

Photocatalytic degradation of indigo carmine dye using TiO₂ impregnated activated carbon

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Abstract. The photocatalytic degradation of indigo carmine dye was studied using hydrothermally prepared TiO₂ impregnated activated carbon (TiO₂ : AC). A comparison between the degradation of the indigo carmine dye using commercial TiO₂ and TiO₂ : AC revealed the efficiency of the title compound. The degradation reaction was optimized with respect to the dye concentration and catalyst amount. The reduction in the chemical oxygen demand (COD) revealed the mineralization of dye along with colour removal. The active compound like TiO₂ was impregnated onto the activated carbon surface under mild hydrothermal conditions (< 250°C, P ~ 40 bars). The impregnated activated carbon samples were characterized using powder X-ray diffraction (XRD) and scanning electron microscope (SEM).

Keywords. Hydrothermal preparation; photocatalysis; indigo carmine; activated carbon; TiO₂.

1. Introduction

The past two decades have witnessed intensive studies related to the light induced mineralization of hazardous organic pollutants with the use of TiO₂ photocatalysts (Crittender *et al* 1997; Yamashita *et al* 2000; Panduranga *et al* 2001; Di Paola *et al* 2002). Photodegradation process, in general, occurs with the attack of organic substances by the activated oxygen species, such as hydroxyl radical and super oxide radical, generated on TiO₂ particulate surface by the reduction of dissolved oxygen in solution and/or oxidation of surface hydroxyl by TiO₂ (Poulios and Aetopoulon 1999; Carlos Gouvea *et al* 2000). The photocatalysis process can break down a large variety of organic compounds to CO₂, water and mineral salts, as the degradation products (Byrappa *et al* 2000). Complete mineralization of the organic substance is the greatest advantage over the conventional techniques of waste treatment (Ding *et al* 2000). The TiO₂ semiconductor has been reported to be the most promising photocatalyst because of its low cost and relatively high efficiency (Ding *et al* 2000; Neppolian *et al* 2002; Baetz and Iangphasuk 1997; Wang 2000). Most of the previous studies illustrate the use of pure TiO₂ particulates, however, TiO₂ supported or coated photocatalyst is becoming more popular in water and air purification in the recent days (Tsumura *et al* 2002). One strategy to

enhance the rate of photodegradation efficiency of TiO₂ is the use of adsorbent-like activated carbon as the support for TiO₂, which provides high concentration of target substances around the catalyst particulate (Matos *et al* 1998; Ferraz *et al* 1999). In the present work, we have used an environmentally benign and cost effective hydrothermal technology to impregnate TiO₂ onto the activated carbon surface (TiO₂ : AC) and also studied the photodegradation efficiency of the prepared TiO₂ : AC.

Removal of colour and organics by photocatalytic degradation is emerging as an effective treatment technique (Wang 2000; Neppolian *et al* 2002). Baetz and Iangphasuk (1997) and Wang (2000) reported the photocatalytic degradation of reactive azo dyes in an aqueous solution and destruction of several classes of organic dyes using TiO₂, respectively. In the present work, photocatalytic degradation of indigo carmine dye using as-prepared TiO₂ : AC has been reported.

2. Experimental

In the preparation of TiO₂ : AC, commercially available activated carbon, 1 g (BET surface area = 1025 m²/g) and TiO₂, 0.2 g (anatase) were taken in definite ratio in a Teflon liner. A required amount of an effective mineralizer (1.5 M HNO₃) was added into this mixture in the Teflon liner, which was later placed inside an autoclave. The autoclave assembly was then placed inside the furnace

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and the temperature of the furnace was set to 150°C. After the experimental run, the autoclave was quenched and the liner was taken out. The resultant product inside the liner was separated from the solution and washed with double distilled water till the pH of the wash became neutral, and then ultrasonicated. Then the product was centrifuged in three or more cycles to remove the undesired components and finally dried at 35–40°C in a dust proof environment. Further, different TiO₂ to AC ratios were considered for impregnation and the results were published elsewhere (Byrappa *et al* 2006a, b; Subramani *et al* 2007).

The TiO₂:AC prepared was characterized using a high-resolution SEM (Cameca, SX-500, France). The X-ray powder diffraction pattern was obtained using Rigaku Miniflex X-ray diffractometer, Model IGC2, Rigaku Denki Co. Ltd., Japan. The scanning range was 10–70° (2θ). The crystalline phase of TiO₂ was identified by comparison with JCPDS files (PCPDF WIN-2-01). The activated carbon used for impregnation was from M/s Ranbaxy, India and TiO₂ from M/s Sigma Aldrich. The indigo carmine dye and other chemical reagents used in the present work were from M/s Loba Chemie, India. The precursors were prepared using double distilled water.

In the photocatalytic treatment of indigo carmine dye, a known concentration (samples were prepared in molar concentration) of the dye solution (50 ml) was taken in a 500 ml clean beaker. To this dye solution a known amount of catalyst (TiO₂:AC) was added. Then the beaker was placed in a closed chamber with a UV source (Sankyo Denki, Japan, 8W), so that the solution was illuminated from the top. The distance between the UV light and the dye solution was 18 cm. The intensity of the UV light was estimated by photolysis of uranyl oxalate (Steven 1973) and it was found to be 2.3775×10^{15} quanta/s. Dye samples of about 2–3 ml were taken out at a regular interval from the test solution, centrifuged for 4–5 min at 1000 rpm and then used in the measurement of percentage transmission (%T) at 610 nm using Spectrophotometer (Model: Minispec SL 171, Elico, India). Chemical oxygen demand (COD) was estimated before and after the treatment (using the K₂Cr₂O₇ oxidation method). The photodegradation efficiency was calculated by (1). For all the photocatalytic experiments in the present work, 5×10^{-5} M indigo carmine dye, and 30 mg TiO₂:AC/commercial AC/commercial TiO₂ were used and UV light was used as the source of illumination unless specified.

$$\text{Photodegradation} = \frac{\text{Initial}_{\text{COD}} - \text{Final}_{\text{COD}}}{\text{Initial}_{\text{COD}}} \times 100. \quad (1)$$

3. Results and discussion

3.1 Characterization of TiO₂:AC

The X-ray powder diffraction patterns of TiO₂:AC and commercial AC are shown in figure 1. The identification

of crystalline phase of TiO₂ as anatase was accomplished by comparison with JCPDS file (PDF: 83-2243, PCPDFWIN-2-01), with a prominent (101) plane. High-resolution SEM studies have shown the impregnation of the TiO₂ particulates onto the carbon surface. Figure 2a shows the TiO₂ particulates adhered onto the activated carbon surface. Figure 2b shows the surface of untreated activated carbon.

3.2 Effect of TiO₂ impregnation on activated carbon

The adsorption of indigo carmine dye by untreated activated carbon (AC) and TiO₂:AC was studied, in order to determine the effect of TiO₂ impregnation on the physical properties of activated carbon, particularly, adsorption capacity. To the known concentration of dye solution, untreated AC and TiO₂:AC were added and kept in a small closed dark chamber without any light source for a period of 10 h. Figure 3 shows the adsorption of indigo carmine vs time for untreated AC and TiO₂:AC. It can be seen that between TiO₂:AC and untreated carbon, there is no prominent change in the adsorption capacity. This indicates that the TiO₂ impregnation has no much influence on the adsorption capacity of activated carbon.

3.3 Efficiency of TiO₂:AC over untreated commercial TiO₂

We have studied the degradation of indigo carmine dye using commercially available TiO₂ and compared the efficiency with that of TiO₂:AC. It was found that hydrothermally prepared TiO₂:AC shows very high efficiency when compared with the untreated commercial TiO₂. Figure 4 shows the plot of decomposition vs irradiation time for untreated TiO₂ and TiO₂:AC with varying amounts of the catalyst (10–50 mg).

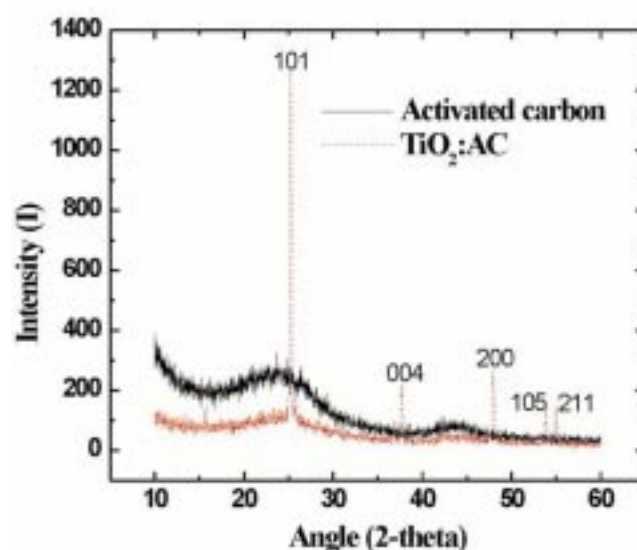


Figure 1. XRD patterns of TiO₂:AC and untreated activated carbon.

3.4 Effect of initial dye concentration

Figure 5 shows the plot of decomposition vs time with respect to different initial concentrations of the dye. It shows a high efficiency at mere low initial concentration of the dye (1×10^{-5} M), which is due to the adsorption of dye molecules onto the carbon surface and immediate degradation of the same. As the initial concentration of the dye increases, the degradation efficiency reduces (Baetz and Iangphasuk 1997; Neppolian *et al* 2002). The possible reason is that, as the initial concentration of the dye is increased, more dye molecules are adsorbed onto the surface of TiO_2 :AC. But the adsorbed dye molecules are not degraded immediately because the intensity of the light and the catalyst amount is constant and also the light

penetration is less. Also with an increase in the dye concentration, the solution becomes more intense coloured and the path length of the photons entering the solution is decreased thereby fewer photons reached the catalyst surface. Hence, the production of hydroxyl and superoxide radicals are limited or reduced. Therefore, the photodegradation efficiency is reduced. Still at higher concentration of the dye, the path length was further reduced and the photodegradation was found to be negligible.

3.5 Effect of catalyst (TiO_2 :AC)

Experiments were carried out taking different amounts of TiO_2 :AC, keeping the dye concentration constant ($5 \times$

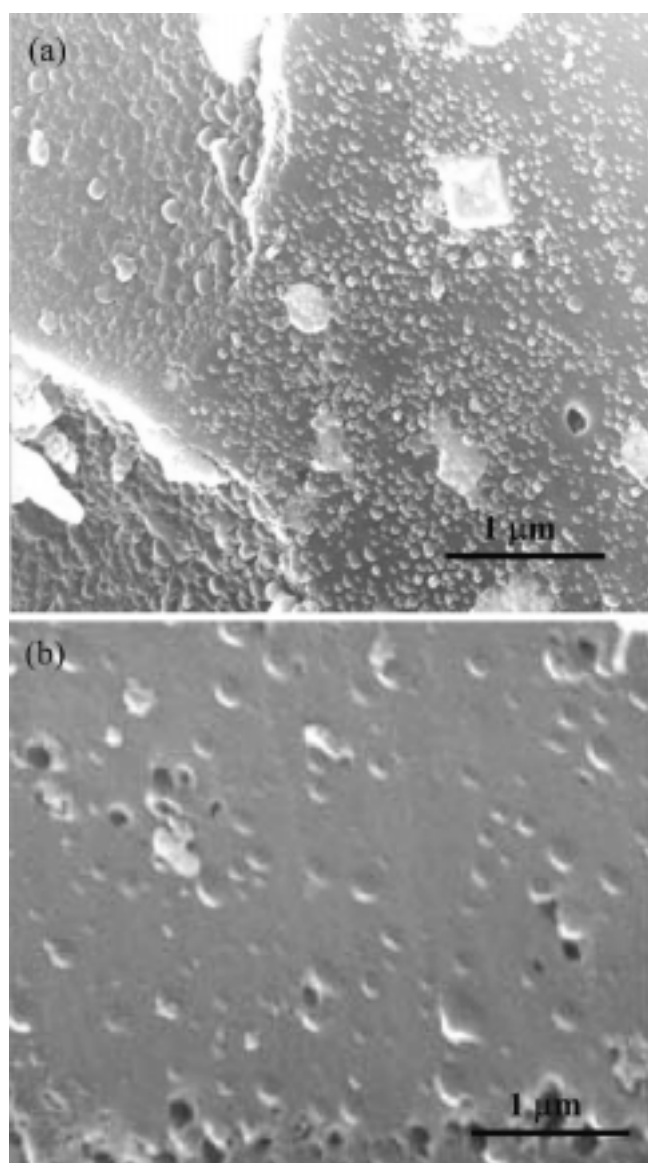


Figure 2. SEM photographs of TiO_2 :AC. (a) TiO_2 particulates adhered onto activated carbon surface and (b) surface of untreated activated carbon.

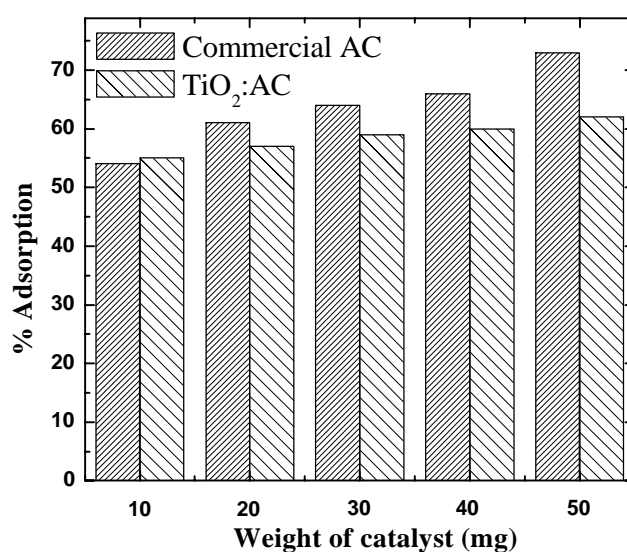


Figure 3. Percentage adsorption of indigo carmine onto TiO_2 :AC and commercial activated carbon with different weights.

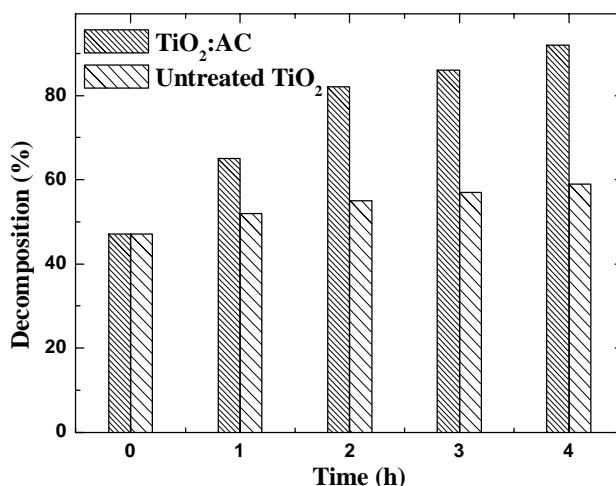


Figure 4. Comparison of TiO_2 :AC and commercial TiO_2 photodegradation efficiency with different exposure durations.

10^{-5} M), in order to obtain an optimum condition with respect to the amount of catalyst used at which the photodegradation efficiency is maximum that can save unnecessary use of excess of photocatalyst quantity-wise. Figure 6 illustrates the effect of different amounts (10–70 mg) of TiO_2 :AC on the decomposition of the dye molecules. It is clear from figure 6 that the efficiency increases up to 30 mg/50 ml of the dye, beyond which it shows a gradual reduction in the rate constant. An increase in the efficiency is due to an increase in the number of active sites on TiO_2 :AC available for the reaction, which in turn increases the rate of radical formation. The reduction in the rate constant may be due to the reduction in the penetration of light with surplus amount of TiO_2 :AC. The surplus addition of the catalyst makes the solution more turbid and light penetration is retarded. The addition of surplus catalyst also results in the deactivation of activated molecules by collision with ground state molecules. 30 mg of

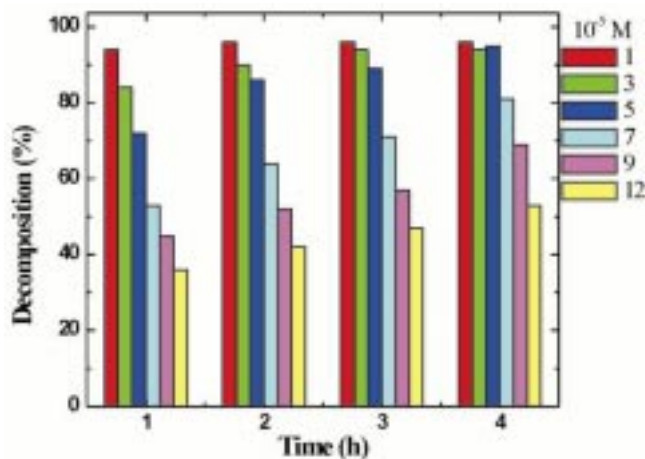


Figure 5. Effect of initial dye concentration on the photodegradation efficiency with different exposure durations.

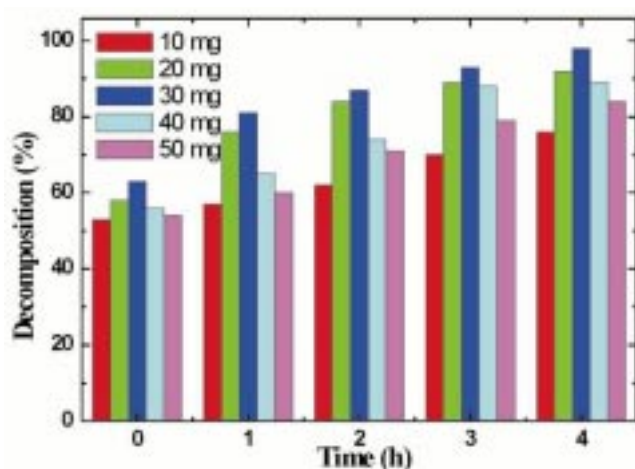


Figure 6. Effect of TiO_2 :AC weight on the photodegradation efficiency with different exposure durations.

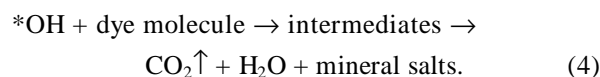
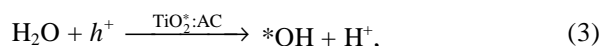
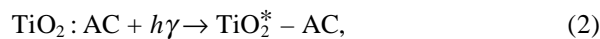
Table 1. COD values of initial and treated indigo carmine dye solution.

Dye concentration (M)	Initial COD (mg/l)	Final COD (mg/l)	Photodegradation efficiency (%)
5×10^{-5}	25.59	7.5	70.69
8×10^{-5}	40.95	7.5	81.68
1×10^{-4}	52.5	15.02	71.3
2×10^{-4}	105.0	11.26	89.27
4×10^{-4}	210.24	18.78	91.06

TiO_2 :AC/50 ml of the dye solution was found to be the optimum condition for treatment, which shows maximum photodegradation efficiency.

3.6 Reaction scheme

The possible reaction scheme for the photocatalytic degradation of indigo carmine dye is given in (2)–(4).



3.7 Estimation of chemical oxygen demand (COD)

The chemical oxygen demand (COD) is widely used as an effective technique to measure the organic strength of wastewater. The test allows measurement of waste in terms of the total quantity of oxygen required for oxidation of organic matter to CO_2 and water. The COD of the dye solution was estimated before and after treatment. The reduction in the COD values of the treated dye solution indicates the mineralization of dye molecules along with colour removal. Table 1 gives the COD values of blank and treated dye solutions. The photodegradation efficiency is calculated from (1). A maximum of 91.06% of degradation efficiency was obtained in the present study. Dye solutions treated with commercial AC in dark for a similar duration was analysed for COD, which shows an average efficiency of 48%.

4. Conclusions

Impregnation of TiO_2 onto activated carbon surface was carried out under mild hydrothermal conditions. The crystal structure and surface morphology were revealed by XRD and SEM studies. TiO_2 :AC was employed in the degradation of indigo carmine dye. A comparative study of the degradation efficiency of commercial TiO_2 and TiO_2 :AC has shown the efficiency of prepared catalyst. The optimization studies revealed the dependence of the degradation of indigo carmine on initial dye concentration

and amount of the catalyst. This study highlights that the TiO_2 :AC can be used as an alternative for the conventional isolated use of the TiO_2 photocatalyst.

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References

- Baetz R L and Iangphasuk M 1997 *Chemosphere* **35** 585
- Byrappa K, Lokanatha Rai K M and Yoshimura M 2000 *Environ. Tech.* **21** 1085
- Byrappa K, Subramani A K, Ananda S, Lokanatha Rai K M, Dinesh R and Yoshimura M 2006a *Bull. Mater. Sci.* **29** 433
- Byrappa K, Subramani A K, Ananda S, Lokanatha Rai K M, Sunitha M H, Basavalingu B and Soga K 2006b *J. Mater. Sci.* **41** 1355
- Carlos Gouvea A K, Wypych F, Sandra Mores G, Duran N, Nagata N and Peralta-Zamona P 2000 *Chemosphere* **40** 433
- Crittender J C, Rominder Suri P S, David Perram L and Hand D W 1997 *Wat. Res.* **1** 411
- Ding Z, Lu G Q and Green Field P F 2000 *J. Colloid Interf. Sci.* **232** 1
- Di Paola A, Garcia-Lopez E, Keda S I, Marchi G and Ohtani B 2002 *Catalysis Today* **75** 87
- Ferraz M C M, Maser S and Jonhaeuser M 1999 *Fuel* 1567
- Matos J, Laine J and Hermann J M 1998 *Appl. Catal. B: Environ.* **18** 281
- Neppolian B, Choi H C, Sakthivel S, Arabindoo B and Murugesan V 2002 *J. Hazard. Mater.* **89** 303
- Panduranga A, Kamala S, Uma S, Palanichamy M and Murgesa V 2001 *Indian J. Chem. Technol.* **8** 96
- Poulios I and Aetopoulon I 1999 *Environ. Tech.* **20** 79
- Steven L M 1973 *Handbook of photochemistry* (New York: Marcel Dekker) pp 124–125
- Subramani A K, Byrappa K, Kumaraswamy G N, Ravikumar H B, Ranganathaiah C, Lokanatha Rai K M, Ananda S and Yoshimura M 2007 *Mater. Letts* (submitted)
- Tsumura T, Kojitani N, Umemura H, Toyoda M and Inagaku M 2002 *Appl. Surf. Sci.* **196** 492
- Wang Y 2000 *Wat. Res.* **34** 990
- Yamashita H *et al* 2000 *Catalysis Today* **63** 63