Enhanced Photocatalystic Activity of TiO₂/SiO₂ Composite Catalysts for the Degradation of Reactive Orange 16 Under UV and Sunlight Irradiations†

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Photocatalytic decolourization and degradation of reactive orange 16 under UV and sunlight irradiations have been studied using titania catalyst synthesized *via* sol-gel method. As-synthesized TiO₂ decolourized the dye solution completely in 130 min under UV irradiation. Under sunlight irradiation, only 25-30 % of decolourization was observed in the same irradiation time. In order to improve the efficiency of titania, TiO₂/SiO₂ composites of ratio 10:90, 20:80, 30:70, 40:60, 50:50 and 60:40 have been synthesized. As synthesized catalysts have been characterized by XRD and BET analyses. Their activity towards the decolourization and degradation of reactive orange 16 were studied. As synthesized TiO₂-SiO₂ composite catalysts showed better activity than bare TiO₂. Optimization of substrate concentration, weight of catalyst and solution pH was carried out under UV irradiation. Total organic carbon analysis was carried out to determine the extent of mineralization of reactive orange 16.

Key Words: Composite catalysts, Decolourization, Degradation, Mineralization, Titania.

INTRODUCTION

Titanium dioxide (TiO₂) has been widely used as a photocatalyst for solar energy conversion and environmental applications because of its low cost, non-toxicity and good photoactivity. Even though it is an excellent catalyst, its wide band gap (3.2 eV) limits its usage in visible light[1]. The normal 3-5 % share of UV light in typical sun-light 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 pair[2,3]. More over the addition of a second metal oxide such as SiO₂, ZrO₂ or Al₂O₃, *etc.*, was also found to be an effective and excellent way of improving the photocatalytic activity of TiO₂[4-6]. Among them, SiO₂-TiO₂ materials were most widely investigated in the photocatalysis field because they exhibited higher photo-catalytic activity than pure TiO₂[7].

In general, reactive dyes are found to be the most harmful compounds in textile wastewater. Since they are water soluble, 10 % to 20 % of reactive dyes remains in the wastewater at its production level[8] and nearly 50 % of reactive dyes may lost to the effluent in the dyeing processes of cellulose fibers[9]. More-

over industrial effluents containing reactive dye has limited biodegradability under aerobic environment and many azo dyes under anaerobic conditions produce aromatic amines[10] which are highly toxic and carcinogenic nature.

In our earlier study, we reported the photocatalytic degradation of RR 120 using silver modified titania under UV and sunlight irradiations[11]. Herein we report the improved photocatalytic activity of TiO₂/SiO₂ composites towards the degradation of reactive orange 16 (Fig. 1) under UV and sunlight irradiations.
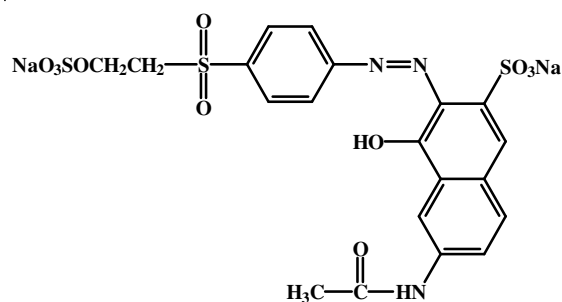

Fig. 1. Structure of reactive orange 16

EXPERIMENTAL

Commercial azo dye reactive orange 16 was purchased from Colourband Dyestuff Pvt. Ltd., Mumbai-34. Titanium tetraisopropoxide (Spectrochem, 98 % pure), acetic acid (Merck, 99 % pure), silver nitrate (Merck, 98 % pure), tetraethyl orthosilicate (TEOS), ammonia solution (25 %), ethanol and propanol were used as received. All the chemicals and dyes were used without any further purification. Double distilled water was used throughout the experimental work.

Synthesis of photocatalysts: Titania catalyst was synthesized through sol-gel method[12]. 25 mL of titanium tetra isopropoxide was mixed with 48 mL of acetic acid with constant stirring. With these, 150 mL of water was added drop wise 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 ºC followed by calcination at different temperatures at a ramp rate of 5 º/min. Monodisperse silica particles were prepared by Stober method[13] from tetraethyl orthosilicate (TEOS, BDH), ammonia (25 % NH_3 solution) and double distilled water. As synthesized silica particle was added to the titania sol to prepare 10, 20, 30, 40, 50 and 60 % of TiO_2/SiO_2 catalysts. The mixture was stirred for 8 h. Then the sol was allowed to dry at 100 ºC for 12 h followed by calcination at 200 ºC.

Characterization of photocatalyst: Powder XRD patterns were taken for all the TiO_2/SiO_2 composite catalysts using XD-2 power X-ray diffractometer (JSO-DEBYEFLEX 2002) using CuKα radiation of wavelength 1.54 nm in the range 10-70º. BET surface area of bare titania and TiO_2/SiO_2 composite catalysts were measured by N_2 physisorption at -196 ºC using Micromeritics ASAP 2020 system. Total organic carbon at different time intervals was measured using total organic carbon analyzer (Shimadzu TOC-5000) by directly injecting the aqueous dye solution after centrifugation.

Studies on photocatalytic decolourization of reactive orange 16: The photocatalytic decolourization and degradation of reactive orange 16 were carried out using bare TiO_2 and TiO_2/SiO_2 composite catalysts under UV and sunlight irradiations. For UV irradiation, a multi lamp photoreactor was used. The reactor consists of four medium pressure mercury lamps (8 W), which could emit the radiation of wave length 365 nm. Also the reactor has the reaction chamber specially designed reflector made of highly polished aluminium, provided with cooling fan at the bottom and magnetic stirrer at the center. Quartz glass tube of 100 mL capacity, 100 cm height at 40 mm diameter was used as a reaction vessel. The dye solution and the photocatalyst were continuously aerated by a pump to furnish oxygen. Also the aerator helps in mixing the dye solution and TiO_2 completely. For sunlight irrradiation, experiments were carried out under open sunlight during the month of May 2011 between 10.00 am and 2.00 pm.

100 mL of RO16 (4.05×10^{-4} M) and required amount of photocatalyst were taken in the reaction vessel. Then the suspensions were stirred for 45 min in dark so as to attain the equilibrium of adsorption of dye over the photocatalyst. The solutions were irradiated using four mercury lamps (8 W) which could emit the radiation of wave length 365 nm. At various time intervals, constant quantity of samples were withdrawn and centrifuged to remove the catalyst. The absorbance was measured at 490 nm respectively using UV-visible spectrophotometer (Hitachi U-2000) in order to determine their percentage decolourization. Total organic carbon analysis was carried out to determine the degree of mineralization of reactive orange 16.

RESULTS AND DISCUSSION

X-ray diffraction analysis: Fig. 2a shows the XRD pattern of TiO_2 with characteristic stronger anatase diffraction peaks of 101, 004, 200, 211 and 204 at 2θ values of 25.3º, 37.7º, 47.8º, 54.8º and 62.4º respectively. Using Debye Scherrer's equation ($d_{hkl} = k\lambda/(\beta \cos \theta)$) the average crystalline size of TiO_2 was determined and it was found to be 6.6 nm. Fig. 2b shows the XRD patterns of TiO_2/SiO_2 materials of ratio 10:90, 20:80, 30:70, 40:60, 50:50 and 60:40. The anatase peaks were identified at 2θ = 25.3º for all the TiO_2/SiO_2 composites. Increase in number of anatase peaks and an increase in its intensity are evident for the increase of amount of titania.
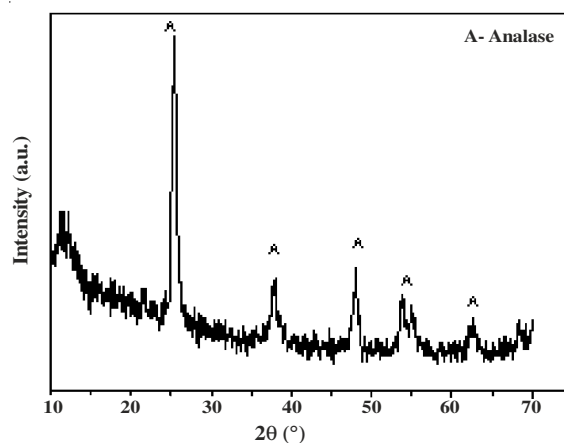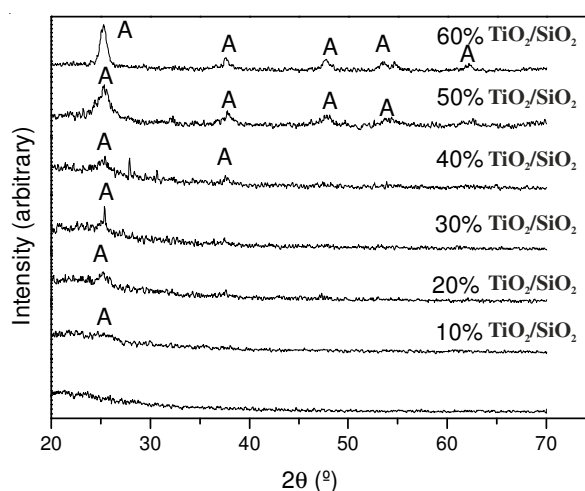

Fig. 2a. XRD pattern of TiO_2

Fig. 2b. XRD patterns of TiO_2-SiO_2 composites

BET analysis: BET surface area values of the bare TiO_2 and TiO_2/SiO_2 are given in the Table-1. The surface area of composite catalysts was found to be higher than the bare titania. This increase in surface area for the composite catalysts may

be due to the absorption ability of silica in the composite catalysts. Among the composite catalysts 40 % TiO₂/SiO₂ showed a very high surface area of 500 m²/g. But on increasing TiO₂ content further to 50 % and 60 % resulted in decrease in surface area. This can be explained by the fact that the several adsorption sites of silica are masked by TiO₂ while impregnation.

TABLE-1
BET SURFACE AREA VALUES OF ALL THE
PHOTOCATALYSTS

Photocatalysts	BET surface area (m²/g)
TiO₂	256
Ag/TiO₂	248
10 % TiO₂/SiO₂	417
20 % TiO₂/SiO₂	452
30 % TiO₂/SiO₂	474
40 % TiO₂/SiO₂	500
50 % TiO₂/SiO₂	441
60 % TiO₂/SiO₂	395

Effect of initial concentration of dye: The effects of initial concentrations for the photocatalytic decolourization of RO16 using TiO₂ were studied under UV irradiation using four mercury lamps (8 W). The initial concentration of dye varying from 4.86×10^{-4}-1.62×10^{-4} M has been analyzed for its decolourization using constant catalyst weight (1 g/L). It was observed that increase in dye concentration decreased the percentage removal[14]. This is due to a strong adsorption of dye molecule on the catalytic surface at higher concentration. This causes decrease in the path length of photon entering into the dye solution which results poor catalytic activity of TiO₂. 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[15].

Effect of weight of catalyst: The influence of the catalyst weight towards the decolourization of RO16 under UV irradiation was investigated by varying the amount of TiO₂ from 0.5-4.0 g/L. It was observed that in the absence of catalyst no decolourization occurred. Further, percentage decolourization increased with an increase of catalyst weight up to 2.5 g/L, above which efficiency decreased moderately[16] as shown in the Fig. 3. The increase in catalyst activity with the increase of weight up to 2.5 g/L may be attributed to the availability of more active sites which increases the absorption of photons. A slight decrease in the photocatalytic activity at high concentration of catalyst may be due (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 TiO₂ may take place.

$$TiO_2^* + TiO_2 \rightarrow TiO_2^\# + TiO_2 \qquad (1)$$
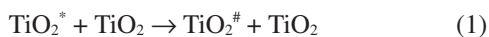
where, TiO_2^* is the dye adsorbed activated TiO₂ species and $TiO_2^\#$ is the deactivated form of TiO₂ and (iv) homogeneity of suspension disappears due to particles agglomeration and sedimentation which decreases the number of active sites. These

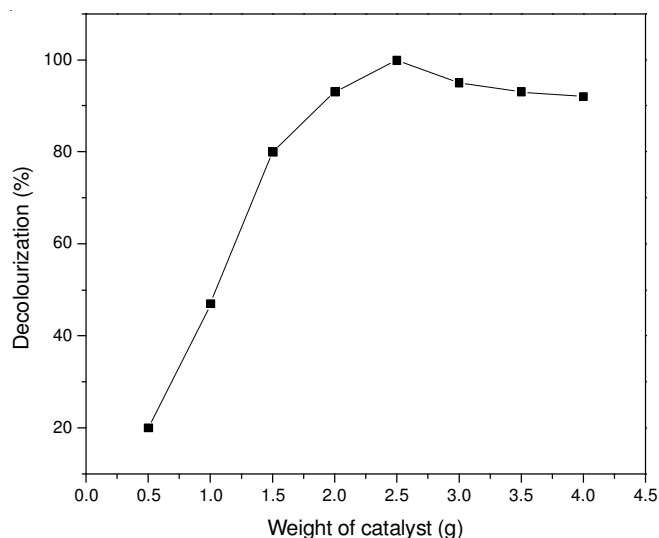cause a part of catalyst surface become unavailable for photon absorption and dye adsorption.

Fig. 3. Effect of weight of catalyst for the decolourization of RO16 under UV irradiation {Reaction conditions: [RO16] = 4.05×10^{-4} M, volume of dye solution = 100 mL, irradiation time = 120 min, T = 298 K, pH = 5}

It was noticed that there is no much difference in the percentage decolourization of RO16 for the catalyst amount ranges from 2 to 4 g/L. Hence 2 g/L was taken as an optimized amount for the decolourization process.

Effect of substrate pH: pH is one of the important parameters in determining the rate of decolourization and degradation of organic compounds. Hence the effect of pH for the photocatalytic decolourization of RO16 has been studied by varying the pH of solution using dil. H₂SO₄ and NH₄OH for acidic and basic ranges respectively. The maximum percentage decolourization of RO16 was observed at its actual pH of 5 as shown in the Fig. 4. At higher and lower pH values, the percentage decolourization decreased. Change in pH generally 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. It is well known that surface of TiO₂ becomes positively charged in acidic suspension and negatively charged in basic suspension. Since RO16 is an anionic dye, it could be attracted effectively in acidic suspension on titania surface. But stronger adsorption causes decrease of active centers on TiO₂ surface which in turn decreases the adsorption of light by the catalyst and so the initial rate of decolourization was lower in acidic solution. A decrease in percentage decolourization at higher pH was observed. This may be due to the repulsion between the anionic dye and negatively charged catalyst. Similar results were reported for several dyes[17,18].

Effect of variation of titania loading over SiO₂: In order to avoid the usage of excess catalyst it is necessary to find out the optimum loading of TiO₂ over SiO₂ for the efficient removal of pollutant. Hence TiO₂/SiO₂ materials of ratio 10:90, 20:80, 30:70, 40:60, 50:50 and 60:40 were synthesized and the optimum level of titania loading over silica material was determined in the photocatalytic decolourization of RO16.
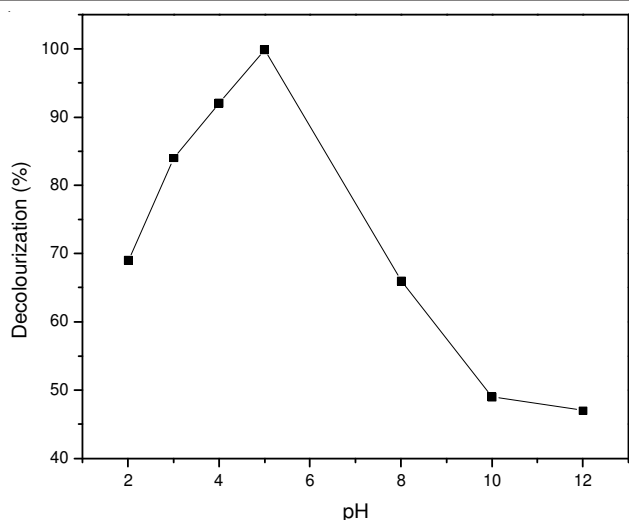
Fig. 4. Effect of pH on the decolourization of RO16 under UV irradiation {Reaction conditions: TiO_2 = 2 g/L, [RO16] = 4.05×10^{-4} M, volume of dye solution = 100 mL, irradiation time = 130 min, T = 298 K, pH = 5}

When the amount of TiO_2 loading increased, the efficiency of the photocatalyst was also increased up to a certain level (Table-2). This behaviour has been frequently observed in photocatalysis[19] and is interpreted to indicate that maximum light absorption can be achieved with sufficient amount of TiO_2 loading and the further addition of titania cannot cause an effective reaction. Further the increase in activity can be attributed to an increased surface area of titania and also the facilitation by SiO_2 through preferential adsorption of dye molecule. The decrease in the concentration of dye over TiO_2/SiO_2 catalyst is due to adsorption and photocatalytic conversion. At higher content of silica, adsorption becomes predominant than photocatalytic activity. But at higher loading of TiO_2, the active adsorption sites of SiO_2 are masked and hence the reaction is governed only by the photocatalytic activity of TiO_2. Among the composites catalysts 30 % TiO_2/SiO_2 showed a very high activity which may be due to both adsorption and photocatalytic activity. Among the composite catalysts 20 % TiO_2/SiO_2 and 30 % TiO_2/SiO_2 showed very high percentage decolourization of of RO16 (94-100 %) and hence 20 % TiO_2/SiO_2 composite catalyst was used for further photocatalytic studies.

TABLE-2
EFFECT OF AMOUNT OF TITANIA IN TiO_2/SiO_2 COMPOSITES OVER THE DECOLOURIZATION OF RO16 UNDER UV IRRADIATION

Amount of Titania (Wt. %)	10	20	30	40	50	60	100
Decolourization (%)	88	94	99.9	69	61	54	60
Irradiation time, t = 70 min							

Photocatalytic decolourization studies under sunlight irradiation: Photocatalytic activities of bare TiO_2 and 20 % TiO_2/SiO_2 were also evaluated towards the decolourization of RO16 under sunlight irradiation. As expected 20 % TiO_2/SiO_2 composite catalyst showed better decolourization efficiency than bare TiO_2. 25-30 % of decolourization could be observed in 130 min and the percentage decolourization has been increased to 65 % by 20 % TiO_2/SiO_2. More over a complete decolourization of dye solution could be achieved by 20 %/ TiO_2/SiO_2 after a prolonged sunlight irradiation (3.5 h).

Total organic carbon analysis: Total organic carbon analysis has been carried out to determine the extent of mineralization of RO16 over TiO_2 and 20 % TiO_2/SiO_2 under UV and sun light irradiations. Results show that 69 % mineralization could be achieved by TiO_2 in 6 h whereas silica composite degraded up to 78 % under UV irradiation. Under sunlight irradiation percentage degradation was measured as 39 % and 51 % for TiO_2 and 20 % TiO_2/SiO_2 respectively.

Conclusion

The reaction parameters such as substrate concentration, weight of catalyst and solution pH were optimized for the decolourization of RO16. The photocatalytic activity of TiO_2 has been compared with the activity of silica-titania composites. The activity of TiO_2/SiO_2 was found to be better. Among the composite catalysts 20 % TiO_2/SiO_2 showed very good decolourizing efficiency under both UV and sunlight irradiations.

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