EFFECT OF OPERATIONAL PARAMETERS ON DEGRADATION OF CORALENE NAVY BLUE 3G DYE BY SOLAR AND ULTRAVIOLET IRRADIATION

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Abstract:

The photocatalytic degradation of Coralene Navy Blue 3B have been studied in the presence of titanium dioxide powder illuminated with a solar light and UV light. The effect of hydrogen peroxide on the degradation process was also determined. It was found that the color removal efficiency was affected by the concentration of dye, amount of TiO_2 added, and the pH of the solution. The degradation of dyes obeys first-order kinetics, with the apparent first-order rate constant increasing with decreasing dye concentration. The rate constants were evaluated as a function of the concentration of dye, amount of TiO_2, and pH.

Keywords: UV irradiation, Coralene Navy Blue 3G, H_2O_2, TiO_2.

1. Introduction:

Textile dyes are an abundant source of coloured organic compounds that present an increasing environmental danger. During dye production and textile manufacturing processes a large quantity of wastewater containing dyestuffs with intensive colour and toxicity can be introduced into the aquatic systems [1]. Ankleshwar is known as textile city of Gujarat. There are many major textile processing units which use million liter of water every day and generate huge quantity of effluent containing dyes [2]. For the removal of dye pollutants, many traditional physical techniques (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, etc.) can generally be used efficiently [3]. Since sunlight is abundantly available natural energy source, its energy can be conveniently exploited for the irradiation of semiconducting materials. UV irradiation is yet another high energy source for degradation of organics present in the effluents. In photocatalytic process, electron–hole recombination is a major problem to circumvent. In photocatalysis, UV irradiation source stands up among other sources to avoid this problem. So it was decided to study the influence of solar light and UV light independently on the photocatalytic degradation of dyes [4].

Recently, advanced oxidation processes (AOPs) were developed to oxidize organic compound into CO_2, H_2O & inorganic ions or biodegradable compound. These methods are environmentally friendly. There for, AOPs are considered as promising treatment methods for waste waters [5]. TiO_2 semiconductor is often used as catalytic agents because of their high stability, low costs, high efficiency and nil toxicity [6]. Hydroxyl radical (H•) and superoxide radical anions (O_2•−) are suggested the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the bleaching of the dye [7].

In the present study, aqueous solutions of Coralene Navy Blue 3G dye were treated with solar and UV rays-H_2O_2 and TiO_2 Advanced Oxidation Process. The influence of parameters like exposure time with concentration of dye, H_2O_2 dose, TiO_2 dose, and change in pH was explored.

2. Experimental:

2.1 Chemicals

The Coralene Navy Blue 3G dye (λ max-540 nm) was used without any further purification. The commercially available photocatalysts TiO_2 (Degussa P25), 30 % H_2O_2 were used as received. All the solutions were prepared fresh using double distilled water.

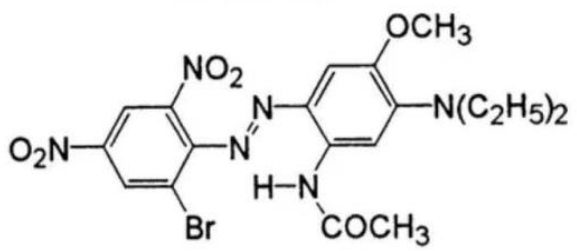


Figure 1 Structure of Coralene Navy Blue 3G dye.

2.2 Photocatalytic Study

The experiments were carried out in 100 ml beaker. Sunlight and UV light were used as the energy source. The experiments were performed at ambient temperature between 40°C and 45°C. Stock solutions of dye at different concentrations were prepared in double distilled water with pH 6.8. 30, 40, 50, 60 and 70 mg/L dye concentration was used for the present study. pH of the dye solution was adjusted by adding 0.1N NaOH or 0.1N HCl. In each sample 30 to 70 mg/L 100ml dye solution is added to 2250 mg/L H_2O_2 (30%) + 100 mg TiO_2 in a 150 ml beaker. The whole set-up was placed in sunlight and UV light between 9

a.m. and 4 p.m. and the average intensity of sunlight during this period is 410 × 100 Lux unit and 3.9 lux Unit respectively. The progress of photocatalytic degradation of the Coralene Navy blue 3G was monitored by withdrawing definite quantity of aliquot at regular intervals and measuring the absorbance in UV–Vis spectrophotometer for decoloration.

2.3 Calculations

The percentage of degradation was determined by using the following equation,

$$\% \text{ Discoloration} = ((A_0 - A_t) \div A_0) \times 100 \qquad (1)$$

Where, A_0 is the initial absorbance of dye solution & At is absorbance at time interval't' (0, 30, 60, 90, 120, 150, 180, 210, 240 min).

3. Results and Discussion

3.1 Typical Run

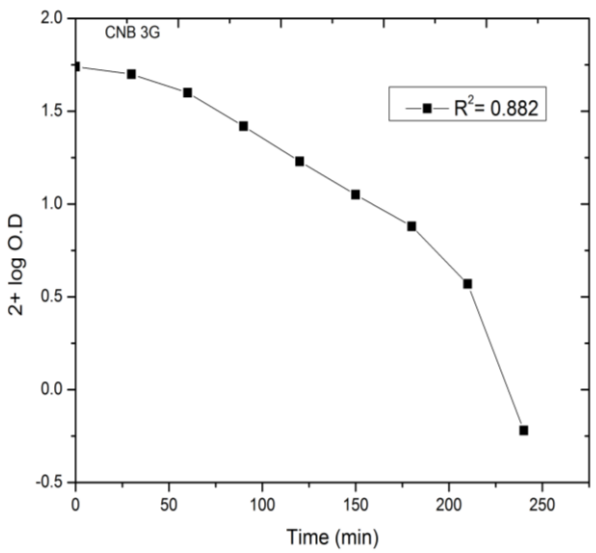


Figure 2 A Typical Run [50mg/L dye, 2250mg/L H_2O_2, 100mg TiO_2, 470×100 LUX Solar Light Intensity, 4.3 pH, 240 min Reaction Time]

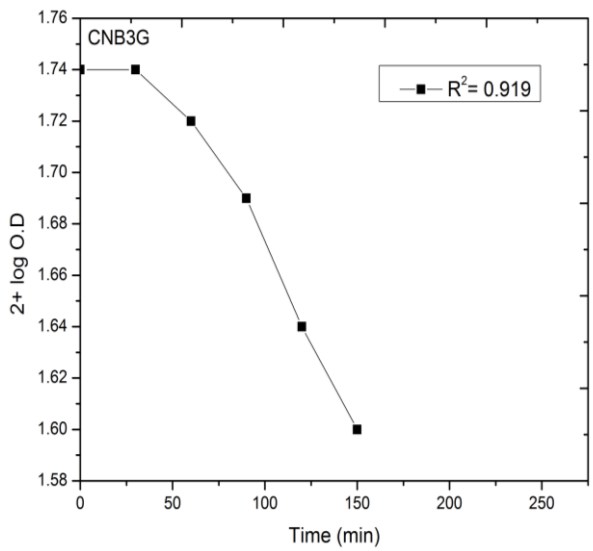


Figure 3 A Typical Run [50mg/L dye, 2250mg/L of H_2O_2, 100mg TiO_2, 9.2×100 LUX UV Light Intensity, 4.2 pH, 150 min Reaction Time]

Photocatalytically degraded sample of coralene Navy Blue 3G were studied at 540 nm in UV-Visible spectrophotometer. The results of Solar and UV irradiation method typical run are graphically given in Fig. 2 and Fig. 3. The plot of 2+ log O.D Vs exposure time is a straight line and rate constant (K) for this reaction are 1.10×10^{-2}

sec^{-1} and 2.26×10^{-3} sec^{-1} respectively. The optical density of the reaction mixture decreases with increasing time intervals.

3.2 Effect of concentration of Dye

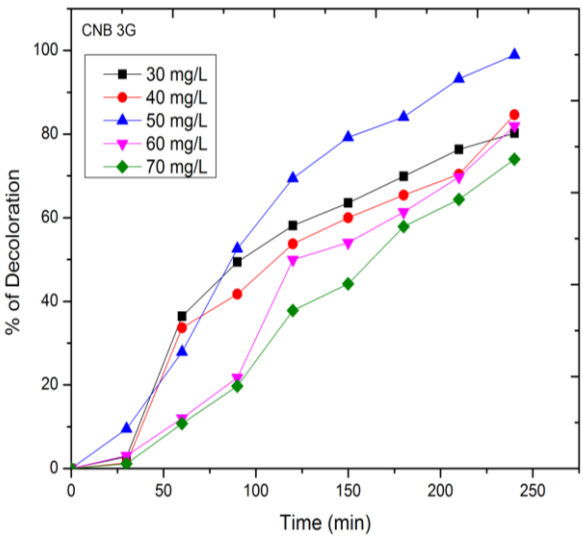


Figure 4 Effect of Concentration of Dye [30mg/L to 50 mg/L dye, 2250mg/L H_2O_2, 100mg TiO_2, 470×100 LUX Solar Light Intensity, 240 min Reaction Time]

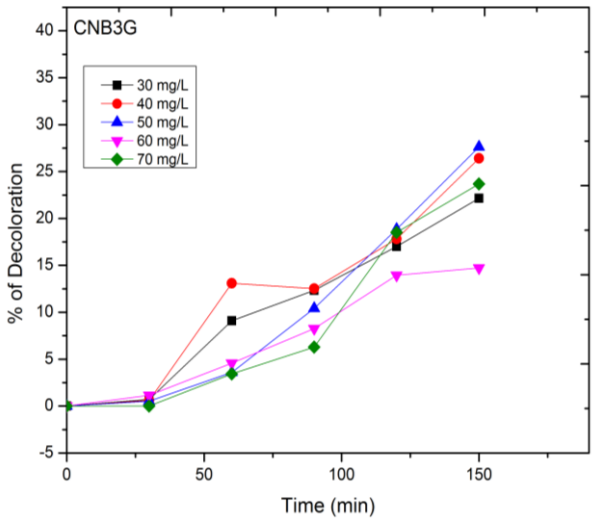


Figure 5 Effect of concentration of Dye [30mg/L to 70 mg/L dye, 2250mg/L H_2O_2, 100mg TiO_2, 9.2×100 LUX UV Light Intensity, 150 min Reaction Time]

Effect of dye concentration of dye was studied by varying the concentrations of dye from 30 to 70 mg/L in order to check the appropriate amount of dye concentration in both methods. Fig. 4 and Fig.5 shows that with increase of dye concentration, the degradation process becomes faster up to 50 mg/L, where efficiency value of decoloration is 98.92% and 27.64% respectively. In solar irradiation method fast degradation compare to UV irradiation method. This may be due to the fact that as the concentration of dyes increase, more dyes molecules may be available for on catalyst surface so there is an increase in the rate. The rate of photocatalytic degradation is found to decrease above dye concentration of 50 mg/L because the intense color of dye solution reduces the percolation of light in solution.

3.3 Effect of pH

To study the effect of pH on decolorization efficiency, the pH value was varied from 2.0 to 10 at the constant dye concentration of 50 mg/L. Fig. 6 and Fig. 7 clearly observed that the lower pH medium are more suitable for the decoloration process of Coralene Navy Blue 3G dye. Highest percentages of decoloration are observed with the value of 99.79% at 2 pH in

solar method and 42.90% at 2 pH in UV method. The effect of pH on the photocatalytic reaction can be explained by the surface charge of TiO_2. Under acidic conditions, the titanium dioxide surface is positively charged. Dye could be adsorbed to the surface of TiO_2, thus strongly allowing hydroxyl radicals to more easily attack the dye molecule. The higher color removal efficiency was obtained with the pH level of 2.0 for dye solution. This result could be attributed to more dye ions adsorbed on the surface of titanium dioxide and reacted with free radicals at the level of pH.

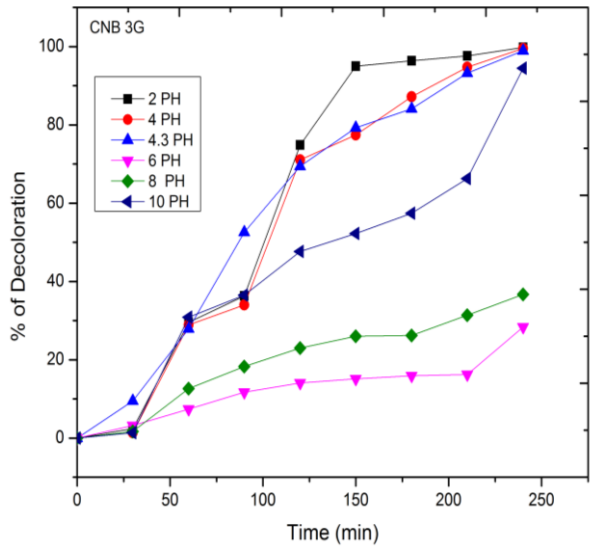


Figure 6 Effect of pH [Change of pH from 2 to 10, 50mg/L dye, 2250mg/L H_2O_2, 100mg TiO_2, 470×100 LUX Solar Light Intensity, 240 min Reaction Time]

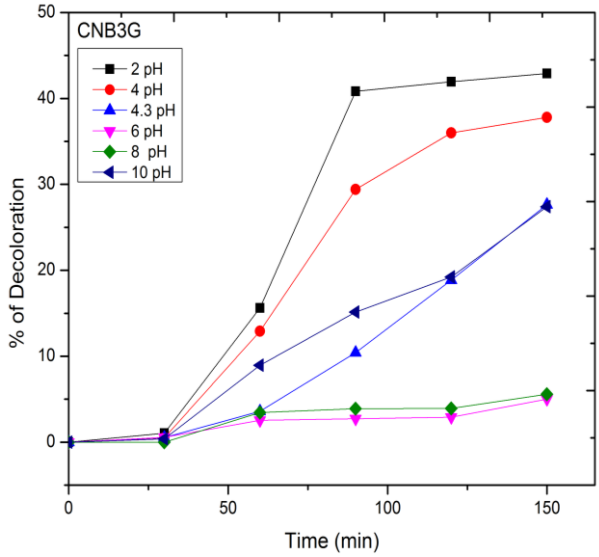
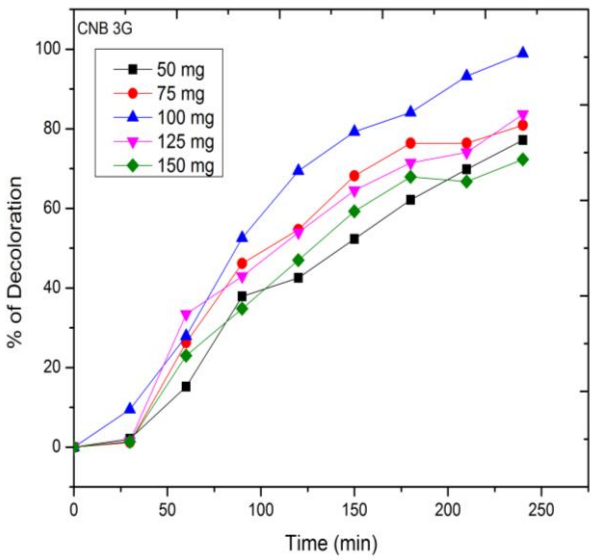


Figure 7 Effect of pH [Change of pH from 2 to 10, 50mg/L dye, 2250mg/L H_2O_2, 100mg TiO_2, 9.2×100 LUX UV Light Intensity, 150 min Reaction Time]

3.4 Effect of Variation of Semiconductor



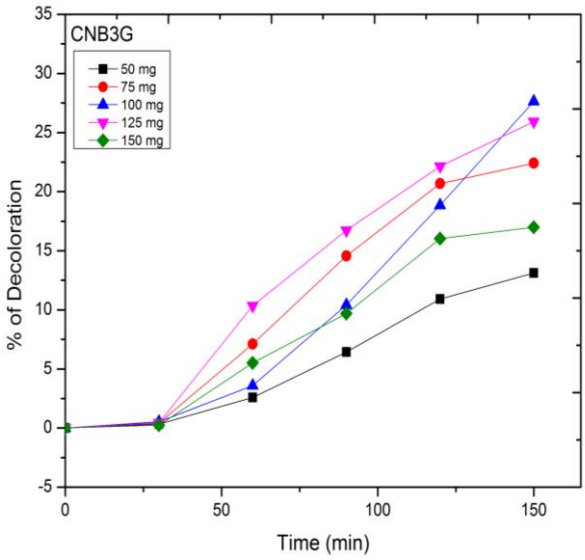
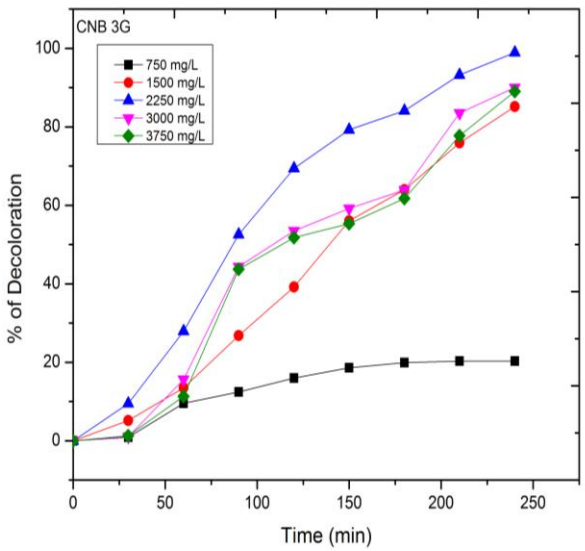


Figure 8 Effect of Variation of Semiconductor [50mg/L dye, 2250mg/L H_2O_2, 50mg to 150mg TiO_2, 470×100 LUX Solar Light Intensity, 240 min Reaction Time]

Figure 9 Effect of Variation of semiconductor [50mg/L dye, 2250mg/L H_2O_2, 50mg to 150mg TiO_2, 9.2×100 LUX UV Light Intensity, 150 min Reaction Time]

Varying amount of TiO_2 from 50 to 150 mg/100mL in the reaction solution, rate constant values increase with the increase of catalyst loading. The maximum decoloration value is 98.92% in solar and 27.64% in UV irradiation method and it is observed at 100mg / 100mL of catalyst concentration. As the amount of catalyst is increased, the number of photons and the number of dye molecules adsorbed are increased as the result of an increase in the number of TiO_2 particles. The density of particles in the area of illumination also increases and thus the rate is enhanced Photo catalytic degradation efficiency increased with the increase of catalyst concentration at up to concentration to 100 mg. After the optimum amount of TiO_2, the activity of photocatalytic decoloration decreased with increase of catalyst concentration because solution becomes milky and do not allow light to pass through it.

3.5 Effect of Variation in H_2O_2 concentration on dye degradation



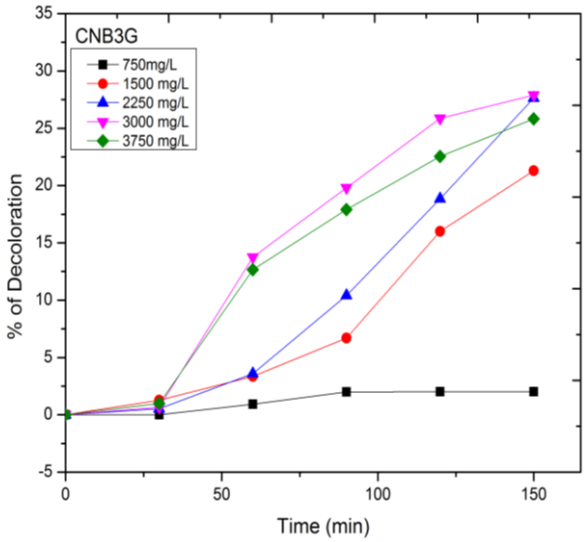


Figure 10 Effect of Variation of Hydrogen Peroxide [50mg/L dye, 750mg/L to 3750 mg/L H_2O_2, 100mg TiO_2, 470×100 LUX solar Light Intensity, 240 min Reaction Time]

Figure 11 Effect of Variation of Hydrogen peroxide [50mg/L dye, 750mg/L to 3750 mg/L H_2O_2, 100mg TiO_2, 9.2×100 LUX UV Light Intensity, 150 min Reaction Time]

The percentage decoloration by variation in hydrogen peroxide concentration is shown in Fig. 10 and Fig. 11 Variation range of H_2O_2 concentration is studied in a 750 to 3750mg/L. The highest degradation are observed at 2250 mg/L with value are 98.92% in solar and 27.64% in UV irradiation. The more availability of hydroxyl radicals means faster reduction. But at concentration higher than 2250 mg/L, the produced $OH^{\cdot}$ radicals that may recombine and that can decrease in efficiency of discoloration.

The higher reaction rates after the addition of peroxide were attributed to the increase in the concentration of hydroxyl radical. At low concentration of hydrogen peroxide, it inhibits the electron–hole recombination, according to Eq. (2) and it could act as an alternative electron acceptor to oxygen (Eq. (3), because hydrogen peroxide is a better electron acceptor than molecular oxygen. Hydrogen peroxide may also be split photolytically to produce hydroxyl radical directly, as cited in the studies of homogeneous photooxidation using UV/H_2O_2 (Eq. (4)). But at high concentration, H_2O_2 is a powerful OH• scavenger.

$$TiO_2\,(e^-) + H_2O_2 \rightarrow TiO_2 + OH^- + \bullet OH \qquad (2)$$

$$\bullet O^{-2} + H_2O_2 \rightarrow OH^- + \bullet OH + O_2 \qquad (3)$$

$$H_2O_2 + hv \rightarrow 2\bullet OH \qquad (4)$$

$$H_2O_2 + \bullet OH \rightarrow HO_2\bullet + H_2O \qquad (5)$$

$$HO_2\bullet + \bullet OH \rightarrow H_2O + O_2 \qquad (6)$$

Therefore, the proper addition of hydrogen per oxide could accelerate the photo degradation rate of CNB 3G. However, in order to keep the efficiency of the added hydrogen peroxide, it was necessary to choose the proper concentration of hydrogen peroxide according to the kinds and the concentrations of the pollutants.

3.6 Mechanism

Following steps are possible in the degradation of coralene dyes.

Photocatalytic reaction begin when the catalyst absorbs equal or greater energy than its band gaps and an electron in the valance

$TiO_2 + hv \rightarrow H^+ + OH^-$ (7)

$h^+_{vb} + OH^- \rightarrow OH^\bullet$ (8)

$h^+_{vb} + H_2O \rightarrow H^+ + OH^-$ (9)

$e^-_{CB} + O_2 \rightarrow O_2^-$ (10)

$e^-_{CB} + h^+_{VB} \rightarrow$ Heat (11)

$OH^\bullet$ radicals attacks the dye in aqueous medium

$OH^\bullet$ + Dye $\rightarrow$ decomposed (12)

$H_2O + O_2^{\bullet -} \rightarrow OOH^\bullet + OH^-$ (13)

$2\ OOH^\bullet \rightarrow O_2 + H_2O_2$ (14)

$O_2^\bullet - +$ dye $\rightarrow$ dye – $OO^\bullet$ (15)

Hydrogen peroxide can be generated in another path

$OOH^\bullet + H_2O + e\ c_B \rightarrow H_2O_2 + OH^\bullet$ (16)

Hydrogen peroxide can form hydroxyl radicals which act as powerful oxidizing agent

$H_2O_2 + e^-_{CB} \rightarrow OH^\bullet + OH^-$ (17)

$H_2O_2 + O_2^\bullet - \rightarrow OH^\bullet + OH^- + O_2$ (18)

$OH / O_2^\bullet - / TiO_2 +$ dye $\rightarrow$ Degradation (19)

$H_2O_2 + hv \rightarrow 2\ OH^\bullet$ (20)

$H_2O_2 + 2\ e \rightarrow 2\ OH^-$ (21)

$OH^\bullet + H^+ + e^- \rightarrow H_2O$ (22)

$H_2O_2 + OH^\bullet \rightarrow HO_2 + H_2O$ (23)

$HO_2^\bullet + OH^\bullet \rightarrow H_2O + O_2$ (24)

4. Conclusion

Advanced oxidation processes are better treatment options than the conventional treatment methods commonly adopted in wastewater treatment plants. These methods provide complete removal of refractory organics like dyes and reduce the toxicity of the effluent discharged into the streams and rivers. Various combinations of AOP processes like ozone, UV, H_2O_2 etc. may provide efficient treatment of textile wastewater depending upon the characteristics of wastewater to be treated. Further, the economic

optimization of these processes must be worked out for treating voluminous amount of wastewater by AOPs.

The photocatalytic degradation of navy blue 3G dye was studied by using Advance oxidation process in presence of sunlight. The results show that the maximum of 99 % degradation efficiency was achieved in 240 minutes in case 50ppm solution. Further it was also noticed that the extent of degradation was found to depend on concentration of dye, pH of dye solutions, concentration of H_2O_2, amount of TiO_2. Thus, based on the degradation results, it was concluded that, since the degradation was achieved in presence of sunlight, the present protocol can be adapted to the large scale industrial discoloration processes and may reduce the water pollution to a certain extent.

This study shows that photocatalysis under UV or sunlight irradiation, the removal rate follows pseudo-first order kinetic with respect to Coralene Navy Blue 3G dye concentration and decreases with increasing initial concentration and maximum degradation achieved in solar irradiation method. It is found that degradation is dependent on various reaction parameters such as pH, dye concentration, amount of catalyst and amount of H_2O_2. It was also found that pH is an important parameter in determining the degradation rate; the acidic condition was favorable for both methods. The results indicated that the color removal rate of Coralene Navy Blue 3G dye with solar light irradiation was higher than that with UV light irradiation.

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