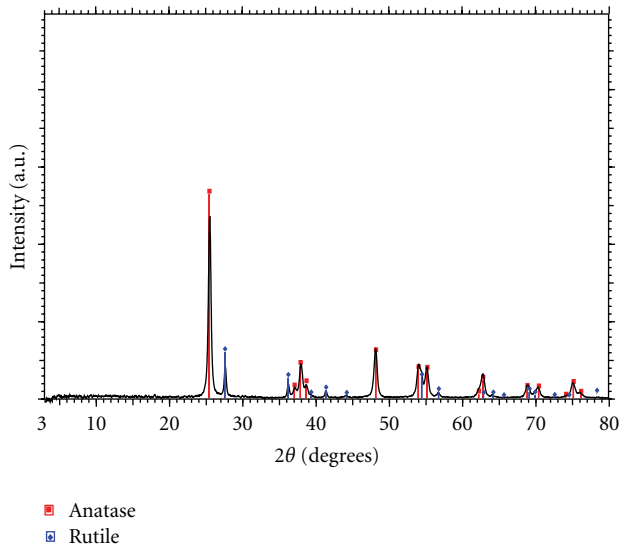


FIGURE 1: XRD pattern Pt/TiO₂ coated on the surface of the ceramic tile.

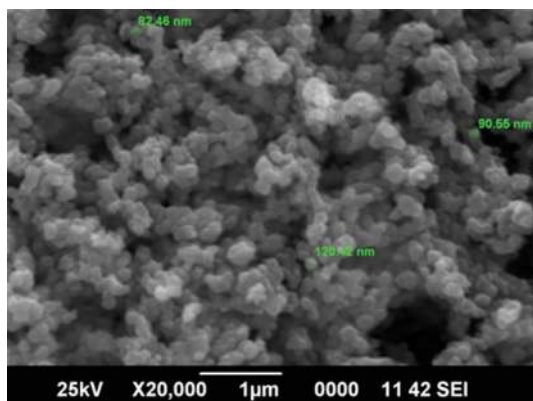


FIGURE 2: SEM of Pt (0.5 wt%)—deposited on TiO₂.

the sample with 0.5 weight % of Pt dispersed on TiO₂ (Figure 2) shows that the particles are approximately spherical in nature. Elemental mapping of Pt by EDAX (Figure 3) shows that the metal particles are uniformly distributed on the surface of TiO₂, even though the characteristic peaks are not quite distinct possibly due to the very low concentration of Pt.

The DRS spectrum of the Pt/TiO₂ sample shown in Figure 4 indicates that the optical absorption of TiO₂ is enhanced significantly from 360 nm onwards. This extension towards the visible region of the optical spectrum is consistent with the findings reported by earlier investigators [25, 26].

According to F. B. Li and X. Z. Li [25] and Chen et al. [26], deposition of Pt on TiO₂ results in the formation of Ti³⁺, possibly due to the interaction between Pt and TiO₂ during photo reduction. The presence of Ti³⁺ sites in the lattice may form a defect energy level in the band gap of TiO₂ thereby absorbing visible light more efficiently and resulting in enhanced photocatalytic activity. The dispersion of Pt

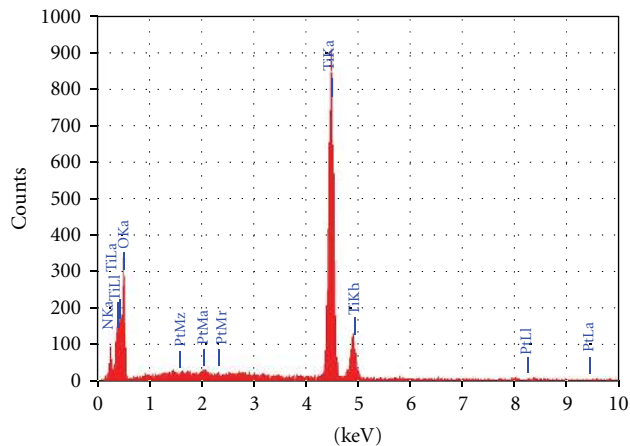


FIGURE 3: EDAX spectrum of Pt/TiO₂.

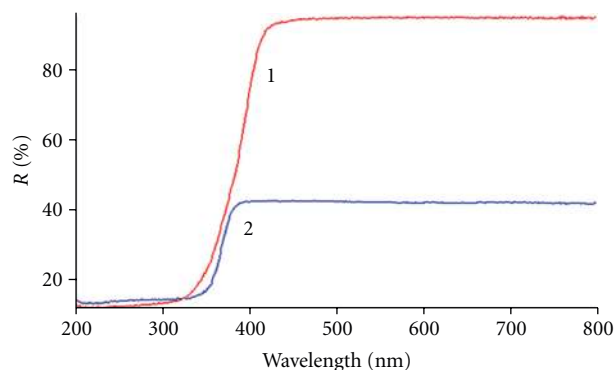


FIGURE 4: DRS spectra of (1) TiO₂ (P-25) and (2) Pt/TiO₂.

nanoparticles in the TiO₂ matrix can also produce some energy levels in the band gap of the latter [25]. Sakthivel et al. [23] also concluded from similar studies that defect sites on the TiO₂ surface, identified as Ti³⁺, 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 in situ transformation of Ti³⁺ to Ti⁴⁺ by oxygen can be ruled out. However, in presence of the platinum salt, the photogenerated Ti³⁺ 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 TiO₂ surface (Pt/TiO₂). The surface plasmon resonance in Pt/TiO₂ under visible light irradiation enables the transfer of photogenerated electrons from the metal particles to TiO₂ conduction band by crossing the metal-semiconductor interface and surmounting the Schottky barrier [28]. This will reduce the recombination of the electron-hole pair. The electrons are taken up by adsorbed oxygen forming active species which interact with the organic substrate, leading to eventual mineralisation. In the process, the substrate can compensate the depleted electron, and the SPR is fully restored, thereby ensuring continued efficient photocatalytic activity.

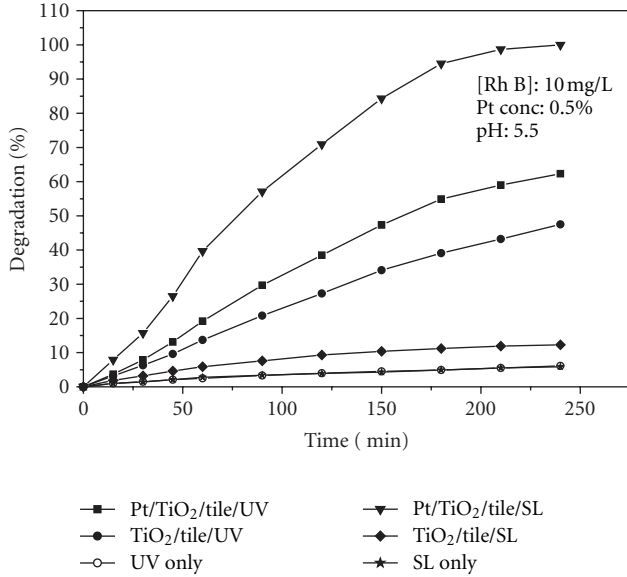


FIGURE 5: Photocatalytic degradation of Rhodamine B under various conditions in presence of UV and sunlight (SL).

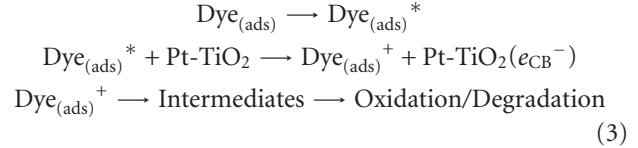
3.2. Photocatalytic Degradation of Rhodamine B on Pt/TiO₂-Coated Tiles. Photocatalytic degradation of the highly soluble basic red dye of the xanthenes class, Rhodamine B, is evaluated using TiO₂/tile and Pt/TiO₂/tile. Earlier studies reported on the degradation of the dye involved the use of catalyst suspensions, which are not quite convenient in terms of practical application. The advantage of the immobilized catalyst over suspension is that it needs not be separated from water every time and can be recycled. Degradation of the dye takes place even in the absence of catalyst, though slowly. The degradation is 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.

As expected, Pt/TiO₂ is more active in the visible sunlight as well as in the UV region compared to TiO₂. Degradation/decolorisation in the absence of catalysts may be due to the natural self-fading of the dye.

The percentage degradation of the dye in presence of Pt/TiO₂/tile is about 60% more compared to TiO₂/tile under UV irradiation. However, the degradation is approximately 5 times more in the case of Pt/TiO₂/tile compared to TiO₂/tile in presence of sunlight. The comparative enhancement in this case increases as the irradiation progresses, possibly due to the inability of pure TiO₂ to get activated significantly in sunlight. At the same time, Pt nanoparticles absorb visible light resulting in the formation of electron-hole pairs and subsequent activation of adsorbed oxygen as explained earlier. The superoxide/hydroperoxide (O₂^{-•}/HO₂[•]) radicals thus formed initiate degradation of the dye. Repeated attacks by the (O₂^{-•}/HO₂[•]) radicals on the dye nuclei will lead to mineralization producing mainly CO₂ and water.



In the case of pure TiO₂ also, the degradation of the dye is significant in sunlight unlike in the case of substrates like phenol, alcohol, cresol, and so forth where the degradation is much slower [35]. This might be because the dye Rhodamine B can absorb visible light and act as a sensitizer thereby transferring electrons from the excited dye molecule to the conduction band of TiO₂,



The electrons are scavenged by the oxygen adsorbed on the surface of TiO₂ as in (1) above. Thus, the dye behaves like an electron donor at the excited state and injects electron directly to the conduction band upon irradiation. Anandan et al. [36] also suggested similar pathway for the degradation of dyes on Ag/TiO₂ catalysts.

The study further shows that, in the presence of sunlight, the photocatalytic activity of dye sensitized TiO₂ is much less compared to Pt/TiO₂. Deposition of Pt enhances the photocatalytic activity of TiO₂ in two ways, that is, by the prevention of electron hole recombination and the extension of the light absorption range as discussed earlier. Modification of the surface of TiO₂ 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 of TiO₂ 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 [37].

The effect of concentration of Pt in Pt/TiO₂ on the rate of degradation of the dye is tested by varying the loading of the former in TiO₂, that is, 0.1, 0.25, 0.75, and 1.0%. The rate constant of degradation in sunlight at various Pt concentrations is plotted in Figure 6. The rate increases with Pt loading initially. However, it levels off or even decreases slightly beyond the optimum.

The detrimental effect of higher content of Pt in photocatalytic degradation was reported earlier also [25]. At lower concentration, Pt clusters can act as charge separation centres. As explained earlier, one of the reasons for the enhanced photocatalytic activity of Pt/TiO₂ is the separation of the photogenerated electrons and holes by the metal-semiconductor interface 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 et al. [38] also observed that there is an optimal metal

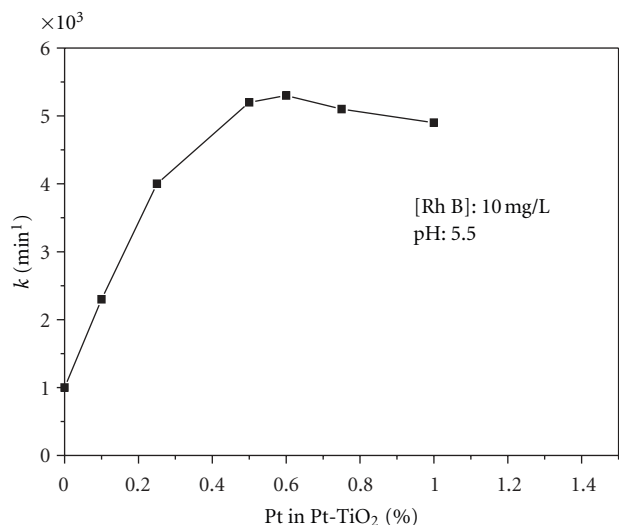


FIGURE 6: Effect of Pt concentration in Pt/TiO₂/Tile on the rate constant of Rhodamine B degradation under sunlight.

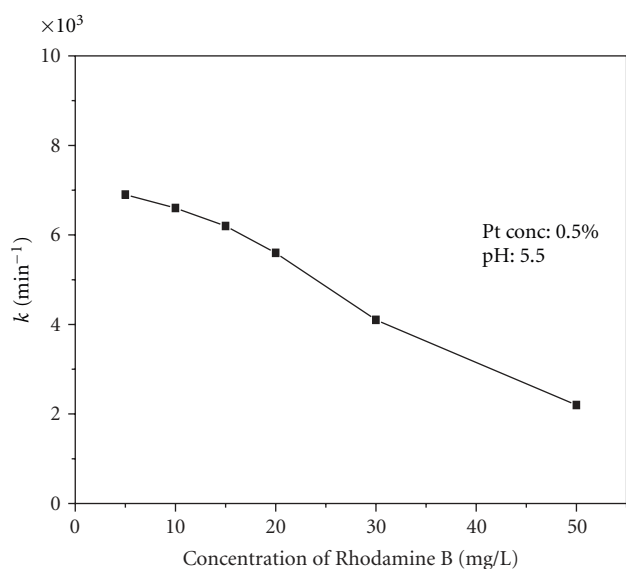


FIGURE 7: Effect of concentration of the Rhodamine B on its photocatalytic degradation in presence of Pt/TiO₂/Tile under sunlight.

dopant concentration above which the photocatalytic activity decreases.

Studies on the effect of concentration of the dye on the rate of photocatalytic degradation showed that the degradation decreased with increasing initial concentration. The results are plotted in Figure 7.

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 stronger adsorption of the dye on the surface of the catalyst. This will inhibit the direct absorption of light by Pt/TiO₂, thereby affecting its ability to generate active radicals. In the

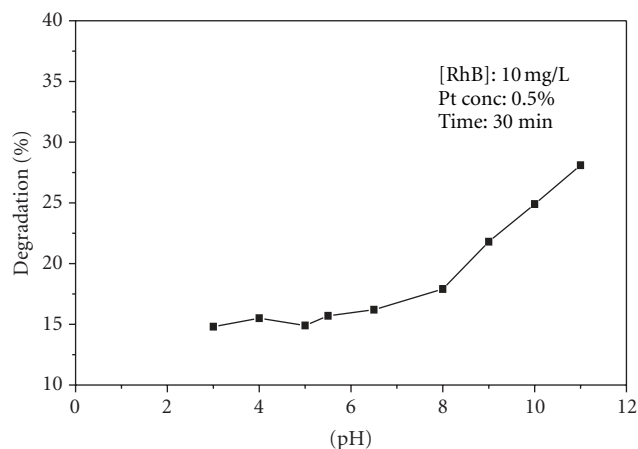


FIGURE 8: Effect of pH on the solar photocatalytic degradation of Rhodamine B in presence of Pt/TiO₂/Tile.

absence of significant continued degradation, the adsorbed dye will not leave the surface sites, thus preventing the adsorption of new molecules and consequent degradation. Thus, the 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 [39].

The pH is an important factor in the case of wastewater, and hence, its effect on the photocatalytic degradation of the dye in water is investigated. The degradation remains more or less the same in the range of 3–6.5 and increases thereafter. The results are shown in Figure 8.

The increased degradation at higher pH is not due to any change in the absorption of light as the λ_{max} for the dye changes very little (551–553 nm) in the pH range of 1–13 [40], even though Rhodamine exists in two principal forms in water, that is, cationic (RhB⁺) or in zwitterionic (RhB[±]). At pH value less than the point of zero charge (PZC) of TiO₂ (6.5), the surface will be positively charged. In the acidic range, the dye will be in cationic form (RhB⁺). Hence, in this range, 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 zwitterion is formed. This can get adsorbed onto the negatively charged catalyst surface resulting in increased degradation of the dye. Further, under alkaline conditions, more OH radical formation is possible from the abundant hydroxide ions, which also enhances the degradation.

3.3. Photocatalytic Disinfection of *E. coli* on Pt/TiO₂/Tile. Heterogeneous photocatalysis has been found to be an effective method for the deactivation of bacteria in water [41]. Conventional semiconductors such as ZnO and TiO₂ which are extensively investigated as photocatalysts can be activated only by UV light, which make them inefficient for solar

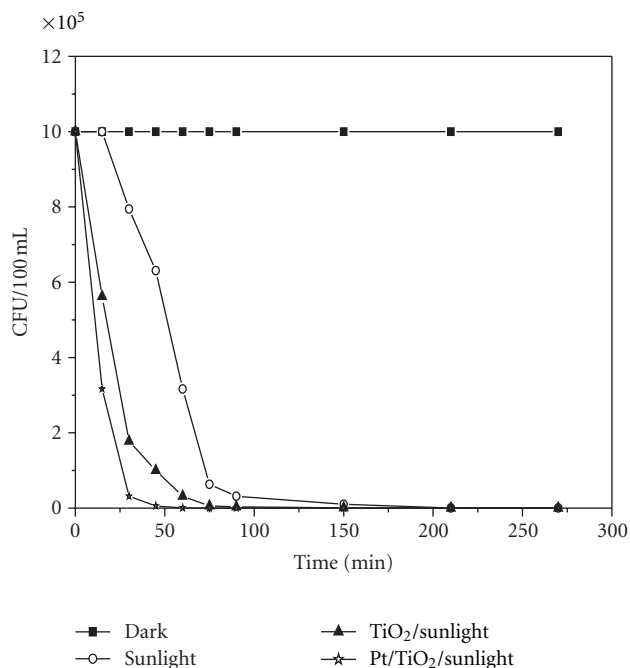


FIGURE 9: Solar deactivation of *E. coli* under different photocatalytic conditions.

energy application. Since Pt/TiO₂/tile is effective for the removal of chemical pollutants in sunlight, the same is tested for the removal of *E. coli* from water.

Results presented in Figure 9 show that the bacteria remain practically unaffected in the dark. However, in presence of sunlight, the population is reduced gradually even in the absence of the catalyst. In the case of Pt/TiO₂/tile, total inactivation takes place in 50 minutes, while it takes 90 minutes in the case of TiO₂/tile. In the absence of catalyst but in presence of light, there is an initial induction period during which the deactivation is negligible. This may be the reason why some of the earlier researchers [42] did not observe any inactivation of *E. coli* in the 60 minutes duration of their study. The deactivation is not due to temperature rise in presence of light as reported by Melian et al. [43] since in our case the temperature was maintained constant at $27 \pm 1^\circ\text{C}$ by circulating water from a thermostat. Since the visible light induced deactivation is more in the presence of Pt/TiO₂/tile compared to direct irradiation in the absence of any catalyst, it is clear that the catalyst plays a significant role in harnessing solar energy for bacterial decontamination. Comparative evaluation of the catalyst in immobilized form as well as in suspension showed that the suspension is more effective [44]. The number of surviving bacteria in the case of the Pt/TiO₂/tile and the suspended catalyst under identical conditions at different time intervals show that the suspension is more effective throughout for bacteria removal.

The pH of natural waters and wastewater will normally be in the range of 5–9. Hence, the effect of pH on the deactivation of *E. coli* mediated by Pt/TiO₂ in presence of sunlight is examined. It is observed that pH has no significant effect on the rate of deactivation in this pH range.

The reason often cited for the convenience of chemical decontamination over other techniques such as photocatalysis is that in the former, the destruction of microorganisms is complete, and hence, the reemergence is not significant. To compare the efficacy of chemical treatment with photocatalysis, the reemergence of *E. coli* in water treated with TiO₂/tile/light, Pt/TiO₂/tile/light, and light alone is examined. After complete inactivation of the bacteria, in experiments with and without catalyst, the reemergence was tested after 2, 24, and 48 hr. There was no bacterial presence detected in any of the systems after 2 hr. However, significant reemergence was noticed after 24 hr in the light alone system. The reemergence was much slower in the system with catalyst, the comparative rate of reemergence being in the order TiO₂/tile/light \gg Pt/TiO₂/tile/light. This indicates that the destruction in presence of the catalyst Pt/TiO₂ is almost as irreversible as in the case of chemical decontamination, while the sunlight alone may not be sufficient for complete destruction.

The mechanism of deactivation of *E. coli* is not known clearly yet. Free radicals have an adverse effect on cell DNA replication and the modification of cellular membrane. Cho et al. [45] demonstrated linear correlation between $\cdot\text{OH}$ concentration and *E. coli* inactivation. Direct photocatalytic oxidation of intracellular coenzyme is also proposed by some authors [42]. The H₂O₂ formed in the system also is a good bactericide [44, 46]. Higher concentration of OH and H₂O₂ in presence of catalyst will lead to higher irreversible destruction of the bacteria. Exposure to reactive oxygen species such as O₂^{-•} and $\cdot\text{OH}$ generated during photocatalysis can result in oxidative damage to cellular components, DNA and RNA [47–49]. The disruption of cell membrane is attributed to peroxidation of the unsaturated phospholipids leading to loss of respiratory activity [50, 51]. Subsequent loss of fluidity and increased ion permeability permit oxidative attack of internal cellular components resulting in cell death.

4. Conclusion

Deposition of noble metal Pt on TiO₂ extends the light absorption of the latter from UV to the visible range which makes the composite a good photocatalyst for solar decontamination of polluted water. In this study, Pt/TiO₂ is immobilized by coating on an ordinary ceramic tile, and its photocatalytic activity is tested for the removal of a chemical pollutant, Rhodamine B, and a bacterial pollutant, *E. coli*. Pt/TiO₂ is more effective than TiO₂ alone for the removal of both types of pollutants. The catalyst is characterized by XRD, DRS, SEM, and EDAX. Higher pH favours the removal of Rhodamine B, while increase in concentration of the dye decreases the rate of removal. There is an optimal concentration of Pt beyond which the rate of enhancement decreases. Suspension system is more efficient compared to the immobilized catalyst. However, problems associated with the separation of the catalyst make the latter more promising for field application. The bacterial contaminant *E. coli* can be removed by light even in the absence of the catalyst. However, the presence of catalyst accelerates the decontamination significantly. Also, the reemergence of the bacteria after

the light is off is inhibited to a great extent by the catalysts. A tentative mechanism for the chemical and bacterial decontamination is proposed and discussed.

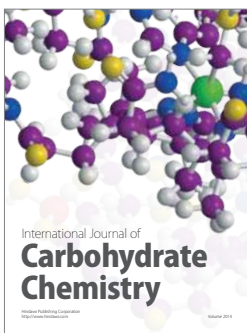
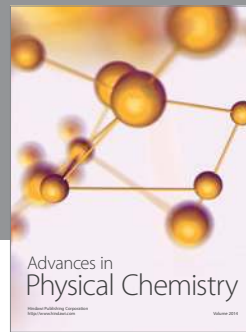
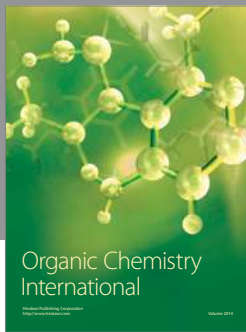
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