Noble metal modified titania catalysts in the degradation of Reactive Black 5: a kinetic approach
A. Valentine Rupa, R. Vaithiyanathan and T. Sivakumar

ABSTRACT

The photocatalytic degradation of Reactive Black 5 (RB 5), a di-azo dye was investigated over M/TiO₂ (M = Ag, Au and Pt) photocatalysts irradiated with UV and visible light. TiO₂ was prepared by sol–gel technique (Syn-TiO₂). Photodeposition of metal salt precursors over Syn-TiO₂ was carried out so as to obtain 1 wt% of M/TiO₂ catalysts. The photodecolourization and photodegradation reactions were also compared with commercial TiO₂ (Degussa P25) catalyst. Kinetic studies for the decolourization of RB 5 showed that it followed pseudo first order. Recycling of catalysts was performed to check the economic feasibility of the photocatalytic process. In order to check the applicability of M/TiO₂ catalyst in the treatment of industrial effluent, real textile effluent was collected from an industry and subjected to photodegradation and the results are presented. Enhanced activity of M/TiO₂ catalyst under visible light irradiation highlights its importance in the field of photocatalysis.

Key words | decolourization, kinetic studies, photodegradation, photodeposition, recycling, reactive black

INTRODUCTION

Textile industries generate large quantities of effluent containing harmful substances and cause water pollution. The increased public concern with these environmental pollutants and the stringent international environmental standards (ISO 14001, October 1996) have prompted the need to develop novel treatment methods for converting dye effluents to harmless compounds. Reactive dyes are used for dyeing cotton fabrics and they add a lot to water pollution. The volume of textile effluent containing reactive dyes discharged from dyeing industries is 300,000–400,000 L ton⁻¹ (approximately) of fabric materials (Blake 1999).

The advanced oxidation process (AOP) has been used as one of the alternative ways to treat dye stuff. Among AOPs, heterogeneous photocatalysis using semiconductor is an attractive method for the degradation of dye pollutants. The semiconductor photocatalyst generates electron and hole pairs (e⁻/h⁺) upon irradiation of light energy that could be utilized in initiating oxidation and reduction reactions respectively. Of all the photocatalysts, TiO₂ has been used effectively and economically in most of the applications in view of its availability and chemical stability (Dutta 1994) and profuse applications of this technique were quoted in the literature and some excellent reviews were published (Hagfeld & Gratzel 1995; Hadjiivanov & Klissurski 1996). However, the semiconductor TiO₂ has its limitations. It can be only activated by UV radiation due to its larger band gap (3.2 eV). A second limitation is that the photogenerated electron and hole pairs are liable to recombine leading to low quantum yields (Fujishima & Honda 1972).

Hence, various attempts have been made to overcome the shortcomings of TiO₂ which include dye sensitization (Hengelin 1989; Zhang et al. 1998) and doping of transitional metal ions on the TiO₂ crystal lattice, etc. (Lakshmi et al. 1995). Even though the modified catalyst was active in visible light, the carrier recombination occurs and low activity of the semiconductor was observed (Lepore et al. 1993). Therefore, the need for a catalyst that could work in visible light and which blends both chemical stability and high activity is sought. This could be accomplished by the deposition of noble metals on TiO₂ (Valentine Rupa et al. 2007a, 2009). The noble metals deposited on TiO₂ perform the task of mediating the electrons away from the TiO₂ surface and preclude them from recombination with the holes.

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Among the reactive dyes, RB 5 has been widely used in various textile industries. As the dye is carcinogenic in nature, it is harmful and causes pollution. Hence degradation of RB 5 carries significance. Muruganandham et al. (2006) observed complete degradation of RB 5 under solar irradiation over TiO2 (Degussa P 25). Photocatalytic degradation of RB 5 carried out by Tang & Chen (2004) and Abdelkahhar et al. (2005) showed that it followed Langmuir–Hinshelwood kinetics.

Herein we report an attempt to improve the catalytic activity of TiO2 towards the photodegradation of Reactive Black 5 (RB 5) in the visible range by surface modification using noble metals. The percentages of decolourization and photodegradation were determined in terms of disappearance of colour and decrease in total organic carbon (TOC). The time taken for complete decolourization of RB 5 and percentage degradation at a fixed time were compared with TiO2 (Degussa P25). M/TiO2 catalysts where, M = Ag (Silver), Au (Gold) and Pt (Platinum) were tested for their photocatalytic activities in the decolourization and photodegradation of the actual industrial effluent and the results were discussed.

**METHODS**

**Synthesis of M/TiO2 (M = Ag, Au and Pt)**

Sol–gel technique was adopted for the synthesis of TiO2 (Sanchez & Lopez 1995). M/TiO2 catalysts were prepared by the photoreduction method (Yang et al. 1997). Calculated amounts of noble metal precursors (0.14 g of AgNO3 for 1% Ag/TiO2 or 0.15 g of AuCl4 for 1% Au/TiO2 or 0.14 g of [Pt (NH3)2]Cl2 for 1% Pt/TiO2) were taken and added to 10 g of synthesized TiO2. The colloidal solution was irradiated with a 125 W halogen lamp until complete reduction was visually observed by the formation of black precipitate for Ag/TiO2 & Pt/TiO2 and purple colored product for Au/TiO2.

**Photodegradation of RB 5**

In order to investigate the effect of noble metal deposition on the photocatalytic activity of TiO2, the experiments were carried out using TiO2 and M/TiO2 catalysts under UV and visible irradiations. 85 W tungsten and 125 W mercury lamps were used as visible and UV sources, respectively. About 200 mL of the dye solution with 1.5 g L−1 of the photocatalyst were taken in an immersion well of photoreactor made up of pyrex glass and the dye solution was stirred for 30 min in the dark to allow equilibration. The zero time reading was obtained from blank solution kept in the dark. Aliquots of 2 mL dye samples were collected at regular intervals of time, centrifuged and subsequently filtered to remove the photocatalyst. The filtrates were subjected to UV–visible spectrophotometric analysis (Hitachi-U-2000) to estimate the percentage of decolourization. TOC analysis was carried out to monitor the extent of mineralization of RB 5 at various time intervals using TOC analyser (Shimadzu, TOC-V CPH). The percentage photodecolourization and photodegradation values are within the experimental error of ±2 and ±1%, respectively.

**RESULTS AND DISCUSSION**

**Photocatalytic activities of TiO2 (Degussa P25), synthesized TiO2 and M/TiO2 catalysts in the decolourization of RB 5**

The photocatalytic decolourization of RB 5 was carried out with TiO2 (Degussa P25), synthesized TiO2 and M/TiO2 (M = Ag, Au or Pt) catalysts. The reaction conditions such as dye concentration, weight of catalyst and pH were optimized for the complete decolourization of RB 5 with TiO2 (Degussa P25). The optimized reaction conditions are pH = 7, catalyst weight 1.5 g, initial concentration of dye = 1 × 10−3 mol/L and the time taken for complete decolourisation is 6 h for UV and 7 h for visible irradiations. Under these optimized conditions photodecolourisation experiments were carried out over synthesized TiO2 and M/TiO2 catalysts under UV and visible irradiations and the results are shown in Figures 1 and 2, respectively.

The photodegradation was also monitored by a TOC analyzer (Figures 3 and 4). The percentage photodegradation of RB 5 at the irradiation time of 8 h is given in Table 1. All the above photocatalytic experiments showed that photodecolourisation and photodegradation efficiency of all the synthesized catalysts followed the trend as mentioned below:


The photocatalytic studies carried out under UV and visible irradiations leads to the following observations:

- Both decolourization and photodegradation of RB 5 by the synthesized TiO2 (Syn-TiO2) catalyst were found to be better than TiO2 (Degussa P25) under both UV and visible irradiations.
Higher percentage of decolourization and photodegradation occurred for both TiO₂ (Degussa P25) and Syn-TiO₂ under UV irradiation when compared to visible irradiation.

The photocatalytic activities of M/TiO₂ catalysts were found to be highest under both UV and visible irradiations.

- The remarkable feature of M/TiO₂ catalysts is that they decolourize and degrade RB 5 to a larger extent even under visible light irradiation than under UV irradiation.

The higher activity of M/TiO₂ catalysts under the visible region may be due to:

Table 1 | Percentage photodegradation (TOC) and apparent rate constant values in the photodecolourisation of RB 5 over different catalysts

<table>
<thead>
<tr>
<th>TiO₂ (P-25 Degussa)</th>
<th>Synthesized TiO₂</th>
<th>Pt/TiO₂</th>
<th>Ag/TiO₂</th>
<th>Au/TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degradation (%)</td>
<td>UV</td>
<td>Visible</td>
<td>UV</td>
<td>Visible</td>
</tr>
<tr>
<td>35</td>
<td>23</td>
<td>51</td>
<td>41</td>
<td>80</td>
</tr>
<tr>
<td>Rate constant k (min⁻¹)</td>
<td>–</td>
<td>$5.416 \times 10^{-3}$</td>
<td>–</td>
<td>$7.716 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
The activity of noble metals which may be attributed to the electronic interaction occurring at the contact region between the metal deposits and the semiconductor surface. This causes the removal of electrons from TiO₂ into the vicinity of the metal particle resulting in the formation of Schottky barriers leading to charge separation (Sadeghi et al. 1999).

The metal deposits acting as electron traps immobilizing the photogenerated electrons in the traps and shortly transferring them to oxygen to form highly oxidative species such as O₂⁻ (Arabatzis et al. 2005).

Further, the trapping of electrons by noble metal from TiO₂ occurring at a faster rate when compared to the electron transfer from TiO₂ to O₂. Enhanced photodegradation of the dye was observed since the recombination of e⁻/h⁺ pairs is prevented (Dawson & Kamat 2001).

Kinetics of decolourization of RB 5 using M/TiO₂ catalysts

Dye solutions (250 mL) containing initial concentrations ranging from 1 × 10⁻⁴ to 5 × 10⁻⁴ mol/L of RB 5 with constant catalyst weight (1.5 g) were decolourized using an 85 W tungsten lamp as visible light source. Since the aim of the present study is to carry decolourization under visible irradiation, experiments under visible light were carried out and the kinetics studies were made under visible light alone. The photocatalytic decolourization followed pseudo-first-order kinetics involving the Langmuir-Hinshelwood model (Sivakumar et al. 1999, 2000; Sivakumar & Shanthi 2000, 2001; Valentine Rupa et al. 2007a, b). The product of equilibrium constant k’ and the limiting rate of reaction kₑ at maximum coverage for the experimental conditions were calculated which represents the apparent rate constant, kₐₚₚ (Annadurai et al. 2000; Sivakumar & Shanthi 2000). The rate constant values (Table 1) showed that M/TiO₂ catalysts were found to be superior to both TiO₂ (Degussa P25) and Syn-TiO₂.

Photocatalytic activity of M/TiO₂ with the actual effluent sample

In order to test the photocatalytic activity of the synthesized M/TiO₂ catalysts (M = Ag, Au or Pt) with the actual effluent, samples, mainly from the dyeing of cotton fabrics using reactive dyes, were collected from a textile industry (M/s Ramkay, Tamilnadu, India). The different parameters such as pH, TOC, TDS, chloride ion concentration and turbidity were found to be 5,750 mg L⁻¹ as CaCO₃, 9,850 mg L⁻¹, 8,600 mg L⁻¹, 1.07 ppm and 110 NTU, respectively.

The industrial effluent (1 L) was first filtered to remove carbonate and hydroxides or any other insoluble matter. The pH of the effluent was increased to 7 by adding dil. NH₄OH then subjected to photocatalytic treatment. Textile dye effluent (1 L) along with 6 g of the M/TiO₂ (M = Ag, Au or Pt) catalyst was taken into the photocatalytic reactor. It was equilibrated for a few minutes with continuous stirring using a magnetic stirrer. The solution was then irradiated using a visible light source and at various time intervals, aliquots of the sample were withdrawn for determining the percentage of decolourization and photodegradation. The effluent studies showed that all the M/TiO₂ catalysts decolourize and degrade the effluent samples significantly (Figures 5 and 6). However,
these catalysts decolourized the effluent to the extent of 65–75% and degraded to the extent of 25–30% after a longer time of irradiation. The lesser percentage of both decolourisation and photodegradation may be due to the presence of an infinite number of dyes, salts, etc. in the effluent.

CONCLUSION

Photocatalytic experiments carried out towards the decolourisation of RB 5 indicated that M/TiO₂ catalysts were found to be more active even under visible irradiation when compared to UV. This significant enhancement of the photocatalytic activity of the M/TiO₂ catalysts under visible irradiation may be due to the simultaneous effects of metal deposits, which act as electron traps and enhance the electron hole separation. Among the noble metals, Au/TiO₂ catalyst was found to be the most active catalyst. This may be attributed to the small band gap value of Au/TiO₂ leading to better visible light absorption. Kinetics studies carried out with M/TiO₂ catalysts showed that the apparent rate constant values were found to be higher than the rate constant values obtained with synthesized TiO₂ and TiO₂ (P-25 Degussa).

REFERENCES


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