

Ag–TiO₂ doped photo catalytic degradation of Procion blue H-B dye in textile washwater

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The photocatalytic degradation of Procion blue H-B dye in biodegraded textile washwater has been investigated for the complete removal of color and maximum reduction of chemical oxygen demand (COD). *Pseudomonas putida* was utilized for obtaining biodegraded textile washwater. In this process, silver-doped TiO₂ photocatalyst was prepared and experiments were carried out to study the effects of UV and mercury lamp irradiations on COD reduction and removal of color. The thus prepared silver-doped TiO₂ catalyst was characterized by thermogravimetric and differential thermal analysis, UV-visible spectrometer, X-ray diffraction, scanning electron microscope, energy dispersive X-ray microanalysis, and BET surface area techniques. Adsorption studies were also carried out to evaluate the fitness of isotherm models. The results show that the silver-doped TiO₂ has enhanced the photodegradation of Procion blue H-B dye under UV and mercury lamp irradiations. The enhanced activity of silver-doped TiO₂ is due to the enrichment of electron–hole separation by electron trapping of silver particles.

Keywords: Procion blue H-B dye; photocatalysis; silver doping; TiO₂; washwater; COD

Introduction

Discharge of dyehouse effluents with biocalcitrant organic pollutants has led to the development of new technologies for the treatment of wastewater. Dye effluents can be treated by biological methods, flocculation, adsorption on activated carbon, chemical oxidation methods, reverse osmosis, and advanced oxidation processes (Slokar and Marechal 1998). Biological methods alone have been proved to be unsuccessful for the treatment of textile wastewater (Pearce, Lloyd, and Guthrie 2003). Flocculation, reverse osmosis, and adsorption methods transfer the pollutants to other media, thus causing secondary pollution (Goutley, Buckley, and Groves 1983). Moreover, chemical oxidation methods are not cost effective (Baban et al. 2003).

In this effort, heterogeneous photocatalysis has been identified as one of the most potential pollution remedial technologies in recent decades (Corma and Garcia 2004; Oller et al. 2006). Semiconductor photocatalyst generates electron and hole

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pair (e^-/h^+) upon irradiation of light energy that could be utilized in initiating oxidation and reduction reactions, respectively. Low electron transfer rate to oxygen and high electron-hole pairs' recombination rate limit the rate of photo-oxidation of organic compounds on the catalyst surface significantly (Linsebiger, Lu, and Yates 1995). The effects of various factors influencing photocatalytic degradation, such as pH, concentration of dye, dosage of photocatalyst on the photodegradation of Procion blue by electro-assisted photocatalytic degradation have been studied (Neelavannan, Revathi, and Basha 2007).

Considerable investigations have been focused on improving photocatalytic activity of titania using dopants and surface deposition of noble metals to broaden the absorption of UV by TiO_2 and reduce recombination odds of photoexcited carriers. Emerging techniques, such as ozonation treatment using Fenton's reagent, electrochemical destruction, and photocatalysis may have considerable potential for discoloration. However, such technologies either usually involve complicated procedures or are economically unfeasible (Chang and Lin 2000). Biological and/or combination treatment systems that can effectively remove dyes from large volumes of wastewater at a low cost are considered to offer a preferable alternative (Robinson et al. 2001). Several researchers have studied the degradation of different textile dyes using silver-doped titanium dioxide by photocatalytic methods (Arabatzis et al. 2003; Ozkan et al. 2004; Sahoo, Gupta, and Pal 2005; Rupa et al. 2007).

The photocatalytic activity with silver deposit was less augmented than with platinum deposit and at times is even detrimental (Vamathevan et al. 2002). It is also found that the presence of nanosized silver particles on the TiO_2 surface could augment the activity of TiO_2 by a factor of 4.0 for the mineralization of sucrose. For the treatment of dye wastewater, TiO_2 modified with silver loading enables the catalyst to be more effective and shortens the illumination period (Sokmen and Ozkan 2002). Separation of TiO_2 from the effluent after dye degradation, however, is difficult due to its fine size. Therefore, it needs a costly filtration process before disposal. To combat this difficulty, TiO_2 is sometimes immobilized on transparent supports (Naskar, Pillay, and Chanda 1998), or it is doped with either metal or metal ions (Arabatzis et al. 2003).

The enhancement of photocatalytic activity of TiO_2 in the oxidative degradation procion by silver deposition may be achieved through the following mechanisms:

- (1) Silver particles deposited on TiO_2 act as electron traps, enhancing the electron-hole separation and the subsequent transfer of the trapped electron to the adsorbed O_2 acting as an electron acceptor (Herrmann 1986).
- (2) More dye molecules were adsorbed on the surface of silver-doped TiO_2 than on the TiO_2 surface, enhancing the photo-excited electron transfer from the visible light sensitized dye molecule to the conduction band of TiO_2 , thereby subsequently increasing the electron transfer to the adsorbed O_2 .

In this work, biodegradation of Procion blue H-B dye in textile washwater is carried out to obtain biodegraded textile washwater, which is amenable for photocatalytic oxidation. For the first time, we report Ag- TiO_2 doped photocatalytic degradation of Procion blue H-B dye in biodegraded textile washwater. All the intermediates and unreacted compounds formed during biodegradation will be oxidized by photocatalytic oxidation and the bacteria presented in the effluent will also be killed. Prepared silver-doped TiO_2 catalyst was characterized by thermo gravimetric and differential thermal analysis (TG and DTA), UV-Visible

spectrometer, X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray microanalysis (EDX), and Brunauer–Emmett–Teller (BET) surface area techniques.

Experimental

Materials

The biodegraded textile washwater containing Procion blue H-B dye (reactive blue 2, C.I. no., 61211 and λ_{max} of Procion blue dye of 605 nm) was used in this study. Titanium dioxide (anatase 98.0%) and silver nitrate (99.5 wt%) analytical grade from Merck were used for the preparation of silver-doped TiO_2 photocatalysts.

Photocatalytic degradation studies

In this study, the washwater after biodegradation was subjected to photocatalytic degradation by two types of irradiation.

Mercury lamp irradiation method

The experimental setup consists of a 500 mL glass beaker that contains washwater with photocatalysts, placed on a magnetic stirrer. This setup is kept inside a reflecting mirror box. A 125 W mercury lamp is provided on top of the mirror box, which serves as the light source. The length, breadth, and height of the reflecting mirror box are 40, 25, and 25 cm, respectively. A volume of 400 mL of the washwater is taken in the beaker and the TiO_2 or silver-doped TiO_2 is added to it. Washwater with a photocatalyst is continuously stirred by a magnetic stirrer for complete mixing of reaction mixture. The volume of washwater taken in the beaker is 400 mL. Figure 1(a) shows the mercury lamp irradiation setup.

UV lamp irradiation method

For this work, washwater containing Procion blue H-B dye is obtained after biodegradation. The experimental setup of pencil-type UV lamp irradiation is shown in Figure 1(b). This setup consists of a 700 mL cylindrical stainless steel reactor placed on a magnetic stirrer. An immersion type 6 W UV lamp of size 2.5 cm diameter and 27 cm height (emitting UV light, $\lambda = 365$ nm) is placed inside the reactor and the same serves as the light source. The height and diameter of the reactor are 21 and 8 cm, respectively. A volume of 700 mL of the washwater is taken in the reactor and to it is added TiO_2 or Ag^+ doped TiO_2 . The washwater with a photocatalyst is continuously stirred by a magnetic stirrer for complete mixing of reaction mixture. The height of the dye solution in the reactor is 20 cm.

Chemical oxygen demand analysis

In order to determine the extent of degradation of the effluent, chemical oxygen demand (COD) was measured. The COD, as the name implies, is the oxygen requirement of a sample for oxidation of organic and inorganic matter. COD is generally considered as the oxygen equivalent of the amount of organic matter

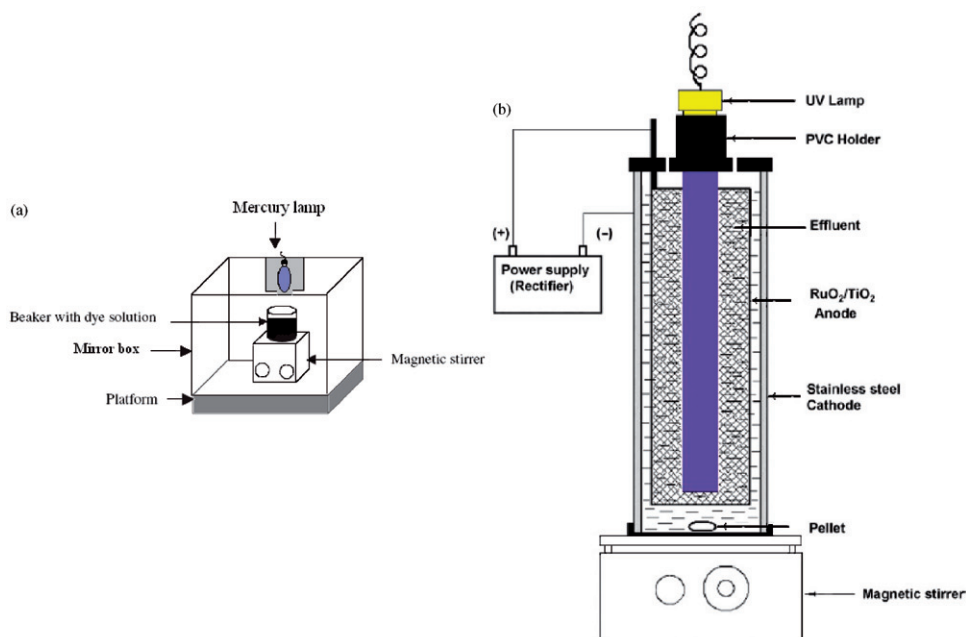


Figure 1. (a) Experimental setup of mercury lamp irradiation process. (b) Experimental setup of UV irradiation treatment process.

oxidizable by potassium dichromate. The organic matter of the sample is oxidized with a known excess of potassium dichromate in a 50% sulfuric acid solution. The excess dichromate is titrated with a standard solution of ferrous ammonium sulfate. The COD of all samples were determined by the dichromate closed reflux method using Thermoreactor TR 620 (Merck). The reaction time was 2 h at 148°C. The experiments are repeated until the difference observed is less than 3%.

Biodegradation

Biodegradation of textile washwater was carried out for 5 days to study the partial removal of color and COD reduction. *Bacillus cereus* and *Pseudomonas putida* was inoculated on the nutrient agar slant and incubated at 37°C for 24 h, and it was maintained in refrigeration condition and it has been subcultured routinely for 15 days.

Nutrient broth culture of 100 mL (*P. putida*) was taken in a 250 mL Erlenmeyer flask and incubated at 37°C for 24 h. Then, textile washwater of 100 mL was taken and added to a flask that contains nutrient broth culture at a pH of 9.0 and shaken at 120 rpm at a temperature of 28°C. The flask was kept in a shaker for 5 days. Discoloration and degradation of washwater in biological treatment based on bacterial activities thus require aerobic condition. For the sequential treatment, aerobic environment can be provided in a rotating biological conductor (orbital shaker). After completion of 24 h, 1 mL of sample was collected every day from the flask for COD analysis, and 5 mL sample was collected for absorbance with the

Table 1. Biodegradation using *P. putida*.

Time (hrs)	COD (mg L ⁻¹)	% of COD removal
24	3280	5
48	2960	14
72	2640	23
96	2480	28
120	2320	33

help of NOVA 60 (Merck). The results thus obtained in a batch setup are shown in Table 1.

Instrumentation

A Varian Cary 500 UV–VIS–NIR spectrophotometer equipped with an integrated sphere was used to record the diffuse reflectance spectra (DRS) and to measure the absorbance data of the solution samples. The baseline correction was performed using a calibrated reference sample of barium sulfate. The reflectance spectra of TiO₂ and silver-doped TiO₂ catalysts were analyzed under ambient conditions in the range $\lambda = 200\text{--}800\text{ nm}$.

Powder XRD patterns of TiO₂ and Ag-doped TiO₂ catalysts were obtained using a Philips PAN analytical X'pert PRO diffractometer equipped with a copper tube for generating a Cu-K α radiation ($\lambda = 1.5406\text{ \AA}$) at 40 kV, 25 mA. The particles were spread on a glass slide specimen holder and the scattered intensity was measured between 20° and 85° at a scanning rate of $2\theta = 1.2^\circ\text{ min}^{-1}$. Peak positions were compared with the standard files to identify the crystalline phases.

SEM analysis was performed on samples using a Hitachi, Model S-3000H, equipped with an INCA EDX probe for the EDX microanalysis.

TG and DTA analyser, TA Instruments Model SDT Q600 Model, was used to measure weight changes in Ag–TiO₂ as a function of temperature (or time) under a controlled nitrogen atmosphere. Its principal uses include measurement of thermal stability and composition of Ag–TiO₂. Data were collected during cooling also.

The specific surface areas of TiO₂ and silver-doped TiO₂ were determined according to the BET method through nitrogen adsorption at liquid nitrogen temperature (77 K) using a NOVA 1000 series instrument.

Preparation of photocatalyst

The Ag-doped TiO₂ catalysts were prepared by photo reducing Ag⁺ ions to Ag metal on the TiO₂ surface as per the following procedure. First, 0.2 g of AgNO₃ was dissolved in 100 mL of water in a glass beaker. Then 10 g of TiO₂ was added to the solution and the solution was stirred well and allowed to stand for 24 h. The system was then irradiated under a 6 W UV lamp with a maximum emission at 365 nm for 2 h. After irradiation, the powder was filtered and washed to remove residual ions and finally dried in vacuum oven at 95°C for 16 h (Liu et al. 2004).

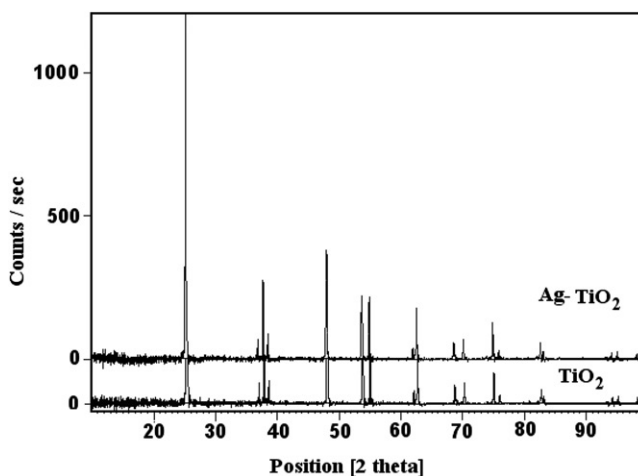


Figure 2. XRD patterns of TiO_2 and Ag-TiO_2 .

Results and discussion

XRD and EDX analysis

Figure 2 shows the XRD patterns of TiO_2 and Ag-TiO_2 . From the figure, we found that the XRD patterns of silver-doped TiO_2 samples almost coincide with that of pure TiO_2 and show no diffraction peaks due to silver species, thus suggesting that the metal particles are well dispersed on the TiO_2 surface. Anatase-type structure is kept in all silver-doped TiO_2 catalysts, indicating that the metal dopants are merely placed on the surface of the crystals without being covalently anchored into the crystal lattice. There are no diffraction patterns characteristics of the doped metals in the XRD patterns. Hence these metal sites are expected to be below the visibility limit of X-ray analysis (Sclafani and Herrmann 1998). The crystallite size was determined from the diffraction peak broadening by employing the following equation:

$$D = \frac{K\lambda}{(\beta_c - \beta_s) \cos \theta},$$

where D is the crystallite size of the catalyst, λ the X-ray wavelength, and β_c and β_s the FWHM of the catalyst and the standard, respectively; $K=0.89$ is a coefficient and θ the diffraction angle. It is noted that all the catalysts are in the form of nanoparticulates with sizes ranging from 20 to 40 nm. The TiO_2 used in this study was pure anatase phase. There was no change in the structure of TiO_2 after the photocatalytic reaction.

We observed maximum photocatalytic degradation of Procion blue by 2% of Ag-doped TiO_2 . We have performed EDX analysis on the Ag-doped TiO_2 catalyst and from the analysis, we notice that in Ag-TiO_2 , the Ag content of 0.42 wt% was present in the selected region. This confirms that the deposition of silver on TiO_2 is non-uniform.

UV-visible DRS

The spectrum of TiO_2 consists of a single absorption around 350 nm, usually ascribed to charge-transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by $3d_{1/2}$ orbital of the Ti^{4+} cations) (Gerischer and Heller 1991). The addition of silver ions and subsequent UV irradiation cause significant changes to the absorption spectrum of TiO_2 resulting in high absorbance from 370 nm to the entire visible region, a characteristic of surface plasmon absorption where a band usually appears at 400 nm. As this band is not as strong as reported in literature (Herrmann et al. 1997; Stathatos et al. 2000), the red shift may not be due to surface plasmon absorption. Hence the extended absorption must be from band gap absorption. This band gap absorption of all silver-doped TiO_2 catalysts slightly shifts to higher wavelength. The absorbance in the visible region for the metallized system shows that lower energy transitions are possible. This is due to the metal clusters giving rise to localized energy levels in the band gap of TiO_2 into which valence band electrons of TiO_2 are excited at wavelength longer than 350 nm. If equal-sized metal clusters are formed, constant absorption in the visible region corresponding to the excitation from the valence band of TiO_2 to the unoccupied level of metal cluster will occur. Since there is a small gradual decrease in absorption from 400 to 800 nm in the DRS of silver-doped TiO_2 catalyst, the metal clusters in the catalyst are not of equal size. The spectra reveal that silver doping has a marked effect on the absorption properties of TiO_2 and that the absorption of light in the visible region by TiO_2 increases with an increase in the silver content.

BET surface area analysis

In general, the surface area of the catalyst is the most important factor in influencing the catalytic activity. The surface area of TiO_2 particles before and after surface modification was determined. It was observed that the surface area decreases with increase in the silver content of the silver-doped TiO_2 catalyst. The surface area of the titanium dioxide and silver-doped TiO_2 were 22.19 and 17.52 m^2/g , respectively. The decrease in the surface area of silver-doped TiO_2 may be due to blocking of fine capillaries of parent TiO_2 surface by metal film islands (Sakthivel et al. 2004).

Thermo gravimetric and differential thermal analysis

Thermal stability is critically important for silver-based multilayered structures such as silver/ TiO_2 . In this work, it has been proved that silver deposition can effectively improve the thermal stability of TiO_2 but does not adversely affect the optical transmission through the multilayer from the near ultraviolet to near infrared spectral region. The TG and DTA patterns were obtained on TiO_2 and silver-doped TiO_2 . An endothermic peak is observed around 35°C with a corresponding weight loss of about 0.5%. This is attributed to the dehydration of the catalyst. No weight loss was observed beyond 1000°C. A similar observation has been reported by Nagaveni et al. (2004) on the photocatalytic degradation of nano TiO_2 . Although the silver-doped TiO_2 gave a similar trend in the latter case, an irreversible decomposition takes place at 1200°C. In both cases, the weight losses observed

between 150 and 500°C are attributed to the strongly bonded water or surface hydroxyl groups (Nagaveni et al. 2004).

Adsorption of Procion blue on TiO₂ and Ag-doped TiO₂ catalysts

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its concentration at constant temperature. For the photodegradation of Procion blue dye on silver-doped TiO₂ under UV irradiation, silver metals act as electron traps, thereby enhancing the charge separation. To find out the mechanism, an adsorption study was carried out with 20–100 mg L⁻¹ of the aqueous solution of Procion blue H-B dye in darkness for 12 h. It was found that there was no measurable decrease in the dye concentration. This indicates that the adsorption of dye is not significant over silver-doped TiO₂.

An adsorption isotherm of TiO₂ is shown in Figure 3(a) and (b). From the figures, a substantial increase in the relative amount adsorption was observed as the dosage was increased from 60 to 100 mg L⁻¹. Linear plots of C_e/q_e versus C_e (Langmuir) and $\ln(q_e)$ versus $\ln(C_e)$ (Freundlich) show that the adsorption obeys both Langmuir and Freundlich isotherm models. The high values of coefficient of regression (R^2) for both the models indicate good agreement between experimental

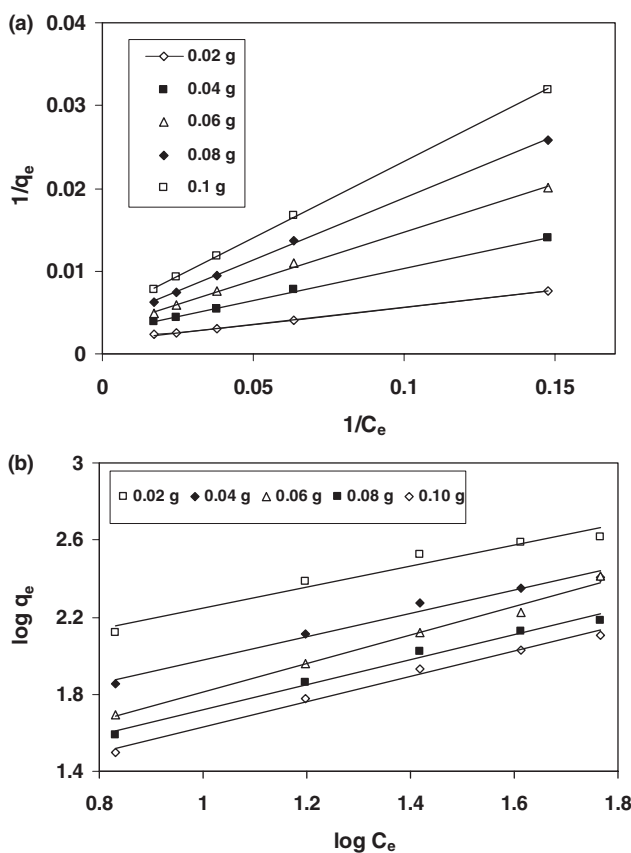


Figure 3. An adsorption isotherm of TiO₂. (a) Langmuir isotherm. (b) Freundlich isotherm.

and predicted data. The applicability of both the isotherm models to TiO_2 and silver-doped TiO_2 system implies that both monolayer sorption and heterogeneous surface conditions exist under the experimental conditions used. The sorption of dye on the TiO_2 and silver-doped TiO_2 is thus complex, involving more than one mechanism. From the measurement, we found that the values of Langmuir constant ' Q^0 ' (Q^0 is the maximum amount of the Procion blue dye adsorbed per unit weight of catalysts to form a complete monolayer, a practical limiting adsorption capacity when the surface is fully covered with Procion blue dye) increases with the increase of dosage of TiO_2 from 8.56 to 47.3, whereas the constant related to the affinity of the binding sites ' b ' decreases from 0.041 to 0.039. In Freundlich isotherm, the values of K_f and n (K_f and n are the Freundlich constants characteristic on the system. K_f and n are indicators of adsorption capacity and adsorption intensity, respectively) increase with the increase of dosage of Procion blue dye from 2.9 to 5.5 and 1.42 to 1.83.

Photocatalytic activities of TiO_2 and Ag-doped TiO_2 catalysts on Procion blue degradation

The degradation profile of Procion blue under various catalysts loading under irradiation is shown in Figure 4. Compared to pure TiO_2 , the silver-doped TiO_2 catalysts with both irradiations exhibited a significant increase in the Procion blue H-B dye degradation. As there is no significant difference in the adsorption of dyes between TiO_2 and the silver-doped TiO_2 catalysts, mechanism (2) is ruled out. Hence the increase in efficiency by Ag deposition is due to mechanism (1).

It is observed that the photonic efficiency increases with an increase in the silver loading up to 600 mg L^{-1} of Ag- TiO_2 (optimum metal loading) and then decreases. There is no considerable change in further loading of catalyst because further addition of catalyst made the effluent dense, and penetration of UV into the effluent was poor. It is also observed that the photonic efficiency increases with an increase in the silver loading up to 600 mg L^{-1} . More silver contents could be detrimental to the photonic

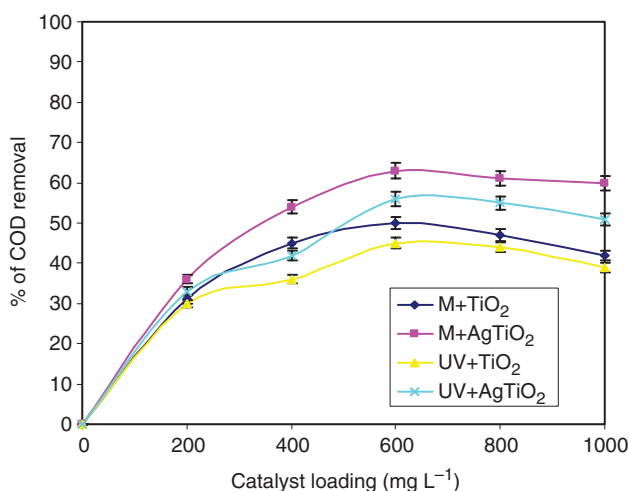


Figure 4. Effect of catalysts loading on COD removal.

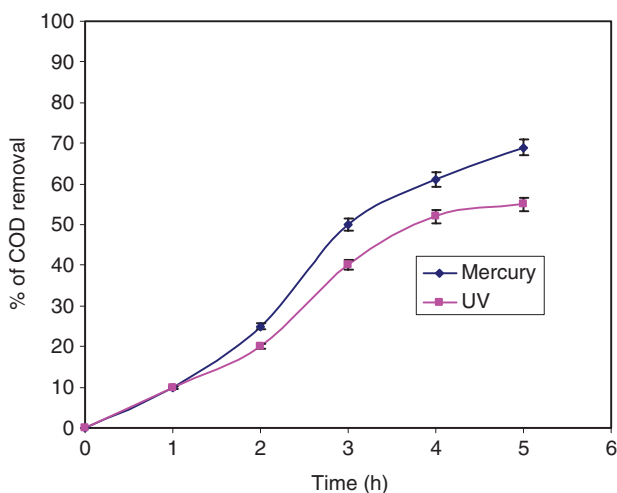


Figure 5. Effect of irradiations on COD removal.

efficiency. It may be explained that up to maximum metal loading, the silver particles deposited on the TiO_2 surface can act as electron-hole separation centers. The electron transfer from the TiO_2 conduction band to metallic silver particles at the interface is thermodynamically possible because the Fermi level of TiO_2 is higher than that of silver metals (Sclafani and Herrmann 1998). This results in the formation of Schottky barrier at the metal-semiconductor contact region, which improves the charge separation and thus enhances the photocatalytic activity of TiO_2 . In contrast, at the silver content above its maximum, the silver particles can also act as recombination centers thereby decreasing the photocatalytic activity of TiO_2 . It has been reported that the probability for the hole capture is increased by the large number of negatively charged silver particles on TiO_2 at high silver content, which reduces the efficiency of charge separation (Zhao et al. 1996; Stathatos and Lianos 2002). The photodegradation of Procion blue H-B Dye against the irradiation time is shown in Figure 5. From this figure, it was found that the rate of photodegradation increased linearly with time of irradiation and mercury lamp with silver-doped TiO_2 irradiation shows maximum Procion blue H-B dye degradation. It is due to the emission area in mercury lamp setup and attained temperature is more than that of UV lamp setup. The source (mercury lamp) was surrounded by mirrors and the reflections influence the photodegradation. The total energy absorbed per unit area during a given exposure time is also more in mercury lamp irradiation setup. Because of the high wattage of the mercury lamp, heat is generated in the reaction chamber, which leads to more photolytic yields. Also the plot reveals that there is no significant difference at each sampling points. During photocatalytic oxidation, all the pollutants (organic contaminants, dyes, and intermediates) were converted to CO_2 .

Conclusion

In this article, silver-doped TiO_2 photocatalyst was prepared and used for the treatment of textile washwater with UV and mercury lamp irradiations. The

characterization of TiO₂ and silver-doped TiO₂ using diffuse reflectance spectroscopy, XRD, SEM, EDX, TG and DTA, and BET surface area techniques revealed the dispersion of silver metal on the surface of TiO₂. The photonic efficiency increases with increase in the metal loading up to 600 mg L⁻¹ due to the effect of decreasing recombination of electron and hole. From this study, we found that the mercury lamp irradiation with silver-doped TiO₂ results in maximum discoloration (86%) and COD removal (69%). Both Langmuir and Freundlich isotherms are fitted well for the degradation of Procion blue H-B dye. An integrated biological–photocatalytic system for the discoloration and COD reduction seems a logical choice for the treatment of textile washwater. The presence of bacteria was checked by plate method and there was no colony found in the photodegraded washwater and can be recycled and used for the rinsing purpose.

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