Studies on photocatalytic activity of the synthesised TiO₂ and Ag/TiO₂ photocatalysts under UV and sunlight irradiations

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ABSTRACT

Photocatalytic decolorisation and degradation of Reactive Red 120 (RR 120) has been investigated under UV (365 nm) and solar light as radiation sources using synthesised nano titania catalyst prepared via sol-gel method. The study encompassed calcination of synthesised titania catalyst at a range of temperature up to 1,000°C. The effects of calcination temperature on titania catalyst have been evaluated on the decolorisation of RR 120. The analysis revealed complete decolorisation of dye solution in 100 min under UV light with the TiO₂ catalyst calcined at 200°C. Only a maximum of 47% dye decolorisation was achieved under sunlight in 4 h with no improvement even after prolonged irradiation. In an endeavour to improve the catalytic activity, bare titania was modified with silver metal and a comprehensive study on the characteristics of silver modified catalyst was made. The result was an enhancement of the rate of decolorisation of dye under both UV and solar light sources. All the catalysts were characterised by XRD and BET analyses. Optimisation of the degradation of RR 120 has been carried out using the unmodified catalyst by varying the amount of catalyst, substrate concentration, pH of dye solution. Effects of addition of small amounts of various oxidants such as H₂O₂, KBrO₃ and (NH₄)₂S₂O₈ have also been studied. Pseudo first order kinetics was observed in the photocatalytic decolorisation of dye. The mineralisation of RR 120 was monitored by TOC analysis.

Key words | mineralisation, nano titania, photocatalysis, reactive red 120, solar light

INTRODUCTION

Our environment has been under serious threat from various contaminations, particularly the ones that pollute water and land. It is understood that the textile industry plays a major detrimental role in polluting water and land. Out of various activities in textile industries, chemical processing employed in dyeing contributes to about 70% of the overall water pollution. Due to various chemical processes involved in textile industries, large volumes of waste water with numerous toxic pollutants are discharged that affects the aquatic ecosystem and land. One of the important groups of dyes are azo compounds that are classified as monoazo, diazo, triazo according to the number of azo bonds (―N=N―) in their structure. Their widespread use makes them one of the principal sources of contamination of effluents. Reactive Red 120 (diazo) is extensively used for dyeing cotton and other cellulosic materials. They are predominantly used in textile processing industries because of their excellent wash-fastness and convenience in application. However, their removal from the effluents is considerably difficult since they are chemically stable towards light and so highly persistent in natural environment. Moreover, the presence of azo bonds is undesirable because of their reduction tendency in anaerobic conditions and nature to promote generation of aromatic amines that are highly toxic and carcinogenic (Chun et al. 2003). Therefore there is a constant need to eliminate them from the effluents discharged out of the textile industry.

The conventional biological treatment processes do not readily remove dyes from textile waste water because of their
resistance to biological degradation and high solubility. Several chemical, physical and biological processes used, such as flocculation, ultra filtration, adsorption, ozonation and chlorination, are not efficient because they form solid wastes. This creates other environmental problems that require further treatment (Ramakrishna & Viraraghavan 1997). Therefore, it is necessary to find an efficacious method of waste water treatment for the removal of hazardous dyes and organics from industrial effluents.

Apart from the above methods, semiconductor photocatalytic techniques have also been worked on and identified to have a greater potential towards addressing challenges related to water and land contamination from effluents. The process involves an interaction of UV light with semiconductor catalyst which is capable of degrading organic pollutants by both oxidative and reductive pathways. Among various semiconductor photocatalysts, titanium dioxide has been proved to be the most suitable photocatalyst for far-reaching environmental applications because of its biological and chemical inertness, strong oxidising power, non-toxicity and long-term stability against photo and chemical corrosion (Sivakumar et al. 1999, 2000; Sivakumar & Shanthi 2000, 2001). Even though it is an excellent catalyst, its wide band gap (3.2 eV) limits its usage in visible light. The normal 3–5% share of UV light in typical sunlight is not sufficient to activate titania catalyst. Numerous studies have been carried out to develop the visible light activity of TiO2 through surface modification using various noble metals (Ag, Au and Pt) as it reduces the rate of recombination of electron-hole pairs (Valentine Rupa et al. 2009). This can be annotated on the basis of formation of Schottky barrier when the work function is greater than that of the semiconductor that facilitates the transfer of electrons from the semiconductor to metal and leaves the holes for the degradation of organic compounds. In our earlier study, we reported the enhanced activity of silver modified titania for the degradation of RY-17 under artificial visible light (Valentine Rupa et al. 2007). The present undertaking comprises the decolorisation and degradation of RR 120 in short duration under natural sunlight irradiations using silver modified titania catalyst.

The degradation of Reactive Red 120 (Figure 1) has been reported using commercial catalyst under UV light (254 nm) by Hyoung & Kyung-Duk 2007. Elaborate research on photocatalytic degradation of RR 120 using synthesised catalysts under UV and solar radiation sources has not been reported so far. Hence this paper is aimed at studying the degradation of RR 120 under UV (365 nm) and solar light sources which stands out for its uniqueness.

**MATERIALS AND METHODS**

**Materials**

The commercial azo dye Reactive Red 120 was purchased from Shrinathajee Enterprises (Ahmedabad, India). Titanium tetraisopropoxide (Lancaster, 97% pure), acetic acid (Merck, 99% pure), and silver nitrate (Merck, 98% pure) were used as received. H2O2, KBrO3 and (NH4)2S2O8 and other chemicals are of analytical grade. All the chemicals and dye were used without any further purification. Double distilled water was used throughout the experimental work.

**Preparation of photocatalyst**

Titania catalyst was prepared through sol-gel method (Suresh et al. 1998). Twenty-five millilitres of titanium tetra isopropoxide was mixed with 48 mL of acetic acid with constant stirring. With these, 150 mL of water was added dropwise to the mixture with vigorous stirring (titanium tetra isopropoxide, acetic acid and water were in 1:10:100 molar ratios). Then the solution was stirred for 8 h to get a clear transparent sol. The sol was allowed to dry at 100°C followed by calcination at different temperatures at a ramp rate of 5°C/min.

In the same way silver modified titania was prepared by adding a desired volume of silver nitrate solution so as to attain 1 wt.% of silver to the titanium dioxide during the addition of water. Then photoreduction of titania sol was carried out with medium pressure mercury lamp (365 nm) for 60 min and designated as Ag/TiO2 after calcination.

![Figure 1](https://iwaponline.com/wst/article-pdf/63/3/377/445215/377.pdf)
Photocatalytic degradation of RR 120

An analysis of the photocatalytic degradation of RR 120 using bare TiO₂ and Ag/TiO₂ was made under UV and sunlight irradiations. For the latter one, experiments were carried out under open sunlight during the month of May 2009 between 10.00 am and 2.00 pm.

One hundred millilitres of dye solution of concentration 250 ppm (1.71 × 10⁻⁴ M) and required amount of TiO₂ were taken in the reaction vessel. Then the suspension was stirred for 45 min in dark so as to attain the equilibrium of adsorption of dye over TiO₂. The solution was irradiated using four mercury lamps (8 W) which could emit the radiation of wavelength 365 nm. At various time intervals, a constant quantity of sample was withdrawn and centrifuged to remove the catalyst. The absorbance was measured at 530 nm using UV-visible spectrophotometer (Hitachi U-2000) in order to determine the percentage decolorisation of RR 120. TOC measurements were carried out to investigate the extent of mineralisation of RR 120.

Characterisation

BET surface area of unmodified titania samples calcined at different temperatures was measured by N₂ physisorption at −196°C using Micromeritics ASAP 2020 system. Powder XRD patterns were taken for all the calcined samples using XD-2 power X-ray diffractometer (ISO-DEBYEFLEX 2002) using Cu Kα radiation of wavelength 1.54 nm in the range 10–70°. Total Organic Carbon (TOC) at different time intervals was determined using Micro C Analytical Jena TOC analyser by directly injecting the aqueous dye solution after centrifugation.

RESULTS AND DISCUSSION

XRD analysis

XRD patterns of unmodified and modified titania calcined at various temperatures are shown in Figure 2(a). Samples calcined at 200°C, 400°C and 600°C exhibit stronger anatase diffraction peaks of 101, 004, 200, 211 and 204 at 20 values of 25.3°, 37.7°, 47.8°, 54.8° and 62.4° respectively. Using Debye Scherrer’s equation (\(d_{hkl} = \frac{k \lambda}{B \cos \theta}\)) the average crystalline size of TiO₂ was determined and it was found to be 6.6 nm. At higher calcination temperature, the rutile phase begins to appear. With increasing temperature, anatase to rutile transformation is evident and it is completely rutile at 1,000°C.

Figure 2(b) shows the XRD patterns of Ag/TiO₂ calcined at different temperatures. No characteristic peaks of silver were observed for Ag/TiO₂ calcined up to 600°C, though 1% was given. But calcination at 700°C produced a material with characteristic XRD pattern of silver at 38.1° and 44.4°. Hence sintering of nano silver particles to yield particles of appropriate dimensions that can be detected by XRD is clearly evident. This observation precludes sintering of silver particles at 200°C, 400°C and 600°C.

BET analysis

Among different catalysts, TiO₂ calcined at 200°C showed the highest surface area. The specific surface area values for both unmodified and silver modified catalysts are given in Table 1. It is evident from the table that BET surface area of both TiO₂ and Ag/TiO₂ catalysts decreased with increase in calcination temperature. It may be due to sintering of particles and decrease in the anatase phase content in the solid matrix. Moreover, silver particles which are to rest on the particle surface might not play any role in preventing the surface from...
going for sintering. Therefore, the silver particles might have very low dimensions to suppress the sintering property of TiO2.

### Effect of calcination temperature on the activity of TiO2

Effect of calcination temperature on the activity of TiO2 over a wide range of 200°C–1,000°C was studied for the decolorisation of RR 120. Percentage removal of dye solution was significantly reduced from 100% to 16% when the calcination temperature was increased from 200°C to 1,000°C (Figure 3). This could be attributed to the decrease in anatase phase content and surface area of the catalyst with increase in temperature. Since TiO2 calcined at 200°C possesses the highest surface area with fully anatase phase, its activity was found to be the highest among all the catalysts. As a result this catalyst was picked up for further investigations.

### Optimisation of substrate concentration, amount of catalyst and pH

#### Effect of substrate concentration

The effect of initial concentration of RR 120 on the percentage of decolorisation was studied by varying the initial concentration over a wide range from 150–400 ppm (1.02 × 10^−4–2.73 × 10^−4 M) with constant catalyst weight (2 g/L). It was observed that increase in dye concentration decreases the percentage removal of RR 120 from 100% to 28% (Figure 4). This is due to strong adsorption of dye molecules on the catalytic surface at higher concentration. This causes decrease in the path length of photons entering into the dye solution, which results in poor catalytic activity of TiO2 (San et al. 2001). Moreover, the colour of the dye becomes more and more intense at higher concentration and prevents the penetration of light to the catalyst surface, eventually affecting the amount of generation of OH· and O2· radicals. Further investigations were made with the dye at a concentration of 1.71 × 10^−4 M.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Calcination temp.</th>
<th>Anatase/rutile (%)</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmod. TiO2</td>
<td>200</td>
<td>100/0</td>
<td>241</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>100/0</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>100/0</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>70/30</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>1,000</td>
<td>0/100</td>
<td>12</td>
</tr>
<tr>
<td>Ag/TiO2</td>
<td>200</td>
<td>100/0</td>
<td>238</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>100/0</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>100/0</td>
<td>36</td>
</tr>
</tbody>
</table>

*Table 1 | BET surface area and anatase phase content of synthesised titania catalyst at different calcination temperatures*
Effect of weight of catalyst

The influence of the catalyst weight on decolorisation of RR 120 was investigated by varying the amount of TiO\(_2\) from 0.5–4.0 g/L (Figure 5). It was observed that in the absence of catalyst no decolorisation occurred. Further, percentage decolorisation increased with an increase of catalyst weight up to 2.5 g/L, above which efficiency decreased moderately (Chen & Chou 1993).

The increase is attributed to the availability of more surface area at higher amount of catalyst, which increases the absorption of photons. Decrease in rate of photocatalytic reaction at high concentration of catalyst may be due to (i) the opacity of the suspension and an enhancement of light reflectance at higher amount of catalyst; (ii) particle–particle interaction becomes predominant as the amount of particles in solution increases, thus reducing the site density for surface holes and electrons; (iii) at higher loading, deactivation of activated molecules by collision with ground state molecules occurs and also shielding by TiO\(_2\) may take place (Bizani et al. 2006).

It was noticed that the rate of decolorisation of dye was almost the same for the catalyst amount ranging from 2 to 2.5 g/L. Hence 2.0 g/L was considered as an optimised amount for complete decolorisation.

Effect of substrate pH

pH is one of the important parameters in determining the rate of decolorisation and degradation of organic compounds. Highest percentage decolorisation was observed at pH 7 (Figure 6) above which decrease in the percentage decolorisation was noted. The effect of pH on the decolorisation of dye could be explained by modifying the electrical double layer of solid–electrolyte interface by means of altering the pH between 1 and 14. This causes a change in acidity of solution, which affects the adsorption–desorption processes and separation of the photo–generated electron–hole pairs in the surface of the semiconductor particles. In general, surface of TiO\(_2\) becomes positively charged in acidic suspension and negatively charged when the medium is base. Since RR 120 is an anionic dye, it could be attracted effectively in acidic suspension on titania surface. Moreover, stronger adsorption leads to major decrease of active centres on TiO\(_2\) surface, which decreases the adsorption of light quanta by the catalyst. This could be the reason why the initial rate of decolorisation was lower in acidic solution. In contrary, decrease in initial rate was observed when the pH was greater than 7. This is due to the repulsion between the anionic dye and negatively charged catalyst. Similar results were reported for several dyes (Reutergardh & Langphasuk 1997).

Since complete decolorisation of dye solution was achieved at its natural pH (~7), further studies were made without the pH adjustment.

Effect of electron acceptors

One of the major problems of photo-induced TiO\(_2\) is electron–hole pair recombination, which plays a major role in suppressing the efficiency of photocatalyst. This can be prevented by...
adding a suitable electron acceptor or donor. In the present study, powerful oxidants such as H2O2, KBrO3, and K2S2O8 were employed and their effect on the photodecolorisation of RR 120 is reported in Table 2. In the absence of oxidant, 68% decolorisation was noted in 60 min.

Addition of small amounts of H2O2 from 1–15 mmol enhanced the percentage of decolourisation from 68% to 99% in 60 min. Further increase from 15–20 mmol lowered the extent of decolourisation to 91%. This decreasing trend beyond the optimum concentration (15 mmol) has been reported in earlier studies (Liu et al. 2009). H2O2 plays two important roles for enhancing the rate of decolourisation. It accepts electrons from conduction band and thus promotes the charge separation with the generation of hydroxyl radicals, equations (1) and (2).

\[ e^{-}_{(CB)} + H_2O_2 \rightarrow TiO_2 + ^{*}OH + OH^{-} \] (1)

\[ H_2O_2 \rightarrow ^{*}OH + ^{*}OH \] (2)

At higher concentration it behaves as hydroxyl scavenger and thereby removal efficiency decreases, equations (3) and (4).

\[ H_2O_2 + ^{*}OH \rightarrow HO_2^{*} + H_2O \] (3)

\[ HO_2^{*} + ^{*}OH \rightarrow H_2O + O_2 \] (4)

Percentage decolourisation upsurged from 68% to 88% in 60 min upon the addition of KBrO3 from 0.5–1.5 g/L. Further increase from 1.5–2 g/L lowered the extent of decolourisation to 85%. This decreasing trend on further increase, the rate of photooxidation declined due to the over coverage of Br− ion on the surface of the catalyst and so a fall in photocatalytic activity of TiO2 (So et al. 2002).

A higher degree of decolourisation was noted (from 68% to 85%) on the addition of (NH4)2S2O8 up to 1.5 g/L. This is due to the inhibition of electron–hole recombination and generation of other oxidising species, namely sulphate radical anion, which can also participate in photodegradation process.

\[ e^{-}_{(CB)} + S_2O_8^{2-} \rightarrow SO_4^{*} + SO_4^{2-} \] (6)

At high concentration, the photodeoxidation is inhibited due to the increase in concentration of SO4^{2-}. Moreover, excess SO4^{2-} ions mask some of the active sites of the photocatalyst.

**Comparative study of photocatalytic activity of TiO2 and Ag/TiO2 catalysts on RR 120 under UV light and sunlight irradiation**

The rate of decolourisation of dye was found to be faster by silver modified titania than the unmodified TiO2. It was observed that the unmodified titania decolours the dye completely under UV irradiation and only 28% under solar irradiation at 100 min whereas the silver modified titania decolours the dye completely (100%) in shorter time (60 min). The enhanced activity of Ag/TiO2 may be attributed to the electronic interaction occurring at the contact region between the metal deposits and semiconductor surface. This causes the removal of electrons from TiO2 into the vicinity of the metal particle leading to the formation of Schottky barriers. As soon as the metal traps the electrons, the latter are transferred to the oxygen shortly to form highly oxidative species O2^{*−}. The trapping of electrons by silver metal from TiO2 occurs at an accelerated rate when compared to the electron transfer from TiO2 to O2. Thus an efficient charge separation which is responsible for the higher catalyst activity is recognised.

**TOC analysis**

For the determination of the degree of mineralisation of RR 120, total organic carbon (TOC) was measured using Micro C Analytical Jena TOC analyser. Decrease in total organic carbon with time under different conditions is presented in Table 3. The maximum amount of TOC removal of about 86% was accomplished with unmodified TiO2 in 10 h under
UV light. Under sunlight irradiation, unmodified TiO$_2$ removes only 25% in 4 h while Ag/TiO$_2$ removes 83%. The results indicate that the Ag/TiO$_2$ shows very high catalytic activity in shorter duration (4 h) under sunlight than under UV light (6 h). Since RR 120 has two triazine groups in its structure, complete mineralisation could not be achieved even after a prolonged irradiation time. According to the data given in the literature (Kontantinou & Albanis 2004), mineralisation was not completely achieved with a dye molecule containing a triazine group because of its high stability and formation of stable cyanuric acid as an intermediate which cannot be degraded by photooxidation method.

**Kinetic analysis**

In general, the influence of initial concentration of organic pollutants on the photocatalytic degradation rate has been described by Langmuir–Hinshelwood kinetic model, equation (8)

$$ r = \frac{dc}{dt} = \frac{kKC}{1 + KC} $$  

(7)

At low substrate concentration, the above equation can be simplified to a pseudo-first order equation as

$$ \ln \frac{C_0}{C} = kkt = k't $$  

(8)

where, $C_0$ is the initial concentration of the reactant (mg/L), $C$ the concentration of the reactant at time (mg/L), $t$ the irradiation time, $k$ the reaction rate constant (min$^{-1}$), and $K$ the adsorption coefficient of the reactant (L/mg).

The $\ln \frac{C_0}{C}$ value increased linearly with time, indicating the photocatalytic reaction follows pseudo-first order rate law (Figure 7).

**CONCLUSIONS**

The higher the calcination temperature, the more is the inhibition activity of titania catalyst, due to sintering of particles. This sintering results in the decrease of surface area and the anatase phase content of titania catalyst. Though tested at various calcination temperatures, the titania catalyst showed its very high activity only at 200 $^\circ$C, since it possessed a greater surface area at this temperature.

Deposition of silver enhanced the activity of titania towards the decolorisation and degradation of RR 120 under sunlight irradiation. This significant increase is due to the tendency of silver metal to trap electrons from the conduction band of titania under irradiation, which suppresses the recombination of electron–hole pairs and causes better charge separation. Various parameters such as concentration of dye, amount of catalyst and pH influenced their effects on the degradation of dye. Better activity of catalyst
was observed at natural pH (~7) of dye solution. Addition of oxidants enhanced the photooxidation process at its optimum level. 83% of TOC removal was achieved with Ag/TiO₂ in 4 h under sunlight irradiation, that clearly indicates the significance of deposition of silver on TiO₂.

REFERENCES


