

## Photocatalytic Degradation of Crystal Violet (C.I. Basic Violet 3) on Nano TiO<sub>2</sub> Containing Anatase and Rutile Phases (3:1)

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### Abstract

The photocatalytic oxidation of crystal violet, a triphenyl methane dye in aqueous solutions was investigated with nanoanatase TiO<sub>2</sub> containing Anatase and rutile phases in the ratio of 3:1, under UV light by using a 125 W high pressure mercury vapor lamp as the source. The dye degradation using Ag<sup>+</sup> doped TiO<sub>2</sub> and nanoanatase TiO<sub>2</sub> was compared. An optimum catalyst dose of 1 g/L was used. It was found that nanoanatase TiO<sub>2</sub> had a higher efficiency than the Ag<sup>+</sup> doped Titanium di Oxide. Nanoanatase TiO<sub>2</sub> was found to be easy to separate from the treated effluent by simple centrifuging. The degradation of the dye of initial concentration: 5×10<sup>-5</sup> mol/L, using nanoanatase TiO<sub>2</sub> was greater than 99.5% on UV illumination for 45 minutes and that with Ag<sup>+</sup> doped Titanium di Oxide as catalyst, was found to be 75% for 45 minutes of illumination. The effects of various parameters such as pH; initial dye concentration and catalyst dose on the reaction rate were studied. The kinetics of degradation fit well to Langmuir-Hinshelwood rate law.

**Keywords:** Crystal violet; Photocatalysis; Anatase

### Introduction

Photolysis is the process of decomposition in the presence of a form of light, whereas photocatalysis is defined as the acceleration of a photochemical reaction in the presence of a catalyst. Catalysts are the substances which are used in order to provide an alternative path for a reaction to take place, which is done in order to enhance the rate of a reaction. Now the removal of the color from the waste water discharge from various industries such as the textile, paper, plastic, leather, ink etc. is an active issue all over the world. Use of dyes in these industries further asserts the issue at hand. There are many classes of dyes such as acidic, basic, neutral, azo, direct, reactive etc. Azo dyes are the most frequently used; these contain one or more azo bonds in their structure (-N=N-). These dyes can be toxic and potentially carcinogenic [1-5].

There have been many ways to treat the dye effluents, viz. biological methods, flocculation, reverse osmosis, adsorption on activated charcoal, chemical oxidation and advanced oxidation processes (AOPs). AOPs have been proven to be the most efficient way to degrade the dye effluents. The term AOP is often used when the oxidative capacity of the parent oxidant is enhanced to make the oxidation process more efficient. In water treatment, AOPs are generally a combination of processes involving O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and UV light [6]. Photocatalysis using TiO<sub>2</sub> is one of the most efficient methods to degrade dyes/pollutants. Crystal violet or Gentian violet is a triarylmethane dye (Figure 1).

Crystal violet has been used for various purposes; it is extensively used in textile dyeing and paper coloring. In the present work the photocatalytic degradation of this dye will be carried out using the nanoanatase TiO<sub>2</sub> catalyst in the photo reactor. Effects of various factors such as concentration of the dye, dose of photocatalyst, presence of light etc. have been studied [7].

### Materials and Methods

Crystal violet dye was purchased from Merck India. Millipore water was used as the solvent for all the studies. A 125 W high pressure mercury vapor lamp was purchased from Samson India and was used as the light source.

### Preparation of photocatalyst

The nanoanatase TiO<sub>2</sub> contains anatase and rutile phases in a

ratio of about 3:1. Transmission electron microscopy showed that the anatase and rutile particles separately form their agglomerates. The average sizes of the anatase and rutile elementary particles are 85 and 25 nm, respectively. Diffuse reflectance spectra of the TiO<sub>2</sub> powder were successfully traced by physically mixing pure anatase and rutile particles in a ratio of 3:1. By the HF treatment of the TiO<sub>2</sub> powder, pure rutile particles were isolated [8]. All these results indicate that the rutile phase does not exist as an over layer on the surface of anatase particles, but it exists separately from anatase particles. The X-ray diffraction (XRD) patterns of catalysts were recorded on a Siemens (D-5005) diffractometer with a scan rate of 2 min<sup>-1</sup>. JEOL JEM-200 CX operated at 200 kV was used to carry out Transmission Electron Microscopy (TEM) studies [9-11]. We also found that photocatalytic oxidation of naphthalene is inefficient on pure anatase and rutile powders. However, the reaction is very efficient on the P-25 powder, as well as on a mixture of pure anatase and rutile particles. Under the conditions of the photocatalytic reactions, the anatase and rutile agglomerates are considered to be decomposed, and the anatase and rutile particles are in contact, leading to a synergy effect.

### Instrumentation

The instruments used for the study were PG Instruments T60 UV-Vis Scanning Spectrophotometer, 125 W high pressure mercury vapor lamp (Samson India), General Purpose Laboratory Centrifuge (Laboratory Centrifuge) Remi R-40 and Remi magnetic stirrer [12].

The experimental setup consists of a quartz tube along with a jacket with dimensions of 3.4 cm inner diameter, 4 cm outer diameter and

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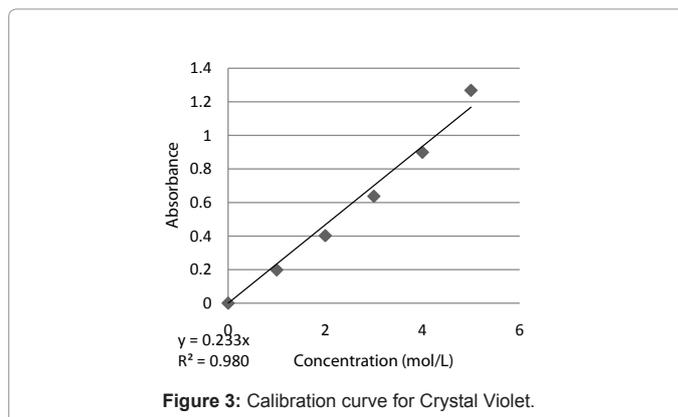
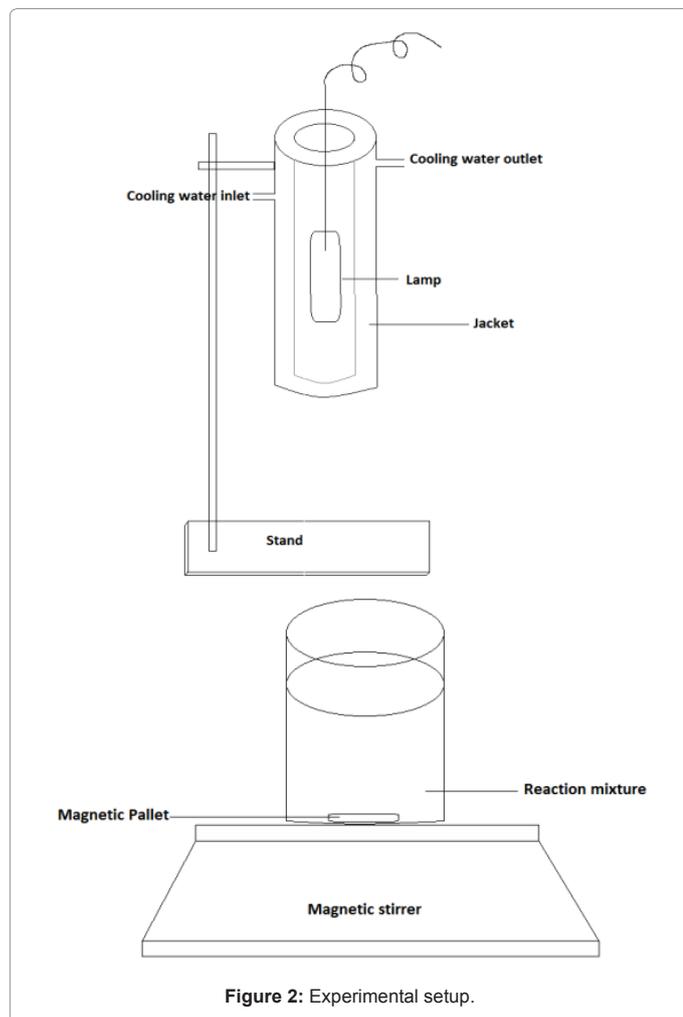
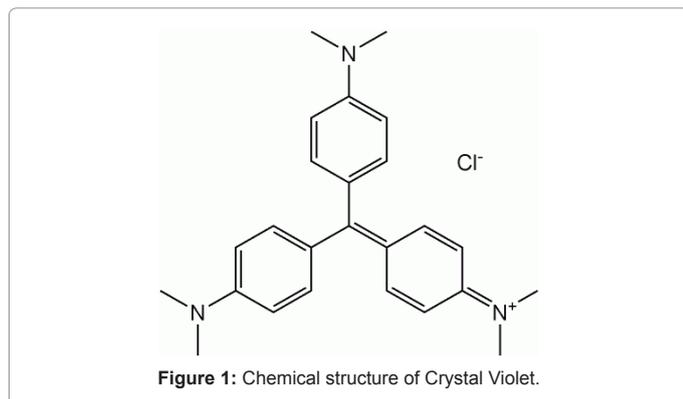
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21 cm length and a glass reactor of 7.2 cm length and 5.2 cm inner diameter. The outer glass shell is removed and placed inside the quartz tube for use. The ballast and capacitor were connected in series with the lamp to avoid fluctuations in the input power supply. Submersible water pump was used for circulating water through the jacket of the quartz tube to avoid heating due to dissipative loss of UV light.

### Adsorption and direct photolysis

The adsorption studies were conducted in the dark conditions using



$5 \times 10^{-5}$  dye solution (100 ml) with 1 g/L nanoanatase TiO<sub>2</sub> catalyst. Aliquots were taken at regular time interval and centrifuged. The dye concentration was measured spectrophotometrically. Direct photolysis of the dye was also studied in the absence of the photocatalyst.

### Photocatalytic degradation

A  $5 \times 10^{-5}$  mol/L stock solution was prepared with millipore water from which an experimental solution was derived of  $2.5 \times 10^{-5}$  mol/L concentration. The experimental setup as shown in figure 2 consists of a 100 ml beaker placed upon a magnetic stirrer on top of which a 125 W high pressure mercury lamp emitting UV light of wavelength  $\sim 365$  nm was placed [13-15]. This served as the light source for the Photocatalysis. 40 ml of the working solution was taken in the beaker and was added nanoanatase TiO<sub>2</sub> to it. Catalyst dose of 1 g/L was added to the dye solution. The height of the solution in the beaker was 4 cm. The solution was stirred in the dark for about 30 min to establish adsorption equilibrium, the zero time reading taken after the equilibrium was reached and the solution was irradiated. Aliquots were taken at regular time intervals and were analyzed using the spectrophotometer. The percentage degradation and the percentage decolouration were calculated [16,17].

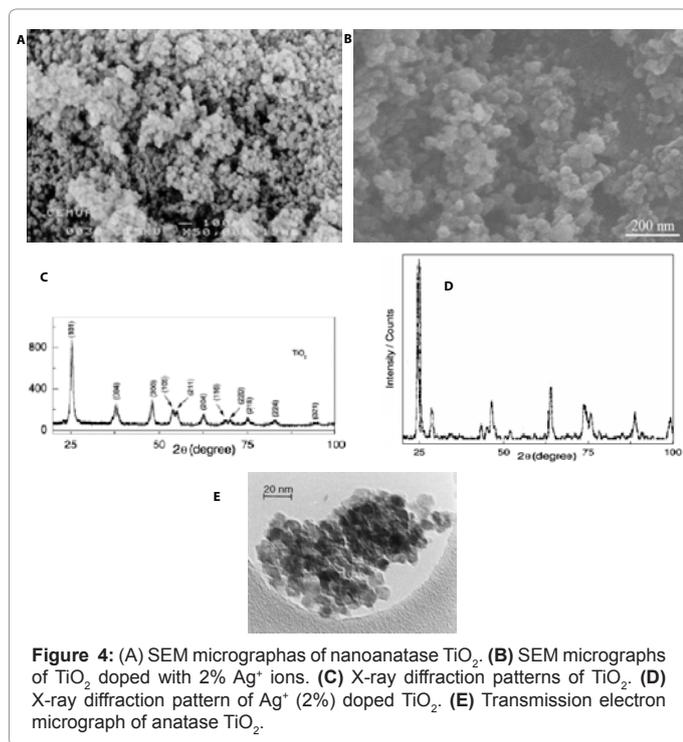
## Results and Discussions

### Calibration

The absorbance of Crystal violet at various dye concentrations was measured. Absorbance vs. Concentration was plotted and it was found to be a linear curve as shown in figure 3.

### Catalyst characterization

The catalyst nanoanatase TiO<sub>2</sub> was characterized by a scanning electron microscope. Scanning electron microscopy affirmed that the anatase and rutile particles separately form their agglomerates. The particle size for nanoanatase TiO<sub>2</sub> was found to be 19 nm as shown in figures 4a and 4b. The SEM micrographs of TiO<sub>2</sub> doped with 2% Ag<sup>+</sup> ions were also analyzed and found to be 200 nm in size. Ag-doping can induce electron-hole separation and as an electrical field aiding electron excitation. Normally, Ag atoms deposit on the surface of TiO<sub>2</sub> or form a core-shell structure such as Ag-TiO<sub>2</sub>. XRD patterns of pure TiO<sub>2</sub> and Ag<sup>+</sup> TiO<sub>2</sub> are shown in figures 4c and 4d respectively. The pattern can be indexed to TiO<sub>2</sub> in anatase phase only. It may be noted that the background of the X-ray pattern is flat indicating that TiO<sub>2</sub> is crystalline. The lattice parameter for pure nanoanatase TiO<sub>2</sub> is  $a=3.7865$  Å and  $c=9.5091$  Å. There was no significant change in the lattice parameters in case of Ag<sup>+</sup> doped TiO<sub>2</sub>.



The crystallite size is determined from XRD pattern using Sherrer formula.

$t = 0.9\lambda / \beta \cos\theta$ . Here "t" is in nm,  $\lambda$  is the wavelength of X-ray in Å,  $\beta$  is FWHM in radians and  $\theta$  is the Bragg angle.

Transmission electron micrographs of TiO<sub>2</sub> show fine crystals with the mean size of  $18 \pm 2$  nm which agrees well with the XRD measurements. Typical TEM image of TiO<sub>2</sub> is shown in figure 4e.

### Photocatalytic degradation

The maximum wavelength observed for the crystal violet was 583 nm and the degradation of the crystal violet solution of  $2.5 \times 10^{-5}$  mol/L was observed to be >99% and the degradation for a concentration of  $5 \times 10^{-5}$  mol/L was found to be >99.9%. These results were obtained after an irradiation time of about 25 min and 45 min respectively, as shown in the figure 5.

When a photon of UV light strikes the surface of TiO<sub>2</sub> a valance bond electron moves into the conduction band thus forming a positively charged hole in the valance band. The conduction band electron and the valance band holes then migrate to the oxide surface and react with the chemisorbed O<sub>2</sub> or OH/H<sub>2</sub>O molecules to generate reactive oxygen species such as O<sub>2</sub><sup>-</sup>, HOO, OH<sup>-</sup> radicals, which attack the dye molecules and the degradation commences. Alternatively, the electron in the conduction band can be picked up by the adsorbed dye molecules, leading to the formation of dye radical anion. When the photocatalyst titanium-di-oxide absorbs ultraviolet radiation from sunlight or illuminated light source (flouroscent lamps), it will produce pairs of electrons and holes. The electron of the valance band of titanium-di-oxide becomes excited when illuminated by light. The excess energy of this excited electron promotes the electron from the valance band to the conduction band of titanium-di-oxide, therefore creating the the negative electron (e<sup>-</sup>) and positive hole (h<sup>+</sup>) pair. This stage is referred to as semiconductor's photo excitation state. The energy difference between the valance band and conduction band is known as band gap.

Wavelength of light necessary for photoexcitation is:

$$= \text{Planck's constant} / \text{Band gap (eV)}$$

$$= 1240 / 3.2$$

$$= 388 \text{ nm.}$$

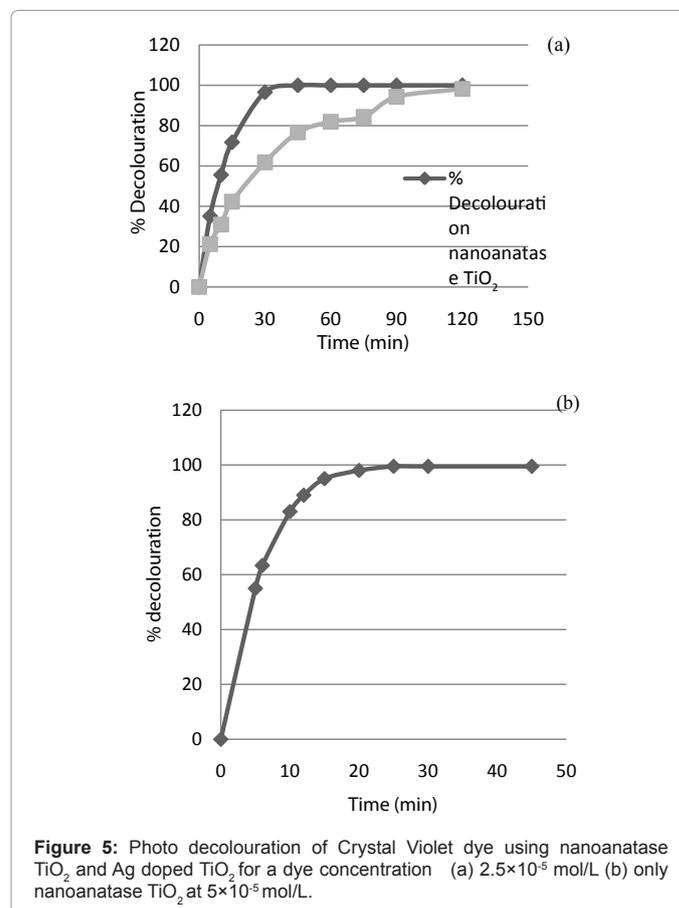
The positive hole of TiO<sub>2</sub> breaks apart the water molecule from the moisture in the air and forms hydrogen H<sub>2</sub> gas and hydroxyl radical (OH<sup>-</sup>). The negative electron reacts with O<sub>2</sub> molecule to form super oxide anion. This cycle continues as long as light is available. Alternatively, the electron in the conduction band can be picked up by the adsorbed dye molecules, leading to the formation of dye radical anion and subsequent reaction of the dye radical anion can lead to the degradation of the dye. Also the adsorbed dye molecules may be directly oxidised by the valence band holes to form dye radical cations which ultimately cause dye degradation [12].

### Adsorption and direct photolysis

The results of adsorption studies of dye solution ( $5 \times 10^{-5}$  mol/L) with nanoanatase TiO<sub>2</sub> (1 g/L), are shown in the figure 6 nanoanatase TiO<sub>2</sub> showed 25% adsorption after 120 min. Direct photolysis of the dye solution by constant stirring and irradiation in the absence of a photocatalyst showed no considerable degradation even after 2 hours (Table 1).

### Kinetic analysis

The Langmuir-Hinshelwood kinetic model illustrates the



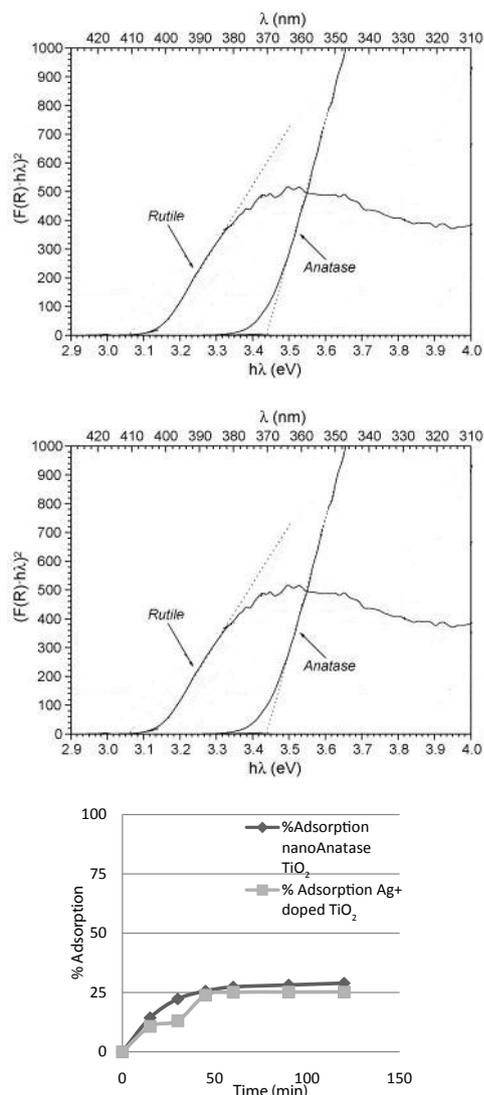


Figure 6: Adsorption of dye using nanoanatase TiO<sub>2</sub> catalyst at dye concentration 5×10<sup>-5</sup> mol/L.

Time	% Adsorption with nanoanatase TiO <sub>2</sub>	% Adsorption with Ag <sup>+</sup> doped TiO <sub>2</sub>
0	0	0
15	14.369	10.73
30	22.3	13.14
45	25.62	23.9
60	27.34	25.12
90	28.17	25.19
120	28.92	25.14

Table 1: Adsorption studies of dye solution with nanoanatase.

dependence of the rate of dye degradation on the concentration of the dye, which is given by

$$r = \frac{dc}{dt} = \frac{kKc}{(1+Kc)}$$

In this equation KC is almost 1, hence we can neglect KC which gives us the equation which can be simplified into a pseudo first order equation

$$\ln\left(\frac{C_0}{C}\right) = kKt = k_{app}t$$

Here, r is the rate of degradation (mol/L/min), C<sub>0</sub> is the initial concentration of the dye solution (mol/L/min) and C is the concentration of the dye solution at a time t (mol/L/min), t is the time of irradiation (min), and K the adsorption coefficient of the dye onto the photocatalyst particles (L/mg). The graphs obtained in the figure 7 were found to be in the pseudo first order as confirmed by the linear transform in the ln (C<sub>0</sub>/C)=k<sub>app</sub>t. The rate constants were obtained as follows,

At 5×10<sup>-5</sup> mol/L: k<sub>app</sub>=0.1237, R<sup>2</sup>=0.9269

At 2.5×10<sup>-5</sup> mol/L: k<sub>app</sub>=0.2022, R<sup>2</sup>=0.9655

### Effect of initial dye concentration

The effect of dye concentration on its degradation was studied. Figure 8 shows the percentage degradation at various initial dye concentrations. At higher concentration, the degradation was found to

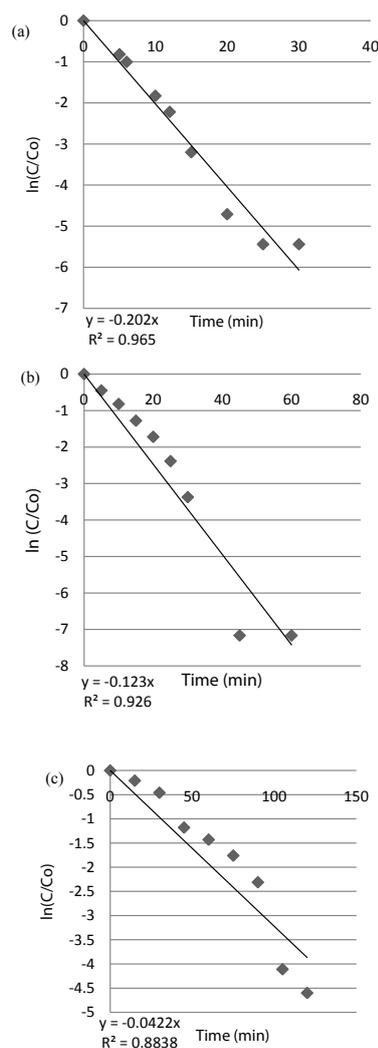


Figure 7: Kinetic analysis (a) 2.5×10<sup>-5</sup> mol/L using nanoanatase TiO<sub>2</sub> (b) 5×10<sup>-5</sup> mol/L. (c) 2.5×10<sup>-5</sup> mol/L using Ag<sup>+</sup> doped TiO<sub>2</sub>.

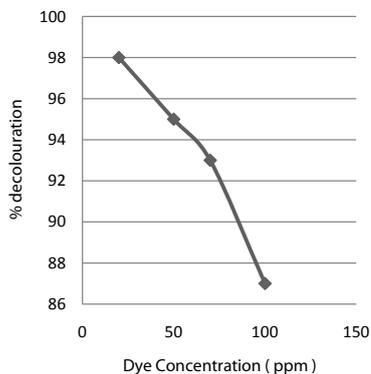


Figure 8: Initial dye concentration vs. percentage decolouration.

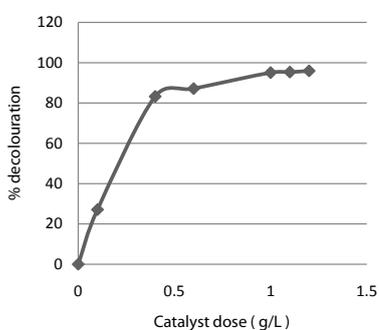


Figure 9: Effect of catalyst dose.

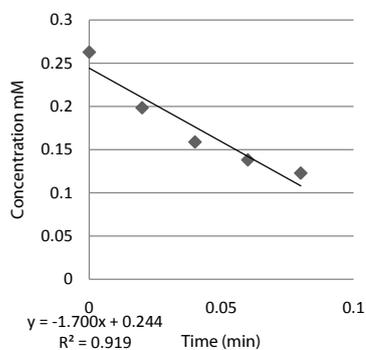


Figure 10: Concentration vs. Time.

be less. This may be because as the concentration of the dye increases, the catalyst particles adsorb more and more dye. Hence, the ultraviolet (UV) light does not reach the catalyst surface. At higher concentration, the light travels up to a smaller distance.

### Effect of catalytic dose

The dye solution (20 ppm) was irradiated for 120 min with different catalytic doses (0.1 g/L, 0.4 g/L, 0.6 g/L, 1 g/L, 1.1 g/L, 1.2 g/L). Figure 9 shows a plot of percentage degradation of dye vs. catalytic dose. The degradation increases with increase in catalytic dose. At 0.8 g/L catalytic dye was found to be almost completely decolourised on irradiation for 120 minutes. Hence, an optimum catalytic dose of 1 g/L was used.

### Effect of pH

Studies were conducted on the effect of pH on the dye degradation.

Parameters	Values	Units
$\phi$	0.5	
$K_0$	2.83333E-07	(mol/L/sec)
$I_0 = K_0/\phi$	5.66667E-07	(einstein/L/s)
$F_0 = (I_0 V N_A E_\lambda) / A$		
$V$	0.05	L
$N_A$	6.023E+23	
$E_\lambda = hc/\lambda$		J / Photon
$h$	6.63E-34	J s / Photon
$\lambda$	0.000000365	m
$c$	300000000	m / s
$E_\lambda$	5.44932E-19	J / Photon
$A = 2\pi r d l / 2$	0.0026847	m <sup>2</sup>
$F_0 = (I_0 V N_A E_\lambda) / A$	3.463830963	W/m <sup>2</sup>

Table 2: Parameter values and its units.

This was done because the effluents of a textile industry are usually at different pH. It was observed that the pH decreased on the photocatalytic degradation. The dye degradation was conducted on a range of pH between 3 and 13 after irradiation for 120 minutes. The initial pH was adjusted by 1 N HNO<sub>3</sub>. It was observed that the dye degradation varied only within 2% by pH change.

### Chemical actinometry

To measure the intensity of the radiation from the lamp, we plotted a graph of average concentration of NBA versus the time and found out the slope of the curve. The plot is as shown below (Figure 10).

The best fit was a straight line. The slope of the line at t=0 was found to be:

$$\text{Slope} = -1.700$$

$$\text{At } R^2 = 0.919$$

The value of the flux for 125 W a high pressure mercury vapour lamp was found to be 3.464 Wm<sup>-2</sup> (Table 2).

### Conclusions

The ultraviolet (UV) light irradiation of the dye by using nanoanatase TiO<sub>2</sub> as a catalyst has yielded percentage decolouration of greater than 99% for a catalyst loading of 1 g/L and initial concentration of the dye solution of 5×10<sup>-5</sup> and 2.5×10<sup>-5</sup> mol/L. The rate constant of degradation was found to be 0.1237 and 0.2022 respectively. This can be an efficient and cost effective method of treating this azo-dye [17].

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