

# Synthesis, Characterization and Photocatalytic Activity of Cobalt Doped TiO<sub>2</sub> Nanophotocatalysts for Rose Bengal Dye Degradation under Day Light Illumination

B. MALINI<sup>1</sup> and G.ALLEN GNANA RAJ<sup>2</sup>

<sup>1</sup>Department of Chemistry, Government College of Engineering,  
Tirunelveli, Tamilnadu, India

<sup>2</sup>Department of Chemistry, Scott Christian College (Autonomous), Nagercoil, (Affiliated to  
Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli), Tamilnadu, India  
*malini@gcetly.ac.in*

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**Abstract:** Cobalt doped TiO<sub>2</sub> nano photocatalysts were synthesized by sol-gel technique and is characterized by SEM, EDX and XRD. The Co-TiO<sub>2</sub> catalyst is evaluated for its photocatalytic activity towards the degradation of Rose bengal under visible light radiations. Then the results were compared with the synthesized nano-TiO<sub>2</sub>. The effect of catalyst loading, initial dye concentration, pH, dissolved O<sub>2</sub> on the photocatalytic activity is studied and the degradation kinetics is also studied. The photodegradation rates of Rose bengal reached 97.50% under visible light irradiation for 150 min.

**Keywords:** Photodegradation, Rose bengal dye, Cobalt doped TiO<sub>2</sub>

## Introduction

Since the accidental discovery of the first commercially successful synthetic dye Mauvin in 1856 by Henry Perkin, about 10,000 different dyes and pigments are generated and over 10<sup>5</sup> tons of these dyes are produced annually worldwide<sup>1</sup>. The dye effluents released from textile industries, due to the presence of metals and other chemicals in their structure are either toxic, carcinogenic or mutagenic<sup>2</sup>. A variety of physical, chemical and biological methods are currently available for the treatment of wastewater containing dye effluents. But these conventional processes are insufficient to treat the wastewaters<sup>3</sup>.

In recent years advanced oxidation processes(AOPs) have been developed to meet the increasing need of an effective wastewater treatment because of the efficiency of their mineralization producing carbon dioxide, water and inorganic mineral ions<sup>4</sup>. Among the various semiconductor materials, maximum attention has been given to TiO<sub>2</sub> because of its

high photocatalytic activity, resistance to photocorrosion, photostability, low cost and non toxicity<sup>5</sup>.  $\text{TiO}_2$  has been used as a photocatalyst for the purification and remediation of contaminated waters loaded with even low concentrations of pollutants<sup>6</sup>. But its wide band gap of 3.2 eV facilitates its sensitization only by UV light and hinders using it indoor<sup>7</sup>.

Meanwhile, the high recombination rate of photogenerated electron hole pair also decreases the photocatalytic activity of  $\text{TiO}_2$ <sup>8</sup>. The development of photocatalysts that can be excited by visible light has received great attention<sup>9</sup>. Enormous doping methods are used for modifying the electronic structures of  $\text{TiO}_2$  to achieve improved catalytic activities<sup>10</sup>. Metal doping can alter the phase transformation and consequently the photocatalytic activity of  $\text{TiO}_2$  and one such dopant of interest for photocatalysis is Co<sup>11</sup>. In this work, preparation and characterization of Co doped  $\text{TiO}_2$  nanoparticles is reported and their catalytic activity for the degradation of environmentally toxic and hazardous Rosebengal dye under daylight illumination is investigated.

## Experimental

Sol-gel technique was used to prepare cobalt doped  $\text{TiO}_2$  samples<sup>12</sup>. 90 mL of 2-propanol was taken as a primary precursor and 10 mL titanium tetra isopropoxide was added to it drop wise with vigorous stirring during the process of  $\text{TiO}_2$  formation. The solution was vigorously stirred for 45 min. to form sols. Liquid solution cobalt nitrate of desired concentration was added slowly drop by drop to that mixture with continued stirring. To obtain nanoparticles, the obtained gels were dried at 80 °C for 5 h to evaporate water and organic material to the maximum extent. Finally the powders were kept in muffle furnace and calcined at 500 °C for 5 h. The particles were pulverized to powder using an agate mortar at room temperature for further characterization.

### *Sample characterization*

The Co-doped  $\text{TiO}_2$  samples are subjected to FESEM with EDX and PXRD characterization using SEM (Vega 3 Tescan) equipped with EDAX (Bruker) and PXRD (Bruker AXS D8 Advance). Absorbance changes of RB during photocatalytic degradation were studied using UV-Visible spectrophotometer (PG Instrument).

### *Photocatalytic degradation procedure*

The photocatalytic degradation of Rose bengal was carried out under clear sky conditions. The light intensity was measured by Luxmeter. The sunlight intensity recorded was about 950  $\text{Wm}^{-2}$  and the mean temperature was 31 °C.

The experiments were performed in a borosilicate glass beaker of 250 mL capacity. Rose bengal dye was dissolved in 100 mL of distilled water resulting in a solution of desired concentration. Prior to irradiation, a suspension containing definite amount of catalyst and 100 mL of Rose bengal dye solution of the particular concentration was stirred continuously in the dark for 30 minutes to achieve the adsorption equilibrium of dye on the surface of the catalyst. The concentration of substrate in bulk solution at this point was taken as the initial one. The solution was irradiated using solar light. At given intervals of irradiation, a sample of the solution along with catalyst particles was collected, centrifuged and then filtered through a Millipore filter. The filtrates were analysed by UV-Visible spectrophotometer. The determination wavelength is 549 nm for Rose bengal, which is the maximum absorption wavelength. The photocatalytic degradation efficiency of Rose bengal was calculated according to the following equation.

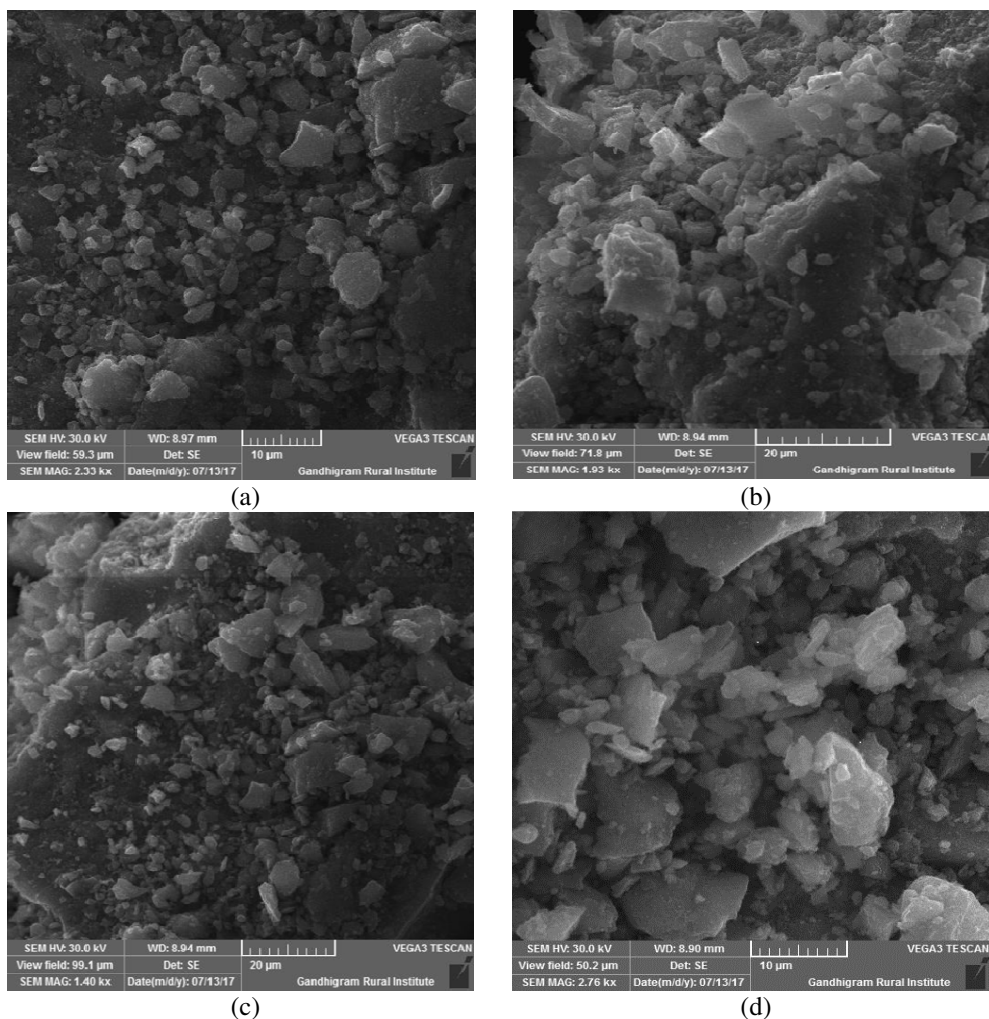
$$\text{Efficiency (\%)} = (C_0 - C) / C_0 \times 100 \quad (1)$$

Where  $C_0$  represents the concentration of Rose bengal solution before irradiation and  $C$  is the concentration of Rose bengal solution after irradiation.

## Results and Discussion

### Scanning electron microscope (SEM with EDX)

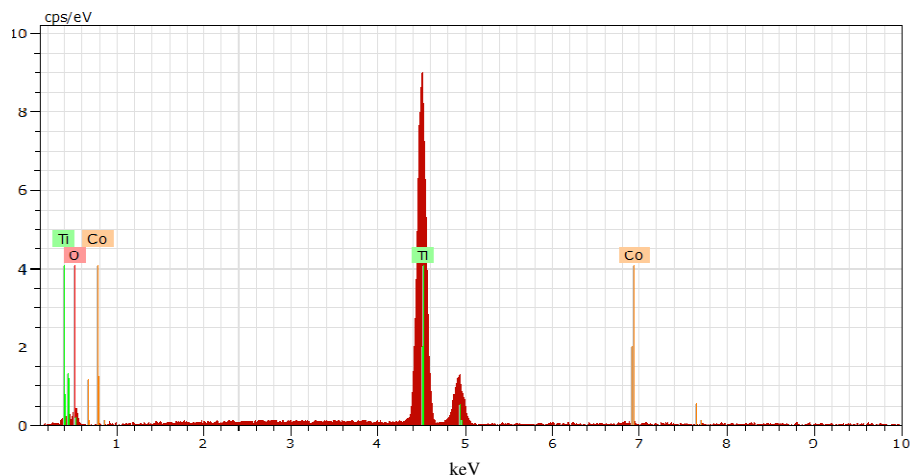
Figure 1 shows the typical SEM images of Co-doped  $\text{TiO}_2$  particles. It is obvious from the figures that most of the particles pebble shaped.



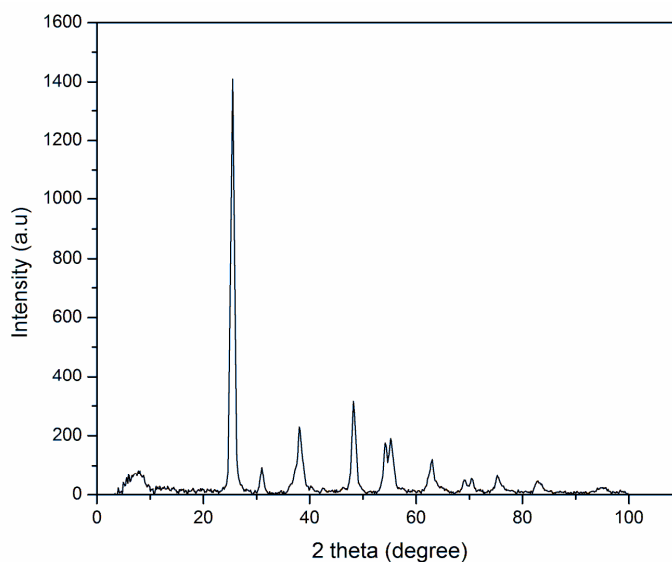
**Figure 1.** SEM images of Co- $\text{TiO}_2$

Energy-dispersive x-ray spectroscopy (EDX) of Co-doped  $\text{TiO}_2$  is shown in Figure 2 which shows the presence of O, Ti and Cobalt.

The XRD patterns as shown in Figure 3 obtained in the present study are identical with the earlier report<sup>12</sup>.



**Figure 2.** EDX of Co-TiO<sub>2</sub>



**Figure 3.** XRD of Co-TiO<sub>2</sub>

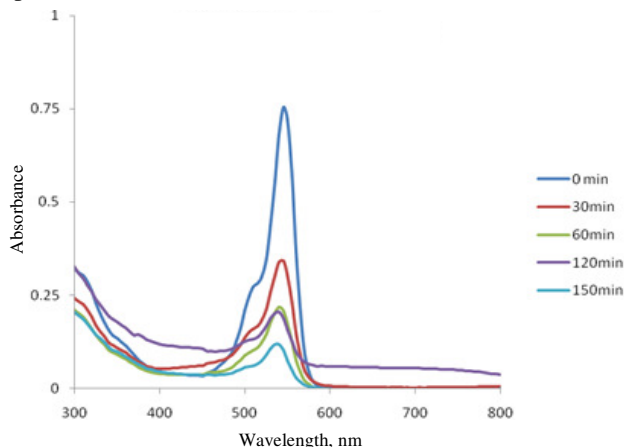
The average crystallite size (*D* in nm) was calculated in accordance with the Scherrer equation<sup>13</sup>

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

Where *k* is the constant (shape factor, about 0.9),  $\lambda$  is the x-ray wavelength (0.15418 nm),  $\beta$  is the full width at half maximum (FWHM) of the diffraction line and  $\theta$  is the diffraction angle. The crystallite size for nano Co-TiO<sub>2</sub> is 19.4 nm.

The photocatalytic degradation of Rose bengal has been investigated using the prepared cobalt doped TiO<sub>2</sub> photocatalyst. Figure 4 shows the time dependent UV-Vis spectra of

Rose bengal in the presence of Co-TiO<sub>2</sub> catalyst. It is evident from the figure that there is a decrease in absorption maximum with time.



**Figure 4.** Time dependent UV-Visible spectra of Rose bengal

#### *Factors influencing the photocatalytic degradation*

The oxidation rates and efficiency of the photocatalytic system are highly dependent on a number of operational parameters.

#### *Effect of catalyst amount*

The increase in catalyst amount actually increases the number of active sites on the photocatalyst surface thus causing an increase in the formation of number of OH radicals that takes part in the actual discolouration of dye solution<sup>14</sup>. Beyond a certain limit of catalyst amount, the solution becomes turbid and thus blocks UV radiation for the reaction to proceed and therefore percentage degradation starts decreasing<sup>15</sup>.

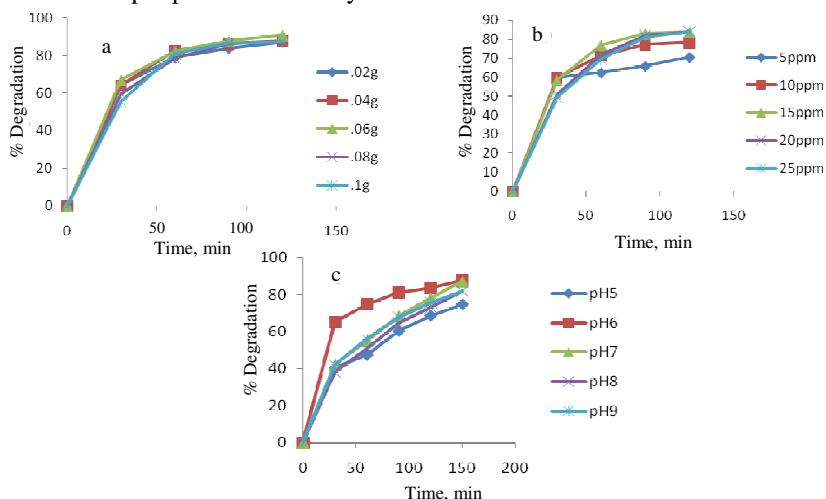
The optimal amount of Co-TiO<sub>2</sub> catalyst for the degradation of Rose bengal was determined by varying the amount of catalyst from 0.02-0.1 g/100 mL at a constant dye concentration of 10 ppm. The percentage of dye degraded at different time intervals at various catalyst loadings is calculated and depicted in Figure 5a. It is evident from figure that with the increase in the amount of catalyst from 0.02-0.1 g/100 mL there is an increase in percentage of dye degraded up to 0.06 g and thereafter there is a decrease in the percentage degradation and hence the optimal amount of catalyst for the dye degradation was taken as 0.06 g/100 mL.

#### *Effect of dye concentration*

In the photocatalysis process, only the amount of dye adsorbed on the surface of photocatalyst contributes and not the one in the bulk of the solution. The adsorption of dye depends on the initial concentration of dye<sup>16</sup>. In general, the percentage degradation decreases with increasing amount of dye concentration, while keeping a fixed amount of catalyst. It is evident from the Figure 5b that as the initial concentration of the dye was varied from 5 ppm to 25 ppm in the steps of 5 ppm at a constant catalyst loading of 0.06 g/100 mL it is seen that at 20 ppm there is maximum dye degradation. With increase in concentration of dye from 5 ppm to 25 ppm initially there was increase in the amount of dye degraded from 5 ppm up to 20 ppm and after that there was a decrease in degradation rate. So, the optimum dye concentration was fixed as 20 ppm.

### Effect of pH

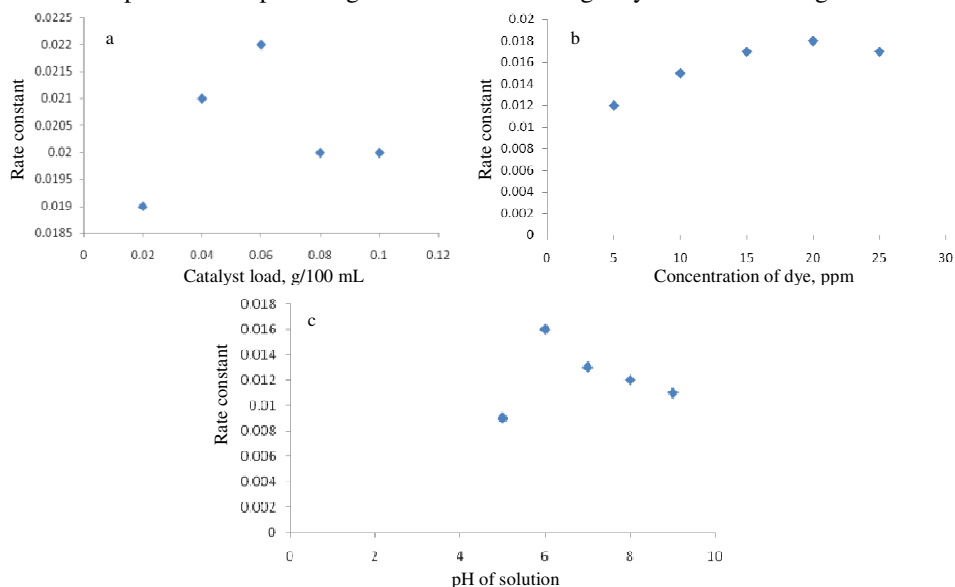
The pH of dye solution is a key factor influencing the rate of degradation. So, the effect of solution pH on the degradation of dye has been investigated in the range 5-9. It is evident from Figure 5c that as pH is increased from 5-9, there is an initial increase in the rate constant values upto pH 6 followed by decrease in rate constant values.



**Figure 5.** Variation of percentage degradation after 120 min irradiation as a function of (a) catalyst loading (b) concentration of dye (c) solution pH

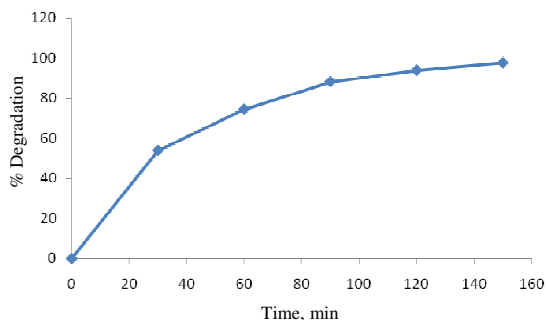
### Kinetics of the photocatalytic degradation of Rose bengal

The kinetics plots for the photodegradation of Rose bengal dye is shown in Figure 6.



**Figure 6.** Variation of rate constant values as a function of (a) catalyst loading (b) concentration of dye (c) solution pH

In order to determine the order of the reaction, the photo degradation reaction of Rose bengal (20 ppm) with photo catalyst (0.06 g) was carried out at pH 6 in sunlight illumination as depicted in Figure 7.



**Figure 7.** Plot of degradation of Rose bengal as a function of irradiation time under optimum conditions

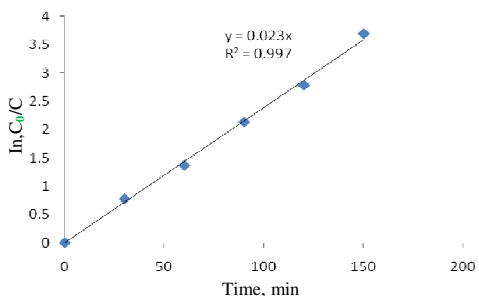
The plot of  $\ln C_0/C$  vs. irradiation time shows a straight line behavior Figure 8. The rate constant for the photo catalytic degradation of Rose bengal was obtained from the first order rate equation

$$\ln C_0/C = Kt \quad (3)$$

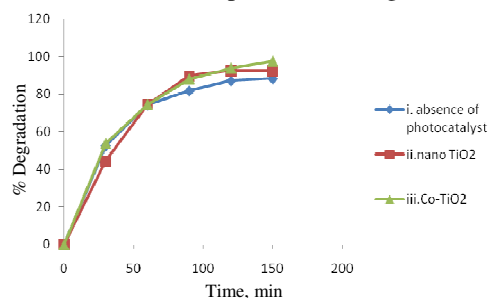
Where  $C_0$  and  $C$  are the concentrations of substrate at time 0 and time  $t$  in minutes.  $K$  is the first order rate constant ( $\text{min}^{-1}$ ) determined from the slope of the straight line. The regression coefficient  $R^2$  of the experimental values were found to be 0.997 which confirms the degradation of the dye molecules principally obeys the pseudo first order linear kinetics.

#### Comparison of degradation rates of Rose bengal

The degradation of Rose bengal was carried out in the absence of photocatalyst, with nanoTiO<sub>2</sub> and Co-TiO<sub>2</sub> under similar conditions and the results are presented in Figure 9.



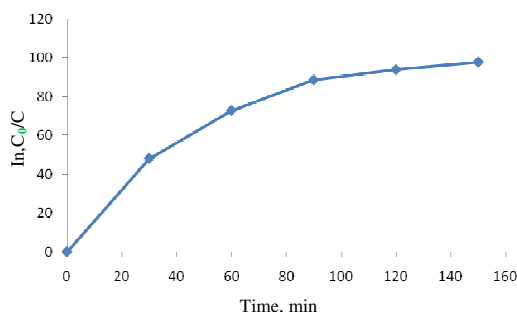
**Figure 8.** Plot of  $\ln(C_0/C)$  versus irradiation time for degradation of Rose bengal using Co-TiO<sub>2</sub> under optimum conditions



**Figure 9.** Plot of degradation of Rose bengal as a function of irradiation time in the (i). absence of photocatalyst (ii). Nano-TiO<sub>2</sub> (iii). Co-TiO<sub>2</sub>

#### Effect of oxygen

The degradation was studied in the presence of atmospheric O<sub>2</sub> by taking Rose bengal (20 ppm) photo catalyst (0.06 g) at pH 6 under sunlight illumination. Figure 10 shows the percent of dye degraded at different time intervals. It is obvious from the figure that the degradation at the end of 150 min irradiation was found to be almost similar to that in the absence of oxygen showing that oxygen has least influence on the rate of degradation in the case.



**Figure 10.** Effect of dissolved oxygen on photocatalytic degradation, initial dye concentration=20 ppm, Co-TiO<sub>2</sub> loading. 06 g/100 mL, pH=6

### Measurement of COD

The total mineralization of Rosebengal has been measured by using the disappearance of COD. The COD varies during the photo catalytic degradation of Rose bengal (20 ppm, 100 mL). Estimation of COD had been done by standard methods. The efficiency of dye mineralization was estimated using the following expressions<sup>17</sup>.

$$\text{Mineralization \%} = \{1 - (\text{COD}/\text{COD}_0)\} * 100 \quad (4)$$

Where COD and COD<sub>0</sub> correspond to CODs at final and initial dye concentration. The suspension was irradiated for 2 h. The percentage mineralization was found to be 96.67 after 2 h.

### Mechanism

The probable mechanism of the photocatalytic degradation of dye in an advanced oxidation process is as follows. Rose bengal molecule being photosensitive absorbs radiations and moves to its singlet excited state. It then undergoes inter system crossing and gives the triplet excited state. The Co-TiO<sub>2</sub> photo catalyst utilizes the incident light energy to excite the electron from its valence band (VB) to the conduction band (CB). The hole left behind on the VB absorbs an e<sup>-</sup> from OH<sup>-</sup> to generate OH<sup>•</sup> radical. The radicals oxidize the dye to its colourless leuco form that gets degraded to harmless compound.

### Conclusion

The Co-doped TiO<sub>2</sub> photocatalysts were prepared by means of sol-gel method at room temperature. The synthesized products were characterized by SEM, EDX and PXRD. The effect of various operational parameters such as the amount of catalyst (0.02-1 g/100 mL), concentration of dye (5-25 ppm) and pH (5-9) of dye solution on the rate of dye degradation has been studied. The dye degradation under optimum conditions on 150 min. irradiation was found to be 97.50% and in the presence of oxygen it was found to be 97.80%. The most favourable results for the degradation of Rosebengal were observed at pH 6 for 20 ppm dye solution at a catalyst loading of 0.06 g/100 mL. Pseudo-first-order reaction kinetics followed the heterogeneous photocatalysis reasonably well. The percentage mineralization achieved on 2 h irradiation was 96.67%.

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