

# Titania Based Catalysts for the Photo catalytic Degradation of Some Common Poluuutants

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## ABSTRACT

Dye effluents from textile industries constitute a major source of environmental problem because of their toxicity, high chemical oxygen demand content, and biological degradation. Photo catalytic degradation offers the complete removal of the pollutants with minimum energy expenditure. The present work attempts an investigation into the efficiency of titania and its modified forms as photo catalysts for the degradation of malachite green and *p*-nitro phenol.

**KEY WORDS:** Malachite green, nitro phenol, photo catalytic degradation, SBA-15, titania.

## 1. INTRODUCTION

With the advent of industrialization, environmental pollution has become a global issue threatening the health of mankind. Discharge of industrial wastes into aquatic bodies has emerged as a hazard for the existence of aquatic as well as human beings. A lot of conventional methods have been proposed to treat industrial effluents, but each method has its shortcomings. Physical methods such as flocculation, reverse osmosis and adsorption on activated charcoal are non - destructive and merely transfer the pollutant to other media, thus causing secondary pollution. In the last decade, photo catalytic degradation processes have been widely applied as a technique for the destruction of organic pollutants in wastewater and effluents, especially for the degradation of dyes. Past few years have witnessed an enormous interest being devoted to heterogeneous photo catalysis by oxide semiconductors owing to its potential applications to both environmental applications and organic synthesis.

Among the various available semiconductor oxides, titania has been the most preferred photo catalyst due to its natural abundance and properties like chemical inertness, mechanical and thermal stability. However, the optical response of titania in UV region and massive recombination of photo generated charge carriers limit its overall photo catalytic efficiency. These can be overcome by modifying the electronic band structure of titania by various strategies like coupling with a narrow band gap semiconductor, metal ion/ nonmetal ion doping, doping with two or more foreign ions, surface sensitization by organic dyes or metal complexes, noble metal deposition etc. The present study includes the synthesis of titania and supported titania systems. SBA-15 has been employed as the support material due to its uniform pore distribution and adsorption characteristics and high surface area. Malachite green and *p*-nitro phenol were selected as substrates for the investigation of photo catalytic activity.

## 2. EXPERIMENTAL

### 2.1. Preparation of Catalysts:

**2.1.1. Pure TiO<sub>2</sub>- Hydrothermal method:** 10 ml Titanium iso propoxide and 20 ml of acetic acid was taken in a beaker and magnetically stirred with drop wise addition of distilled water (200 ml) from a dropping funnel. The clear sol obtained was sonicated for 3 hours and then transferred to an autoclave and placed in the oven for overnight at 110°C. The resultant solution was subjected to solvent evaporation and dried in an air oven at 110°C. It was then finely powdered and calcined at 500°C for about 5 hours.

**2.1.2. Mesoporous SBA-15:** Polycrystalline powders of the mesostructural siliceous SBA-15 were prepared by procedure adopted by Zhao *et al* using tri-block copolymer (Pluronic P123) template. 8 g of tri-block copolymer, poly (ethylene oxide) - poly (propylene oxide) - poly (ethylene oxide) (P123 Aldrich) was dissolved in 60 ml deionized water and 2 M HCl was added with stirring until the pluronic was dissolved completely. This was followed by the addition of Tetra ethoxysilane (TEOS, Aldrich). After stirring for 24 hrs, the mixture was transferred to an autoclave at 110°C for 48 hrs. The precipitate was filtered and then washed with deionized water before being dried at room temperature followed by calcination in a muffle furnace at 550°C for 6 hrs.

**2.1.3. TiO<sub>2</sub>-SBA:** Titania doped with SBA was prepared by *in situ* addition during sol preparation. 1 g SBA was added to the clear sol obtained after drop wise addition of water to mixture of titanium iso propoxide and acetic acid. This was followed by sonication for three hours. The sol after transferring to an autoclave was kept at 110°C overnight followed by solvent evaporation. The powder after oven drying was calcined at 500°C. Different

compositions of TiO<sub>2</sub>-SBA-15 were prepared with SBA: TiO<sub>2</sub> molar ratios 3:1, 1:1 and 1:3 and designated as ST1, ST2 and ST3 respectively.

**2.2. Characterization:** The recent technological advances have resulted in the development of several modern characterization techniques, a proper utilization of which provides a greater insight into the molecular aspects of the adsorbent and the nature of the active sites involved. The prepared samples were characterized by XRD, UV-DRS and TEM.

**2.3. Photo catalytic activity studies:** The photo catalytic activity of the prepared systems (pure titania, SBA-15 doped titania) were scanned towards the degradation of malachite green and nitro phenol under UV light. Stock solutions were prepared by weighing out appropriate quantities of the samples. Solutions of appropriate concentrations were made from this stock solution by dilution with distilled water. Experiments were carried out in a photochemical reactor (PSAW) at lamp intensity of 64 W. 0.01g of the catalyst and 10 ml test solution was used in each run. After exposure to radiation for definite time interval, the solution was centrifuged in a high speed centrifuge and the absorbance of the residual solution was measured using a UV Visible Spectrophotometer (Thermo scientific - Evolution 220) at their respective  $\lambda_{\text{max}}$  values (620 nm for malachite green and 320 nm for nitro phenol). From the absorbance values, the percentage degradation was calculated. Influence of different experimental parameters like initial dye concentration, time of contact, adsorbent amount etc. was determined.

### 3. RESULTS AND DISCUSSION

#### 3.1. Physicochemical characterization:

**3.1.1. XRD:** XRD patterns of pure Titania and representative SBA-TiO<sub>2</sub> are presented in Figure.1. Pure titania showed the presence of only the photo catalytically active anatase phase  $2\theta = 25.5$  (1,0,1 plane), 38 (0,0,4) plane, 48.3 (2,0,0) plane, 54 (1,0,5) plane, 55.2 (2,1,1) plane, 63 (2,0,4) plane, 68.9 (1,1,6) plane. No characteristic peaks of rutile or brookite phase were observed indicating the high purity of the system. Presence of mesoporous support resulted in a lowering of crystallinity which is indicated by the lowering of intensity in XRD pattern. An increase in the amount of mesoporous support resulted in a further lowering of intensity of XRD patterns which implies a lowering of the degree of crystallization. This may be accounted as being due to hindrance to agglomeration of titania particles in presence of the support material. This, in turn, leads to enhancement in surface area of the system. The particle size as calculated from Scherrer equation is given in Table 1

**3.1.2. UV-DRS analysis:** UV-VIS diffuse reflectance spectrum of the samples is sketched in Fig 2. Pure titania shows a sharp reflection peak at around 380 nm. UV-DRS of modified systems also showed a similar pattern indicating that there was not much alteration in the optical response of the system. This was confirmed by the band gap values calculated using KubelkaMunk plots (Table.1)

**3.1.3. TEM analysis:** TEM images (Fig.3) indicate high uniformity and nano dimensions of the samples.

**3.2. Photo degradation studies:** Photocatalytic efficiency of the prepared systems was determined selecting the degradation of *p*-nitrophenol and malachite green as test reactions. The influence of experimental conditions on the activity was also estimated.

The activity of the different prepared systems for the degradation of nitro phenol and Malachite green are shown in Table 2. 10<sup>-4</sup> solutions were used in both the cases. SBA supported systems showed a drastic enhancement in the activity for the degradation of malachite green whereas only a mild improvement was observed in the case of nitro phenol degradation. The enhanced photo degradation of the dye may be partially attributed to the combined effect of adsorption as well as photo degradation.

**3.3. Influence of time:** The degradation of nitro phenol and malachite green was conducted over the different catalysts. The percentage degradation was determined by measurement of absorbance at regular time intervals and the result is presented in Fig 4. Percentage degradation showed an increase with time which leveled off after a certain interval.

**3.4. Influence of dye concentration:** In order to determine effect of dye concentration on catalytic activity, a series of experiments were carried out in presence of Ultra Violet light with different dye concentrations. Time of run was kept constant at 10 minutes and the results are shown in Table 3.

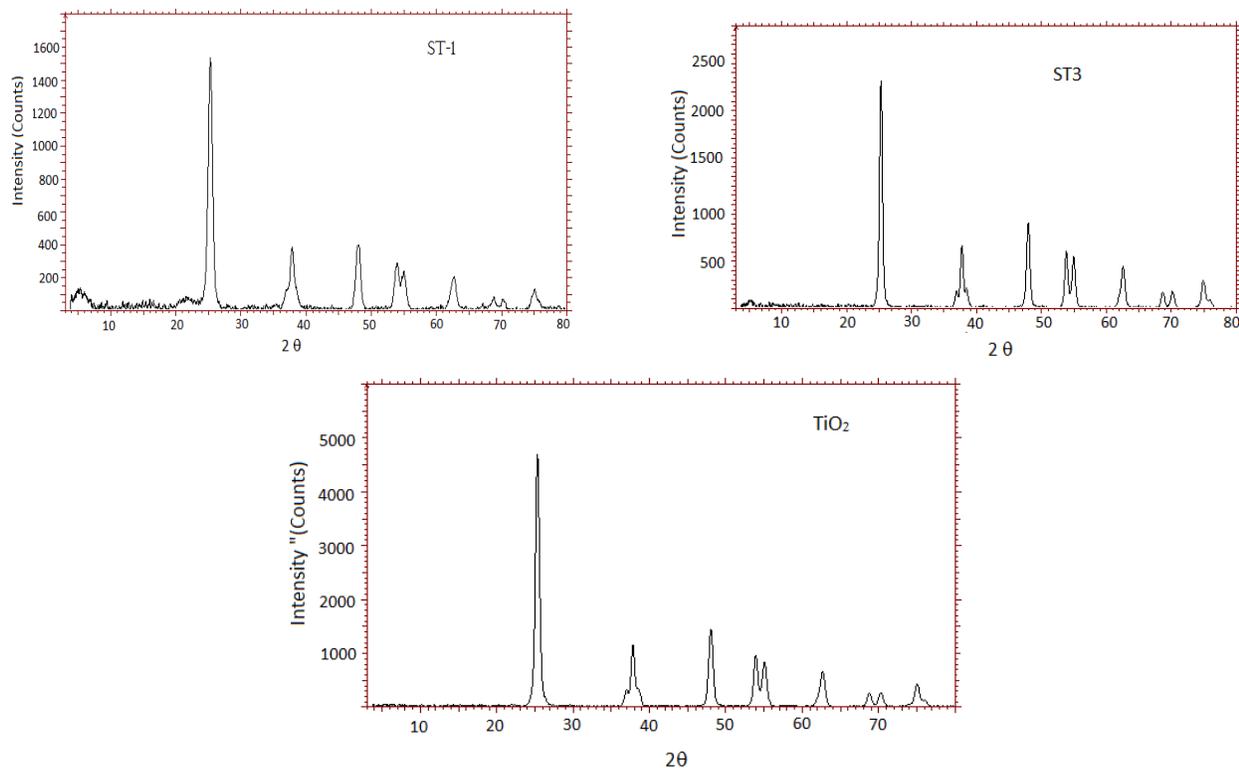


Fig.1.XRD patterns of representative samples

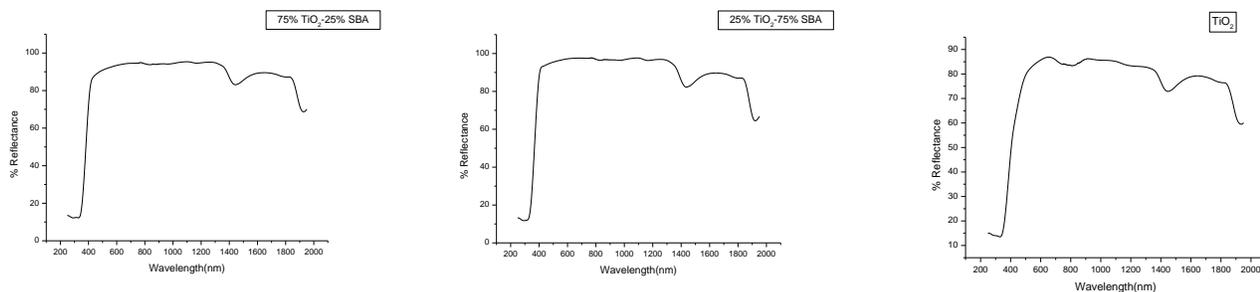


Fig.2. UV-DRS Plots of different samples

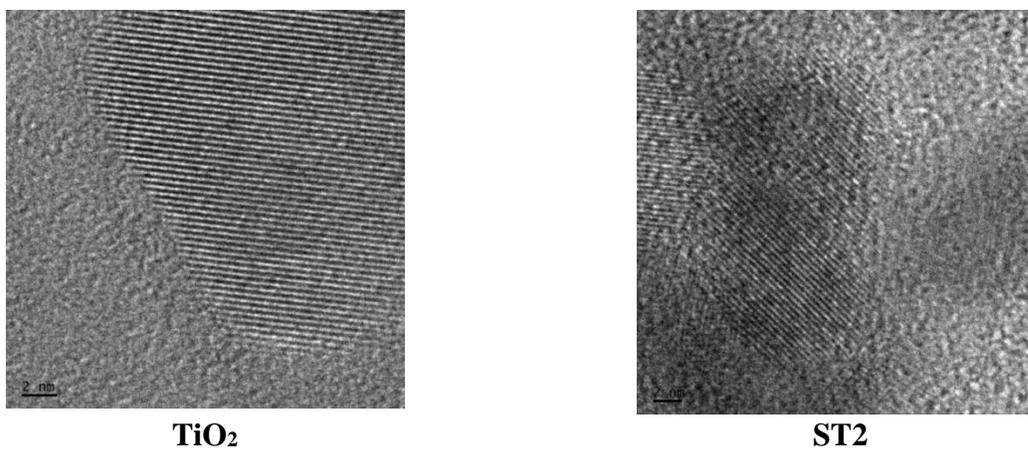


Fig.3.TEM Images of representative samples

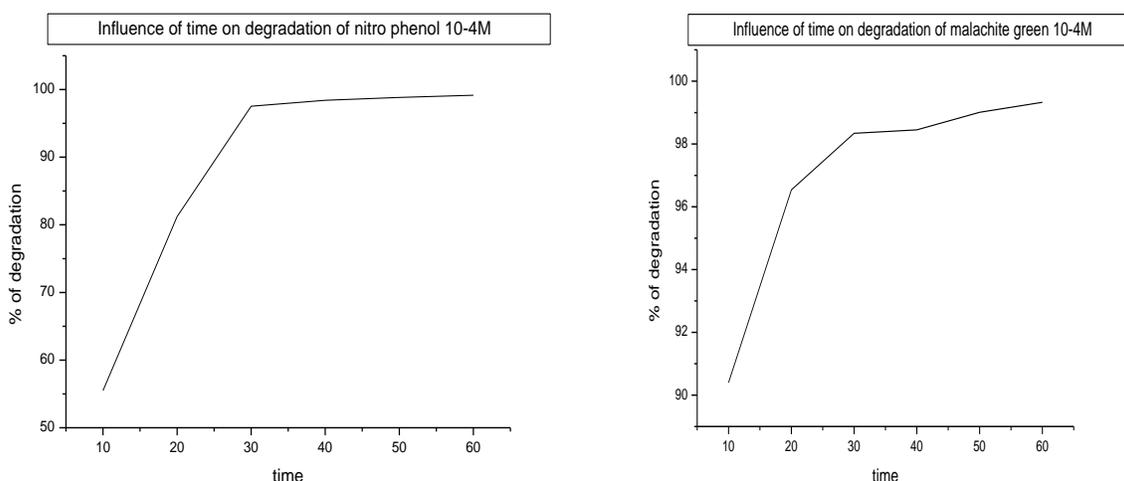


Fig.4. Influence of time on Photodegradation 10<sup>-4</sup> solutions, 0.01 g ST3 catalyst

Table.1. Band Gap and crystallite size of different systems

Samples	Band gap (eV)	Crystallite size (nm)
TiO <sub>2</sub>	3.28	18.5
ST1	3.18	5.8
ST2	3.21	8.3
ST3	3.14	10.7

Table.2. Comparative evaluation of catalytic activity

% of TiO <sub>2</sub>	% Degradation	
	Malachite green	p-Nitrophenol
TiO <sub>2</sub>	25.9	44.93
ST1	56.7	51.55
ST2	87.1	52.40
ST3	90.4	55.49

10<sup>-4</sup> M Solution, Time of run -10 min

Table.3. Variation in activity with concentration

	p- Nitro phenol		Malachite Green	
	Conc	% degradation	Conc	% degradation
ST1 catalyst 10 min	1x10 <sup>-5</sup>	99.15	1x10 <sup>-4</sup>	56.70
	2x10 <sup>-5</sup>	99.06	2x10 <sup>-4</sup>	50.01
	4x10 <sup>-5</sup>	97.11	4x10 <sup>-4</sup>	49.06
	6x10 <sup>-5</sup>	95.85	6x10 <sup>-4</sup>	30.38
	8x10 <sup>-5</sup>	88.97	8x10 <sup>-4</sup>	24.41

#### 4. CONCLUSION

Hydrothermal method was found to be suitable for the formation of ordered mesoporous structures with high surface area. The photo catalytic degradation of malachite green and nitro phenol proceeded effectively over the prepared systems. The catalyst composition as well as the effective surface area plays a significant role in deciding the photo catalytic efficiency. Among the different systems, ST3 was found to be the most efficient which may be due to the relatively high content of titania.

## 5. ACKNOWLEDGEMENT

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## REFERENCES

Ciambelli P, Sannino D, Palma V, Vaiano V, and Mazzei R.S, Intensification of gas-phase photo oxidative dehydrogenation of ethanol to acetaldehyde by using phosphors as light carriers, *Photo chem. Photo biol. Sci.*, 10, 2011, 414.

Lachheb H, Puzenat E, Houas A, Ksibi M, Elaloui E, Guillard C, Herrmann J.M, Photo catalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Brilliant Green, Congo Red, Methylene Blue) in water by UV-irradiated titania, *Appl. Catal. B: Environmental*, 39, 2002, 75.

Li X.Z, Li F.B, Study of Au/Au<sup>3+</sup>-TiO<sub>2</sub> Photo catalysis towards Visible Photo oxidation for Water and Wastewater Treatment, *Environ. Sci. Technol.*, 35, 2001, 2381-2387.

Mohapatra P, Parida K.M, Photo catalytic activity of sulfate modified titania 3: De colorization of methylene blue in aqueous solution, *J. Mol. Catal. A: Chemical*, 258, 2006, 118.

Murcia J.J, Hidalgo M.C, Navyo J.A, Vaiano V, Ciambelli P, Sannino D, Photo catalytic ethanol oxidative dehydrogenation over Pt/TiO<sub>2</sub>: Effect of the addition of blue phosphors, *Int. J. Photo energy*, 2012, Article ID 687262, doi:10.1155/2012/687262.

Tang W.Z, An H, UV/TiO<sub>2</sub>, Photo catalytic oxidation of commercial dyes in aqueous solutions, *Chemosphere*, 31, 1995, 4157.

Yu H, Irie H, Shimodaira Y, Hosogi Y, Kuroda Y, Miyauchi M, Hashimoto K, An efficient visible-light-sensitive Fe(III)-grafted TiO<sub>2</sub> photo catalyst, *J. Phys. Chem. C*, 114, 2010, 16481.

Zhao D, Huo Q, Stucky G.D, Tri block-Copolymer-Directed Syntheses of Large-Pore Mesoporous Silica Fibers, *Chem. Matter.*, 10, 1998, 2033.

Zhao J, Chen C, Ma W, Photo catalytic degradation of organic pollutants under visible light irradiation, *Topics in Catalysis*, 35, 2005, 269-278.