CHAPTER -7
Ag - TiO₂ DOPED PHOTO CATALYTIC DEGRADATION OF PROCION BLUE H-B DYE IN TEXTILE WASHWATER

7.1 INTRODUCTION
7.2 EXPERIMENTAL
7.2.1 Mercury lamp irradiation.
7.2.2 Pencil type immersion UV lamp irradiation
7.2.3 Biodegradation
7.2.4 Instrumentation
7.2.5 Preparation of photocatalyst
7.3 RESULTS AND DISCUSSIONS
7.3.1 SEM analysis and EDX analysis
7.3.2 UV–visible diffuse reflectance spectra
7.3.3 BET surface area analysis
7.3.4 Thermo gravimetric & differential thermal analysis (TG & DTA) analysis
7.3.5 X-ray diffraction (XRD) analysis
7.3.6 Adsorption of Procion blue on TiO₂ and Ag doped TiO₂ catalysts
7.3.7 Photocatalytic activities of TiO₂ and Ag doped TiO₂ catalysts on Procion blue degradation.
7.4 CONCLUSIONS
REFERENCES.
7.1. Introduction

Discharge of dye-house effluents with bio calcitrant organic pollutants have lead to the development of new technologies for the treatment of wastewater. Dye effluents can be treated by biological methods, flocculation, and adsorption on activated carbon, chemical oxidation methods, reverse osmosis and advanced oxidation processes [1]. Biological methods alone have been proved to be unsuccessful for the treatment of textile waste water [2]. Flocculation, reverse osmosis and adsorption methods transfer the pollutants to other media, thus causing secondary pollution [3]. Moreover chemical oxidation methods are not cost effective [4].

In this effort, heterogeneous photocatalysis has been identified as one of the most potential pollution remediation technologies in recent decades [5,6]. Semiconductor photo catalyst generates electron and hole 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 pair recombination rate limit the rate of photo oxidation of organic compounds on the catalyst surface significantly [7]. Effects of various factors influencing photocatalytic degradation such as pH, concentration of dye, dosage of photocatalyst on the photo degradation of Procion blue by electro assisted photocatalytic degradation have been studied [8].
In the recent years, silver ions have attracted the interests of several researchers because of both their novel effects on the improvement of photo activity of semiconductor photocatalysis nano crystallites and their effects on antibacterial activity. These properties can be applied to a tremendous range of applications, for instance, environment, textiles, engineering materials and so on. Emerging techniques, such as ozonation, treatment using Fenton’s reagent, electrochemical destruction and photocatalysis may have potential for decoloration. However, such technologies usually involve complicated procedures or are economically unfeasible [9]. 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 [10]. Several researchers have studied the degradation of different textile dyes using silver doped titanium dioxide by photocatalytic methods [11-14].

The photocatalytic activity with silver deposit was less augmented than with platinum deposit, or at times even detrimental. It is also found that the presence of nano sized silver particles on the TiO₂ surface could augment the activity of TiO₂ by a factor of 4.0 for the mineralization of sucrose [15]. For the treatment of dye wastewater, TiO₂ modified with silver loading enables the catalyst to be more effective and shortens the illumination period [16]. Separation of TiO₂ from 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 or it is doped with either metal or metal ions [17, 18].

The enhancement of photocatalytic activity of TiO$_2$ in the oxidative degradation of Procion blue by silver deposition may be through the following mechanisms:

(i) 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 [19].

(ii) 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 the present 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 photo catalytic 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
TG & DTA, UV–Visible spectrometer, XRD, SEM, EDX, and BET surface area techniques.

7.2. Experimental

The biodegraded textile washwater containing Procion blue H-B dye was used in this study. In this study, the washwater after biodegradation was subjected to photocatalytic degradation by two types of irradiation.

7.2.1 Mercury lamp irradiation.

The experimental setup consists of a 500 mL glass beaker which contains washwater with photocatalysts is placed on a magnetic stirrer. This setup is kept inside a reflecting mirror box. A 125 W mercury lamp is provided on the top of the mirror box which served as the light source. The length, breadth and height of the reflecting mirror box were 40 cm, 25 cm and 25 cm respectively. 400 mL of the washwater was taken in the beaker and to it is added TiO₂ or silver doped TiO₂. Washwater with a photocatalyst was continuously stirred by a magnetic stirrer for complete mixing of reaction mixture. The volume of washwater taken in the beaker is 400 mL. Fig. 1 shows the mercury lamp irradiation setup.
Fig. 1  Mercury lamp irradiation set up  

7.2.2 Pencil type immersion UV lamp irradiation.

For this work, washwater containing of Procion blue H-B dye is obtained after biodegradation. The experimental setup of pencil type UV lamp irradiation is shown in Fig.2. 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 of wavelength 365 nm) is placed inside the reactor and the same served as the light source.
The height and diameter of the reactor are 21 cm and 8 cm, respectively. 700 mL of the washwater is taken in the reactor and to it is added TiO\textsubscript{2} or Ag\textsuperscript{+} doped TiO\textsubscript{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.
7. 2.3 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 hours and it maintained in refrigeration condition and it subcultures routinely for fifteen days.

Nutrient broth culture of 100 mL (Pseudomonas putida) was taken in a 250 mL Erlenmeyer flask and incubated at 37°C for 24 hours. Then textile washwater of 100 mL was taken and added in flask which contains nutrient broth culture at a pH of 9.0 and shaken at 120 rpm at 28°C temperature. The flask was kept in a shaker for five days. Decolorization and degradation of washwater in biological treatment based on bacterial activities thus require aerobic condition. For the sequentially treatment aerobic environment can be provided in a rotating biological conductors (orbitery shaker). After completion of 24 hours, 1 mL of sample was collected every day from the flask for COD analysis and 5 mL sample was collected for absorbance with the help of NOVA 60 (MERK). The results obtained in a batch setup were shown in the Table1.
Table. 1 Biodegradation using Pseudomonas putida

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>COD (mg/L)</th>
<th>% of COD removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>3280</td>
<td>5</td>
</tr>
<tr>
<td>48</td>
<td>2960</td>
<td>14</td>
</tr>
<tr>
<td>72</td>
<td>2640</td>
<td>23</td>
</tr>
<tr>
<td>96</td>
<td>2480</td>
<td>28</td>
</tr>
<tr>
<td>120</td>
<td>2320</td>
<td>33</td>
</tr>
</tbody>
</table>

7.2.4. 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 base line correction was performed using a calibrated reference sample of barium sulfate. The reflectance spectra of TiO$_2$ and silver doped TiO$_2$ catalysts were analyzed under ambient conditions in the wavelength range of 200–800 nm.

Powder X-ray diffraction patterns of TiO$_2$ and Ag doped TiO$_2$ catalysts were obtained using a Philips PAN analytical X per PRO diffractometer equipped with a copper tube for generating a Cu K$_\alpha$ radiation (wavelength 1.5406 Å) at 40 kV, 25 mA. The particles were spread on a glass slide specimen holder and the scattered intensity was measured between 20$^\circ$ and 85$^\circ$ at a scanning rate of 20 = 1.2$^\circ$ min$^{-1}$. Peak positions were compared with the standard files to identify the crystalline phases.
Scanning electron microscope (SEM) analysis was performed on samples using a HITACHI, Model S-3000H, equipped with an INCA EDX probe for the energy dispersive X-ray micro analysis (EDX).

Thermogravimetric & differential thermal analysis (TG & DTA) Analyzer, 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 was collected while cooling also.

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

### 7.2.5. 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 procedure as follows. 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 was allowed to stand for 24 h. The system was then irradiated under a 6W 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).
7.3. Results and discussions

7.3.1. SEM analysis and EDX analysis.

From this work it is observed maximum photocatalytic degradation of Procion blue by 2 at % of Ag doped TiO$_2$. Hence SEM analysis has been carried out for the modification of surface topography of Ag-TiO$_2$ catalysts. The SEM pictures of pure TiO$_2$, and Ag-TiO$_2$ are shown in Fig. 2. The SEM picture of pure TiO$_2$ (Fig.3) shows that the size of titanium dioxide particle is uniform. But the distribution of silver on the surface of TiO$_2$ is not uniform and the SEM picture (Fig. 4) show

![SEM picture of pure TiO$_2$](image)

**Fig. 3** SEM picture of pure TiO$_2$

that Ag doped TiO$_2$ catalyst contains irregular shaped particles which are the aggregation of tiny crystals. However, it cannot be ruled out that some Ag particles are too small to be observed at the resolution of the used microscope. The above figures also reveal that the doping of silver
metal does not leave any change in the topology of the catalyst surface. We have also performed EDX analysis on the Ag doped TiO$_2$ catalyst and presented the spectrum in Fig. 5. From the figure, we notice that, in Ag-TiO$_2$ the Ag content of 0.42 wt. % was there in the selected region. This confirms the deposition of silver on TiO$_2$ is non-uniform.
Fig. 5 EDX spectrum of Ag-TiO₂

7.3.2. UV–visible diffuse reflectance spectra

The reflectance spectra of TiO₂ and Ag doped TiO₂ catalysts are illustrated in Fig 6.

The spectrum of TiO₂ 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,2g orbital of the Ti$^{4+}$ cations) [21]. The addition of silver ions and subsequent UV irradiation causes significant changes to the absorption spectrum of TiO$_2$ resulting in high absorbance from 370 nm to entire visible region, a characteristic of surface plasmon absorption where usually appears a band at 400 nm. As this band is not as strong as reported in literature [22,23]. 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 metallised 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 diffuse reflectance spectrum 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.

### 7.3.3 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 in 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$^{-1}$ 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
[24].

7.3.4 Thermogravimetric & differential thermal analysis (TG & DTA) analysis

Thermal stability is critically important for silver-based multilayered structures such as silver / TiO$_2$. In this work, it has been proved a 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 Thermo gravimetric & differential thermal analysis (TG & DTA) patterns 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. on the photo catalytic degradation of nano TiO$_2$ (Nagaveni et al 2004). 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°C and 500°C are attributed to the strongly bond water or surface hydroxyl groups (Nagaveni et al. 2004).

7.3.5 X-ray diffraction (XRD) analysis

Fig 7 shows the XRD spectrum of pure TiO$_2$ and silver doped TiO$_2$. The X-ray diffraction 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 X-ray diffraction patterns. Hence these metal sites are expected to be below the visibility limit of X-ray analysis [26]. The crystallite size was determined from the diffraction peak broadening by employing the following equation (1):

**Fig. 7. XRD spectrum of pure TiO$_2$ and silver doped TiO$_2$.**
Where “D” is the crystallite size of the catalyst, “λ” the X-ray wavelength, and “βc” and “βs” are the FWHM of the catalyst and the standard, respectively. K= 0.89 is a coefficient and θ is 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 TiO₂ used in the present study was pure anatase phase. There was no change in the structure of TiO₂ after the photocatalytic reaction.

7.3.6. 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 of the aqueous solution of Procion blue H-B dye in darkness for 12 hours. It was found that there was no measurable decrease in the dye concentration. This indicates that adsorption of dye is not significant over silver doped TiO₂.
A substantial increase in the relative amount adsorption was observed as the dosage was increased from 60 to 100 mg/L. Linear plots of Ce/qe versus Ce (Langmuir) and ln(qe) versus ln Ce (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 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 constant related to the affinity of the binding sites “b” decreasing from 0.041 to 0.39. 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) increases with the increase of dosage of Procion blue dye from 2.9 to 5.5 and 1.42 to 1.83.
7.3.7 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 Fig.8. Compared to pure TiO$_2$, the silver doped TiO$_2$ catalysts with both irradiations were 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 silver doped TiO$_2$ catalysts, the mechanism (2) is ruled out. Hence the increase in efficiency by Ag deposition is due to the mechanism (1).
It is observed that the photonic efficiency increases with an increase in the silver loading up to 600 mg/L of Ag-TiO$_2$ (optimum metal loading) and then decreases. There is no considerable change in further loading of catalyst. It is also observed that the photonic efficiency increases with increase in the silver loading up to 600 mg/L. More silver contents could be detrimental to the photonic 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 [26]. 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 [27, 28]. The photo degradation of Procion blue H-B Dye against the irradiation time is shown in Fig.9.
From this figure it was found that mercury lamp with silver doped TiO$_2$ irradiation shows maximum Procion blue H-B dye degradation and decolourization. It may be due to higher intensity of ultraviolet rays in the mercury lamp than UV lamp. Also the plot reveals that there is no significant difference at each sampling points. During photocatalytic oxidation all the pollutants (organic contaminants, dyes & intermediates) were converted to CO$_2$.

7.4. Conclusions

The characterization of TiO$_2$ and silver doped TiO$_2$ using diffuse reflectance spectroscopy, XRD, SEM, EDX, TG & DTA and BET surface
area techniques revealed the dispersion of silver metal on the surface of TiO$_2$. The photonic efficiency increases with increase in the metal loading due to the effect of decreasing recombination of electron and hole.

From this study we found that the mercury lamp irradiation with silver doped TiO$_2$ results maximum decolourization and COD removal. Both Langmuir isotherm and Freundlich isotherms are fitted well for the degradation of Procion blue H-B dye. Also from the results of the present work and the respective literature one could claim that the photocatalytic treatment of the washwater of the textile industry, one of the most polluting industrial sectors, could be employed as a powerful tool for the decolorization and reduction of organic pollutant of the liquid waste. An integrated biological—photocatalytic system for the decolorization and COD reduction, seems a logical choice for the treatment of washwater such as those coming from the textile processing industry. The possibility of reusing the photocatalyst was examined to see the cost effectiveness of the method. It was observed that the used catalyst could be used for the second time also with 90% efficiency [13]. The presence of bacteria was checked by plate method and there was no colony found in the photodegraded washwater. It can be recycled and used for the rinsing purpose.
References


