

Decolorization of Coralene Navy Blue 3G dye using in Textile Wastewater

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Abstract:

Degradation of textile dye coralene navy Blue 3G was carried out using advance oxidation method. In this method catalyst TiO₂ and H₂O₂ were used. The whole experiment was carried out under solar light. The effect of various parameters like photo catalyst, concentration of H₂O₂, concentration of Dye and pH were studied. Process of degradation is faster in solar light when TiO₂ in used as catalyst. The decolorization efficiency was inversely related to dye concentration of the effluent. The maximum decolorization occurred in ≤ 240 min in all cases. A mechanism is proposed for the process of degradation considering the various parameters. This advanced oxidation degradation process was applied to treat textile dye in wastewater.

Keywords: Advance oxidation, Coralene navy Blue 3G, H₂O₂, TiO₂.

1. Introduction:

Azo dyes constitute the largest class of dyes used in industry. In textile industry, it is estimated that 10–15% of the dye is lost during the dyeing process and released as effluent. Azo dyes are the most important class of synthetic organic dyes used in the textile industry and are therefore common industrial pollutants. They are produced in large amounts and enter the environment during the production and manufacturing processes [1]. They are characterized by the presence of one or more azo group (–N=N) bound to aromatic rings. It has been reported that some of them are toxic, mutagenic, and carcinogenic compounds [2]. Azo dyes are resistant to aerobic degradation; however, under anaerobic conditions, the azo linkage is reduced to generate aromatic amines that are colorless but can also be toxic and potentially carcinogenic [3].

There are many kind of dyes available in the market. In view of their chemical structures, dyes can be characterized as azo dyes, anthraquinone dyes, heterocyclic dyes, etc. Dyes can also be characterized according to their application method into Vat dyes, Reactive dyes, Direct dyes, acid dyes, basic dyes, disperse dyes, etc [4]. As these dyes are designed to resist oxidative degradation, they pass through most stages of effluent treatment and ultimately released into environment. Many treatment methods have been reported for dye degradation such as flocculation, coagulation, ultrafiltration, reverse osmosis, biodegradation etc. These methods have their own limitation in terms of high cost, specificity for certain group, disposal of sludge formed, and excessive use of chemicals [5]. Another set of techniques that are relatively newer, more powerful, and very promising called Advanced Oxidation Processes (AOPs) has been developed and employed to treat dye-contaminated wastewater effluents [6].

Advanced Oxidation Processes (AOPs) are alternative techniques of destruction of dyes and many other organics in wastewater and effluents. These processes generally, involve UV/H₂O₂, UV/O₃ or UV/Fenton's reagent for the oxidative degradation of contaminants. Heterogeneous photocatalysis through illumination of UV or solar light on a semiconductor surface is an attractive advanced oxidation process. Titanium dioxide is a wide band gap Semiconductor (3.2 eV) used successfully as a photocatalyst for the degradation of organic and dye pollutants [7]. However, TiO₂ absorbs a small portion of solar spectrum in the UV region (4–6%). Hence, to reap maximum solar energy, it is necessary to shift the absorption threshold towards visible region. Semiconductor photocatalysis is a newly developed AOP, which can be conveniently applied to dye pollutants for their degradation [8].

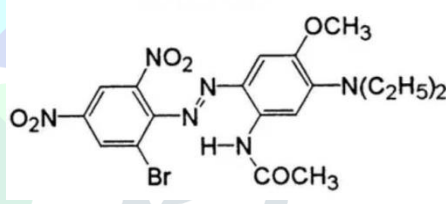
The aim of the present work is to investigate the influence of various parameters on photocatalytic decomposition of an azo dye, Coralene Navy blue 3G, in the presence of TiO₂ irradiated by the solar light [9] and to apply this to treat dye contaminated water.

2. Experimental:

2.1 Chemicals

The commercially available azo dye CNB 3G (λ_{max} - 541 nm), product of Shree Balaji, was used as received. The chemical structure and characterization of the dye was presented in Fig. 1. Titanium dioxide (anatase) was used as photocatalyst and obtained from Chitichem vadodara. H₂O₂ obtained from Samir tech-chem. PVT, LTD. Double distilled water was used to prepare the dye solutions. Sodium hydroxide and hydrochloric acid were used to adjust the pH of dye solutions. Colored wastewater was obtained from a textile industry located in Ankleshwar, Gujarat.

Table 1: characteristics & Molecular structure of CBN 3G

Name	Coralene Navy Blue 3G
Other name	Disperse blue 291
λ max	541 nm
CAS No.	56548-64-2
Molecular Weight	509.31
Molecular Formula	C ₁₉ H ₂₂ BrN ₆ O ₆
Chemical Structure	

2.2 Instruments

Dye concentration was measured by Thermo scientific (Evolution 201), A digital pH-meter (model 361, Systronics, India) was used for pH measurements, Racer stop watch was used for measuring time expose, Digital Lux meter Model- TES 1334 (TES-1332A) was used for measurements of intensity.

2.3 Methods

Stock solutions of dye at different concentrations were prepared in double distilled water with pH 6.8.

2.3.1 Reaction mixture Preparation

30, 40, 50, 60 and 70 mg/L dye concentration was used for the present study. In each sample 30 to 70 mg/L 100ml dye solution is added to 2250 mg/L H₂O₂ (30%) + 100 mg TiO₂ in a 150 ml beaker.

2.3.2 Progress of Reaction

The progress of reaction was observed by measuring optical density of the reaction mixture containing dye at different time intervals during exposure. A decrease in optical density indicates that the dye was bleached during this photocatalytic process. Absorbance maximum for coralene Navy Blue 3G is 541 nm, all the data were collected at this wavelength.

2.3.3 Control Experiments

The optical density of solution was determined with the help of a Spectrophotometer. The dye solution was placed in equal amounts in following set of mixture of dye were prepared. each set has equal amount of dye in it.

- (i) The first beaker containing dye solution was kept in dark.
- (ii) The second beaker containing dye solution was exposed to room temperature.
- (iii) The third beaker containing dye solution was exposed to solar light only.
- (iv) The fourth beaker containing dye solution + TiO₂ was exposed to solar light (no change was observed).
- (v) The fifth beaker contained dye solution + TiO₂ + H₂O₂ was exposed to solar light degradation (AOPs).

After allowing there beakers to stand in 3 hours, the optical density of the solution in each beaker was measured with the help of a spectrophotometer. No change in the optical density was found for the solution of first four beakers (i-iv). Fifth beaker showed a decrease in value of optical density.

2.4 Calculations

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

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

Where, A₀ is the initial absorbance of dye solution & A_t is absorbance at time interval 't' (30, 60, 90, 120, 240 min).

3. Results and Discussion

3.1 Typical Run

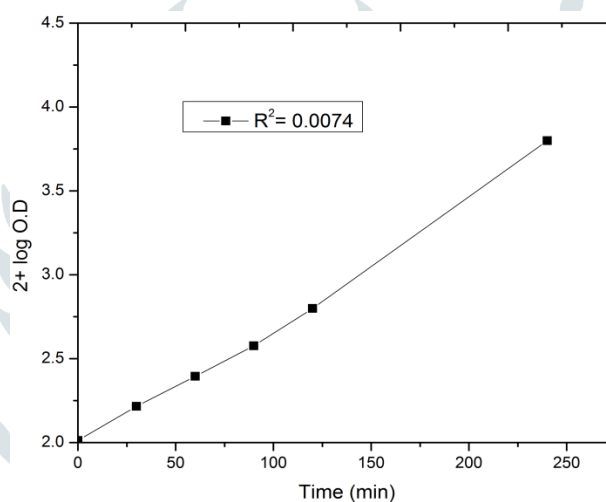


Figure 1 A Typical Run for Degradation of dye coralene Navy Blue 3G.

[50mg/L dye, 2250mg/L H₂O₂, 100mg TiO₂, 504×100 LUX Light Intensity, 4.3 pH, 240 min Reaction Time].

The optical density of the reaction mixture decreases with increases of time intervals which indicate that the concentration of dye decreases in this reaction mixture. Fig. 1 shows A plot of 2 + log O.D vs. exposure Time was a straight line. This indicates that the photocatalytic degradation of dyes follows pseudo Second order kinetics and the rate constant for this reaction was determined using the expression $K = 2.303 \times \text{slope}$.

In this parameter maximum 98.92 % of discoloration achieved in 240 minutes so we can say that the rate of reaction decreases and after 240 min keeping reaction mixture under sun light no change was observed.

3.2 Effect of dye concentration on degradation of dye

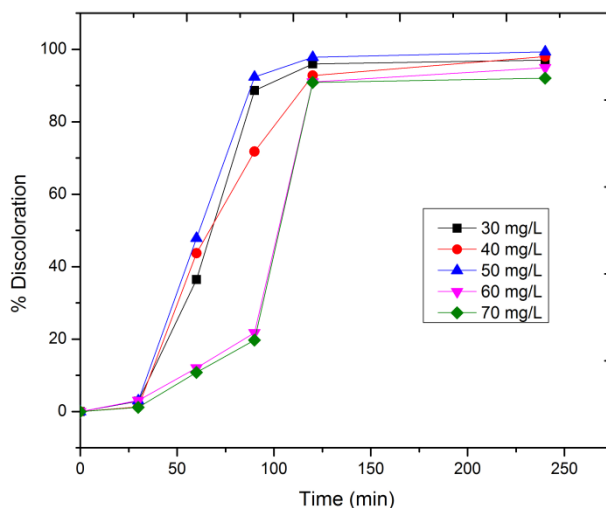


Figure 2 Effect of Concentration on Degradation of dye coralene Navy Blue 3G.

[30mg/L to 50 mg/L dye, 2250mg/L H₂O₂, 100mg TiO₂, 504×100 LUX Light Intensity, 240 min Reaction Time].

Effect of variation of CNB 3G dye concentrations was studied by taking different concentrations from 30 mg/L to 70 mg/L. Figure 2 shows maximum 98.72 % of discoloration achieved within 240 min at 50 mg/L dye solution. This may be attributed to the fact that as the concentration of dyes was increased, more dyes molecules were available for excitation followed by inter system crossing and hence, there was an increase in the concentration of dyes further.

3.3 Effect of pH on degradation of dye

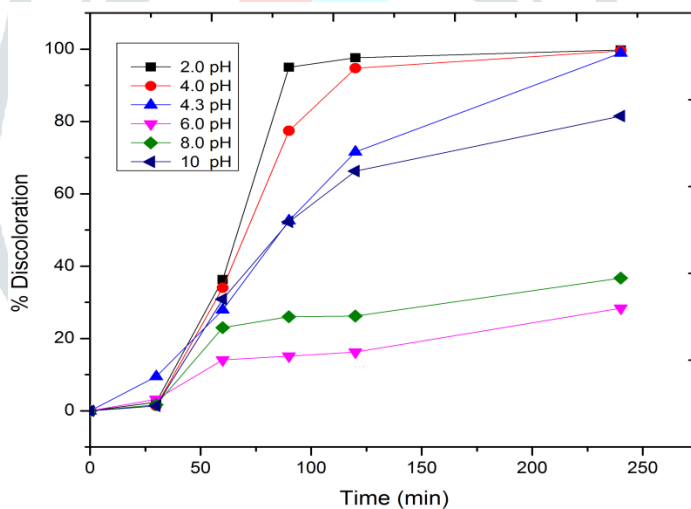


Figure 3 Effect of pH on degradation of dye coralene Navy Blue 3G.

[50mg/L dye, 2250mg/L H₂O₂, 100mg TiO₂, 504×100 LUX Light Intensity, 2 to 10 pH, 240 min Reaction Time].

The photocatalytic experiments were conducted at different pH from 2 to 10 by keeping direct sun light. 0.1N HCL/NaOH solutions were used for adjusted pH solution and the results are presented in Fig. 3. on exposure of reaction volume to sunlight, the highest degradation 99 % at pH 2 was recorded within 240 min for CNB 3G. At pH 10, the rate of discoloration was observed 81%. Hence it is concluded that the degradation in acidic medium, basic medium is higher than that of neutral medium. The increase in rate of photocatalytic degradation may be generated due to the more availability of OH⁻ ions. In range of acidic medium more OH radicals may be generated due to electronic excitation in catalyst. Formation of these hydroxyl radicals is responsible for the high photocatalytic degradation.

3.4 Effect of Amount of Semiconductor on dye degradation

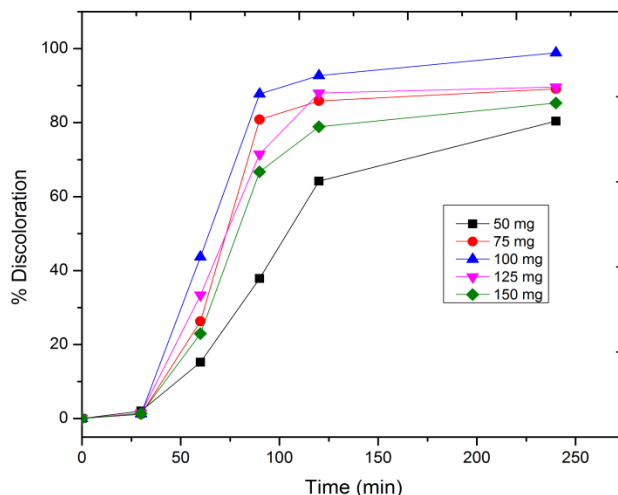


Figure 4 Effect of Amount of Semiconductor on dye degradation.

[50mg/L dye, 2250mg/L H₂O₂, 50mg to 150mg TiO₂, 504×100 LUX Light Intensity, 240 min Reaction Time].

In order to study the effect of amount of catalyst, TiO₂ dosage was varied from 50 mg to 125 mg. At 50 mg/L of CNB 3G dye solutions and the results are presented in Fig. 4. On exposure of reaction volume to sunlight after adding the catalyst, the dye color started to fade by showing the visible signs of decolorization. The highest degradation 98.72% was recorded for 100mg/L of catalyst which was sufficient to degrade CNB 3G dye Solution within 240 min. The results prove that the rate of photo degradation increases with increases catalyst. It further more of catalyst added, solutions become more turbid and reduce the light transmission through the solution.

3.5 Effect of Variation in H₂O₂ concentration on dye degradation

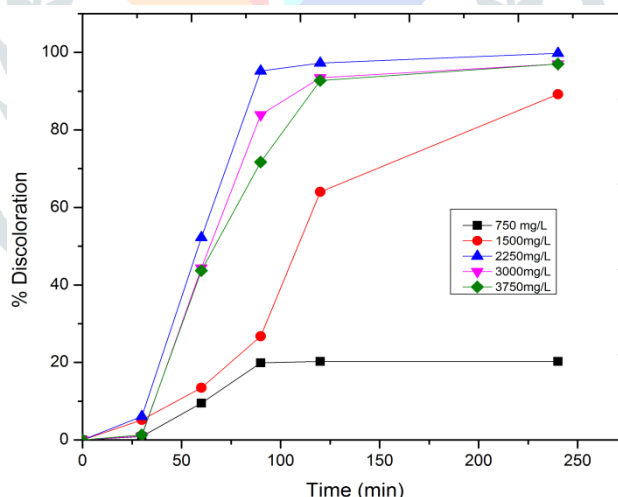


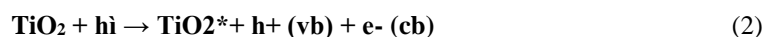
Figure 5 Effect of H₂O₂ on dye degradation coralene Navy Blue 3G.

[50mg/L dye, 750mg/L to 3750 mg/L H₂O₂, 100mg TiO₂, 504×100 LUX Light Intensity, 4.3 pH, 240 min Reaction Time].

Since hydroxyl radicals appear to play an important role in the photocatalytic degradation, electron acceptors such as hydrogen peroxide were added to the dye solution. The degradation rates for the CNB 3G in presence of irradiation/TiO₂/H₂O₂ in order to find the optimal H₂O₂ concentration to be used was shown in Fig. 5. It was observed that the added hydrogen peroxide had a beneficial effect on the degradation of azo dye. The results show that maximum reaction rate was observed at 2250 mg/L of H₂O₂ for dye achieving a 98.72% degradation rate in 240 min. However, when the concentration of H₂O₂ increases, the electron acceptor reacts with hydroxyl radicals, and acts as scavenger of the photo produced holes. In addition, H₂O₂ can modify the TiO₂ surface. This fact probably decreases its photocatalytic efficiency.

3.6 Mechanism

A mechanism is proposed for the degradation of the dye coralene Navy Blue 3G, the participation of OH[·] radical as an active oxidizing agent is proposed. The end product found is a colorless solution indicating for complete degradation of dye.



Where cb is conduction band and vb is valence band.

The photon production holes and electrons may migrate to the particle surface, where the holes can react with surface-bound hydroxyl group (OH⁻).



The electrons in conduction band react with the adsorbed oxygen molecules to form super oxide ions (O₂⁻).

Superoxide ions (O₂⁻) is reduced by H⁺, accounting for hydroxyl radical (HO₂[·]) and hydroxyl radical production.



HO₂[·], OH[·], O₂⁻, are strong oxidizing species and they react with dye molecules to oxidize them.

In the second pathway where a dye absorbs radiation of suitable wavelength and excited to its first singlet state followed by inter system crossing to triplet state.



The excited dye may be oxidize to produce highly reactive hydroxyl radical (OH[·]).



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, H₂O₂ 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.

5. References

- [1] Ge, J. Qu, J. 2004. Ultrasonic irradiation enhanced degradation of azo dye on MnO₂. Journal of Environmental applied catalysis B, 47: 133-140.
- [2] Gümüş, D. Akbal, F. 2011. Photocatalytic degradation of textile dye and wastewater. Journal of Water Air Soil Pollutant, 216:117–124.
- [3] Malik, P. Saha, S. 2003. Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst. Journal of Separation and Purification Technology, 31: 241-250.
- [4] Kaur, S. Singh, V. 2007. Visible light induced sonophotocatalytic degradation of Reactive Red dye 198 using dye sensitized TiO₂, Journal of Ultrasonics Sonochemistry, 14: 531–537.
- [5] Pamecha, K. Mehta, V. and Kabra, B. 2016. Photocatalytic degradation of disperse azo dye coralene dark red 2B by CeFeO₃, Journal of Archives of Applied Science Research, 8 (1): 7-12.
- [6] Giwa, A. Nkeonye, P. Bello, K. Kolawole, K. 2012. Photocatalytic decolorization and Degradation of C. I. Basic Blue 41 Using TiO₂ Nanoparticles, Journal of Environmental Protection, 3: 1063-1069.

- [7] Daneshvar, N. Salari, D. Khataee, A. 2003. Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters, *Journal of Photochemistry and Photobiology A: Chemistry*, 157: 111–116.
- [8] Kalra, S. Mohan, S. Sinha, A. Singh, G. 2011. Advanced Oxidation Processes for Treatment of Textile and Dye Wastewater: A Review, *Journal of International Conference on Environmental Science and Development*, 4: 271-275.
- [9] Sun, J. Sun, S. Sun, J. Sun, R. Qiao, L. Guo, H. Fan, M. 2007. Degradation of azo dye Acid black 1 using low concentration iron of Fenton process facilitated by ultrasonic irradiation, *Journal of Ultrasonics Sonochemistry*, 14: 761-766.
- [10] Saggiaro, E. Oliveira, A. Pavesi, T. Maia, C. Ferreira, L. Moreira, J. 2011. Use of Titanium Dioxide Photocatalysis on the Remediation of Model Textile Wastewaters Containing Azo Dyes. *Journal of Molecules*, 16: 10370-10386.
- [11] Modirshahla, N. Behnajady, M. 2006. Photooxidative degradation of Malachite Green (MG) by UV/H₂O₂: Influence of operational parameters and kinetic modeling, *Journal of dye and Pigments*, 70: 54-59.
- [12] Sakthivel, S. Neppolian, B. Shankar, M. Arabindoo, B. Palanichamy, M. Murugesan, V. 2003. Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO₂, *Journal of Solar Energy Materials & Solar Cells*, 77: 65-82.
- [13] Gupta, V. Jain, R. Mittal, A. Saleh, T. Nayak, A. Agarwal, S. Sikarwar, S. 2012. Photo-catalytic degradation of toxic dye amaranth on TiO₂/UV in aqueous suspensions, *Journal of Materials Science and Engineering, C* 32: 12-17.
- [14] Kavitha, S. Palanisamy, P. 2011. Photocatalytic and Sonophotocatalytic Degradation of Reactive Red 120 using Dye Sensitized TiO₂ under Visible Light, *International Journal of Civil and Environmental Engineering* 3(1): 1-6.
- [15] Shimizu, N. Ogino, C. Dadjour, M. Murata, T. 2007. Sonolytic degradation of methylene blue with TiO₂ pellets in water, *Journal of Ultrasonics Sonochemistry*, 14: 184-190.
- [16] Pare, B. Solanki, V. Singh, P. 2011. Photocatalytic degradation of Acridine Yellow G and Aniline Blue B dyes in a slurry batch reactor using visible light and ZnO suspension, *Journal of Indian chemical society*, 88: 1533-1540.
- [17] Panjabi, P. Ameta, R. kumar, A. Jain, M. 2008. Visible light induced photocatalytic degradation of some Xanthene dyes using immobilized anthracene, *Journal of Bulletin of the chemical society of Ethiopia*, 22(3): 361-368.
- [18] Madhusudhana, N. Yogendra, K. Mahadevan, K. Naik, S. Gopalappa, H. 2011. Photocatalytic degradation of coralene dark red 2b dye using calcium aluminate (CaAl₂O₄) catalyst, *Journal of Environmental Science an Indian*, 6(3): 159-163.
- [19] Malik, P. Saha, S. 2003. Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst, *Journal of separation and purification technology*, 31: 241-250.
- [20] Kambalagere, Y. Channappa, B. Mahadevan, K. Narayanappa, M. 2016. Decolorization of synthetic Coralene Violet 3R and Disperse Blue 2BL azo dyes using photoactive Calcium Aluminates Nanoparticle in presence of sunlight, *Journal of International advanced in chemical engineering & biological science*, 3(1), 108- 112.