



PHOTOCATALYTIC DEGRADATION OF AZO DYE BRILLIANT YELLOW PRESENT IN TEXTILE EFFLUENT USING DEVELOPED MBIR DOWEX-1X8

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Abstract

This study investigated the photocatalytic degradation of textile Azo dye using the photocatalyst immobilized Dowex-1x8. Advanced oxidation processes (AOPs) are the best methods for treating textile effluent. Immobilized Dowex-1x8, a newly developed photocatalyst, is used for the photodegradation of azo dye. The effects of various factors including photocatalyst loading, dye concentration, light intensity and pH on photocatalytic degradation were evaluated. The photo degradation efficiency reached about 98% after 210 min of irradiation. The degradation rate typically follows a first order kinetic reaction. In this study, we found that the photocatalytic degradation treatment of the dye in water is a simple and rapid method.

Keywords: Photocatalyst, Immobilization, Brilliant Yellow (BY) dye, degradation.

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1. INTRODUCTION:

Textile industries are among the largest consumers of water, dyes and various chemicals, resulting in large quantities of highly toxic waste. Pre-treatment of these wastes can be hazardous to the environment. Generally, textile wastes mainly range in color, pH, chemical oxygen demand, inorganic salts, turbidity and temperature [1]. According to the United States Environmental Protection Agency (USEPA), textile waste is mainly classified into four types, namely hard-to-treat, high-volume, dispersible, and hazardous and toxic waste [2].

The textile industry uses water during the dyeing and finishing processes [3]. When both volumes discharged and effluent composition is considered, the wastewater generated by the textile industry is rated as one of the most polluting of all industries. About 1 to 20% of the world's total dye production is lost during the dyeing process and released into textile effluents [4]. The release of these coloured effluents into the environment is a significant cause of pollution and eutrophication, and it can generate dangerous byproducts through oxidation, hydrolysis, or other chemical reactions occurring in the wastewater phase [5].

In view of the carcinogenic or mutagenic character of some azo dyes, the dangerous effect of the colour in the textile effluent, and the traditional resistance of the effluents to biological degradation, the necessity of investigating new alternatives for the adequate treatment of these kinds of residues are evident. Primary (flocculation, adsorption), secondary (biological methods), and chemical processes (ozonization, chlorination) are currently used to degrade the colour of dye-contaminated water [6,7]. However, these techniques are non-destructive because they only transfer non-biodegradable matter into sludge, resulting in a new type of pollution that requires additional treatment [8,9]. Advanced oxidation processes (AOPs) based on heterogeneous catalysis have emerged as a potentially destructive technology capable of completely degrading the majority of organic pollutants [10,11].

As a result, the immobilized resin Dowex-1x8 photocatalyst has been studied as an alternative to conventional processes. Recently, the use of advanced oxidation processes (AOPs) has generated considerable interest in incompletely decomposing dyes. AOP is based on the production of reactive species, such as hydroxide atoms, which rapidly and selectively oxidize a wide range of organic pollutants [12-17]. A significant destructive technology that completely degrades the majority of organic contaminants, including organic colours, is heterogeneous photocatalysis [18-21].

2. Materials and methods:

2.1 Materials:

The dye Brilliant Yellow (BY) purchased from Lobachemie (India), the photocatalyst Dowex resin-1x8 (Sisco chem) and Methylene blue hydrate (Lobachemie, India). Double distilled water was used for preparation of various solution. The pH conditions of the desired solution were adjusted by using standardized 1N H_2SO_4 and 1N NaOH solution. pH of the solution was measured by digital pH meter. All experiments were performed at room temperature and with a magnetic stirrer.

2.2 Photocatalytic studies and design of photoreaction chamber:

The photocatalyst is prepared using Dowex-1x8 materials, and for immobilization, a concentration solution of approximately M/100 of methyl blue is prepared in double-distilled water, and Dowex-1x8 resin is added to the solution and shaken well to immobilize resin pores for up to 24 hours. All this was done in a dark place. Then the resin prepared from the solution is filtered by double-distilled water and used as a photocatalyst. Photochemical degradation experiments were conducted in glass reactors containing solutions of the Brilliant Yellow dye. The characteristics and structure of the Brilliant Yellow dye are listed in Table 1. The reactor solution is continuously agitated by a magnetic stirrer during the experiment. After 10 minutes of darkness, the reactor solution was illuminated on the reactor by 200 watt tungsten lamps (Philips, India) emitting light equivalent to visible light (Figure 1). The lamp is surrounded by an aluminium reflector to avoid radiation loss.

Table -1 Properties of Brilliant Yellow (BY) dye

Dye Name	: Brilliant Yellow(BY)
C.I. Name	: Direct Yellow 4
Molecular Formula	: $C_{26}H_{18}N_4O_8S_2Na_2$
Molecular Weight	: 624.5gm/mol
Class	: Azo dye
Solubility	: Soluble in water
Nature	: Acidic
λ_{max}	: 497 nm
Structure	

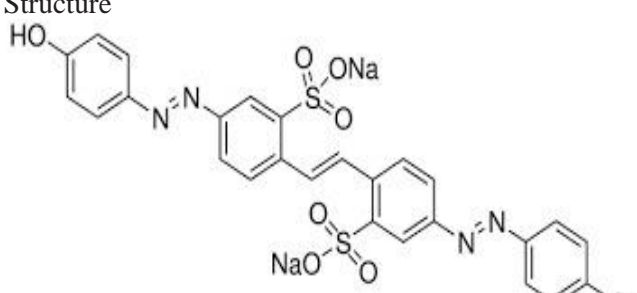
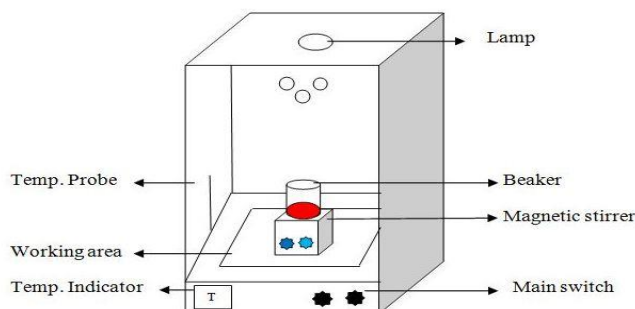
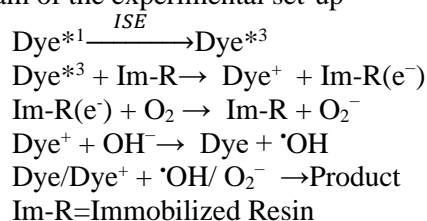
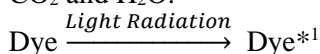



figure 1. Schematic diagram of the experimental set-up

2.3 Mechanism and Method:

The mechanisms of the degradation of Brilliant Yellow(BY) dyes under ultraviolet or solar light include electron excitation and the generation of very active oxygen species that attack dye molecules and result in photo degradation. The Dowex-1x8 is a photocatalyst developed from methyl blue immobilized resin. Due to the photosensitive nature of methylene blue, the electron transitions from the valence band (VB) to the conduction band (CB) and reaches the triple state (Dye^{*3}) of methylene blue by the ISC. After the intermolecular electronic transition begins between the resin, blue dye molecules, water molecules, brilliant yellow dye molecules, and dissolved oxygen, holes, hydroxyl radical ($\cdot OH$), and superoxide ions (O_2^-) form, which are highly oxidized by the action of holes, hydroxyl radical ($\cdot OH$), and superoxide ions on azo dyes. They are converted to simple organic compounds such as CO_2 and H_2O .



The dye concentration change is simply observed by the CSIM 500 microprocessor UV/Visible spectrophotometer at λ_{max} is 497nm. At the 10 minute time interval, we pipette out 5 ml of solution. This equation calculates the degradation efficiency (X%) of dye solution.

$$X \% = (C_i - C_t / C_i) \times 100$$

Where, C_i and C_t are the initial optical density and the optical density at time t of brilliant yellow dye, respectively.

3. Results of dye degradation by photocatalyst under UV/ Visible light

3.1. Effect of photocatalyst loading dose:

The amount of photocatalyst used is the most important parameter affecting the rate of photocatalytic degradation. At a constant pH of 7.5 and an intensity of light of 10.5 mWcm^{-2} , we observed a change in photocatalysts of 1.0 to 2.5 g/100 ml, dye concentrations of 30 mg/L, and photocatalysts. We found that with increasing the number of catalysts, the rate of degradation

increases because the surface area of the photocatalyst is enhanced, the quantity of absorption and interaction of reaction mixture molecules with the photocatalyst is increased, and the number of holes, hydroxyl radicals ($\cdot\text{OH}$) and superoxides (O_2^-) increases. These are the primary oxidizing intermediates in the advanced oxidation process, which increases degradation efficiency. Figure 2 shows the impact of photocatalyst loading on optical density.

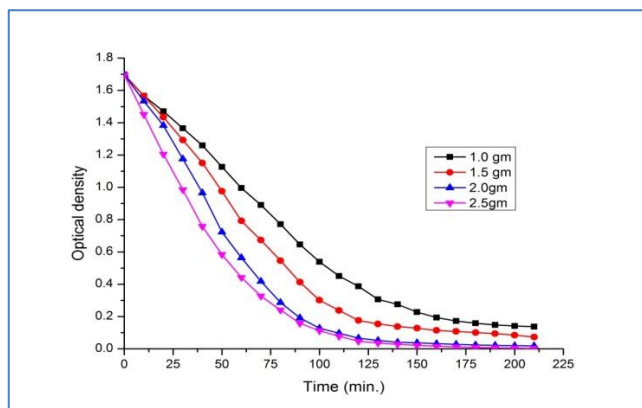


Figure-2 Effect of photocatalyst loading on optical density

3.2. Effect of initial dye concentration:

The initial dye concentrations were influenced by the effect of varying from 30 to 60 mg/L, based on a constant photocatalyst (2.0 g/100 ml), pH 7.5, and light intensity 10.5 mWcm^{-2} , and tested on degradation efficiency. As the concentration of dye increases, the rate of degradation decreases (shown in figure 3). This effect can be caused by the following factors: As dye concentration increases,

the numbers of photons that reach the unit surface area of the photocatalyst decreases. As a result, the formation rate of holes, hydroxyl radicals ($\cdot\text{OH}$) and super oxides (O_2^-) decreases, also the rate of degradation decreases. The photocatalyst active site has a limited number of dye molecules, and the remaining dye molecules persist in the solution until the previously attached molecules degrade.

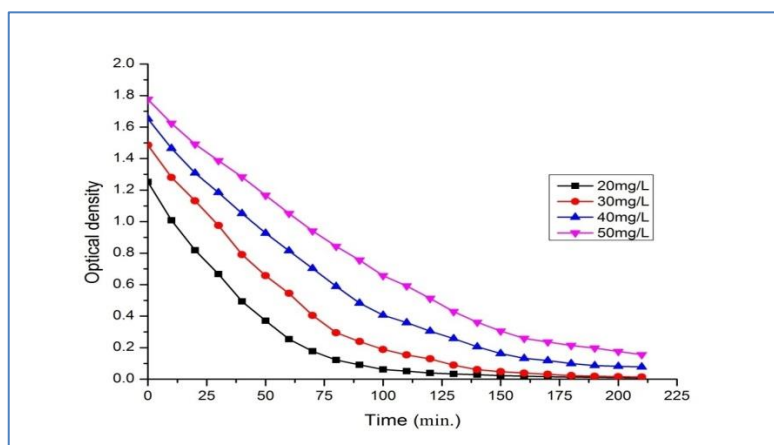


Figure-3 Effect of initial concentration on optical density

3.3. Effect of pH:

The influence of pH on the degradation rate of dye molecules is very interesting for us. The results show that in high acid pH ranges below pH 5, the degradation rate is very slow. When pH reaches the

basic range, the rate of degradation increases rapidly, and in the pH range at 7.3 to 11, the rate of degradation is very good. At constant catalyst amount 2.0g/100ml, dye concentration 30mg/L, and light intensity 10.5 mWcm^{-2} , the rate of degradation

begins to increase as pH increases. As a result, we concluded that the degradation rate of the basic medium is higher than that of the acid medium. The increase in photocatalytic degradation may be due to the increased availability of hydroxyl radical ($\cdot\text{OH}$) in the pH range of 7.3 to 11. The formation of more hydroxyl radicals ($\cdot\text{OH}$) that combined with holes formed by electronic

excitation in photocatalysts. Superoxides (O_2^-) are less likely to cause photocatalytic degradation than hydroxyl radicals. As pH increases above 11, the degradation rate slows down. This effect may be caused by competition between $\cdot\text{OH}$ groups and O_2^- for attachment the active site of the catalyst (Figure 4).

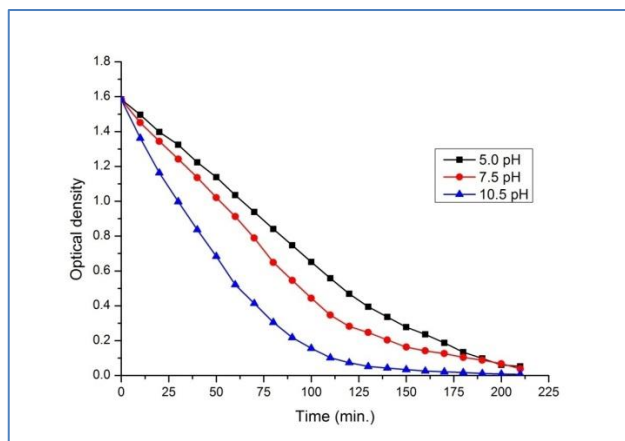


Figure-4 Effect of solution pH on optical density

3.4. Effect of visible light:

The most important factor affecting the rate of degradation is the intensity of the light. We found that as the light intensity increases (dye concentration 30 mg/l, photocatalyst 2.0 g/100 ml, pH 7.5), the rate of degradation of dye molecules increases to a certain point, and above that point, no change in the degradation rate of the dye is observed at the light intensity. This change in the rate of degradation of the dye molecules is due to the change in the intensity of the light. As the intensity of light increases (5.4 – 15.5 mWcm^{-2}), the number of photons reaching the surface of the photocatalyst

increases, the number of pores, hydroxyl radical ($\cdot\text{OH}$), and super oxide ions (O_2^-) increases, and the degradation rate of dye molecules increases. This can result in the availability of the maximum number of photons required for the excitation within a fixed range of light intensity after a significant change in the rate of degradation is observed because the excitation does not require more photons. Since all photocatalyst molecules are active in fixed light intensity ranges, the degradation rate remains unchanged when light intensity increases to any range (Figure 5).

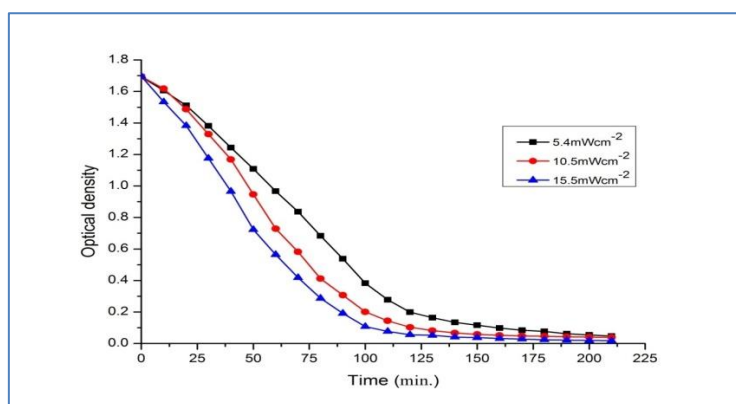


Figure-5 Effect of visible light intensity on optical density

3.4 FTIR Characterizations

The FTIR technique was used to examine the surface group responsible for dye adsorption. The FTIR spectra (Figure 6) of the degraded dye show a

peak at 3585 cm^{-1} –OH stretching vibrations. The absorption peaks at $\sim 2850 \text{ cm}^{-1}$ due to OH stretching vibration.

The absorption peaks at $\sim 2360\text{ cm}^{-1}$ stretching vibration C-H bond. The absorption peak at $\sim 1735\text{ cm}^{-1}$ was due to the observed -NH bending of aromatic amines and C=C in the aromatic stretching vibration peak. The adsorption bands at 702-1480

cm^{-1} were assigned to SO_3 and $-\text{C}=\text{C}$ trans alkene stretching groups on the samples. IR spectra clearly showed that the azo bond ($\text{N}=\text{N}$) is broken, which is mainly responsible for the toxicity of industrial waste textile dye.

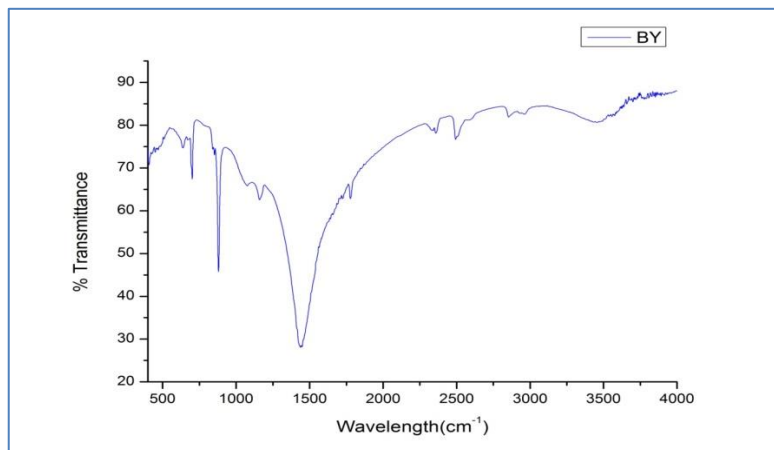


Figure -6 FTIR analysis of degrade dye

3.5 Kinetics study

Figure 7 shows the kinetics of the disappearance of Brilliant Yellow dye at an initial concentration of 30 mg/L under optimised conditions. The results show that photocatalytic degradation of Brilliant Yellow dye in the photocatalyst MBIR Dowex-1x8 can be described by the first-order reaction $\ln a/(a-x)$

$x) = kt$, a being the initial concentration, and x being the constant concentration of t . The semi-logarithmic plot of the concentration data gives a straight line. The rate constant was calculated as $5.909 \times 10^{-2} \text{ min}^{-1}$.

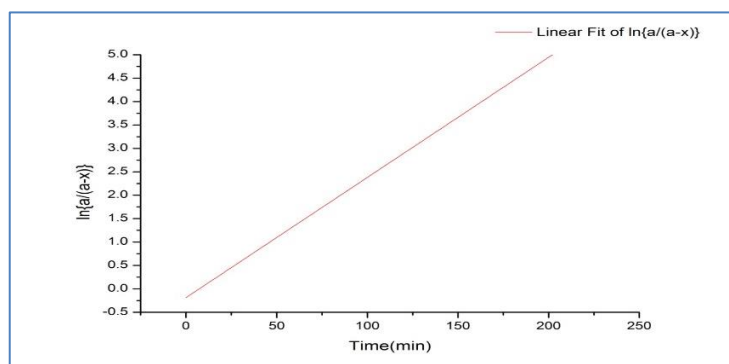


Figure 7 kinetic analysis for the degradation of Brilliant Yellow dye

4. Conclusions:

We found that the methylene blue immobilized resin Dowex-1x8 used as a photocatalyst gives very good results in dye degradation, so the dye degradation efficiency of 99% has been achieved by this photocatalyst under favourable conditions. The degradation of textile azo dyes by the newly developed photocatalyst MBIR Dowex-1x8 is an economical and very good alternative to conventional techniques for industrial application. We observe the effect of various parameters given in order of importance.

- Variation in catalyst dose: As the photocatalyst dose increases, so does the rate of dye degradation increases.
- Variation in dye concentration: As dye concentration increases, the degradation of dye also decreases.
- pH variation: The acidity range of pH is very low. With pH increases, degradation rate increases, and between pH 7.3 and 11, it is a good degradation rate. As pH increases, the rate of degradation increases.
- Variation in light intensity: As the intensity of light increases, the degradation rate of dye

molecules increases to a certain point, and no further changes occur afterwards.

- FTIR analysis of the degraded dye solution using immobilized Dowex-1x8resin is carried out after a photo degradation process of 210 min. The dye was completely degraded in MBIR dowex-1x8, and no azo bonds were detected in the degraded dye. The decolorizing of the solution was due to degradation.
- The photocatalytic degradation followed first order kinetics.

5. REFERENCES

1. A.K.Verma, R.R. Dash, P. Bhunia. A review on chemical coagulation/flocculation technologies for removal of color from textile wastewaters. *J. Environ. Manag.* (2012) 293, 154–168.
2. J. Dasgupta, J. Sikder, S.Chakraborty, S. Curcio, E. Drioli, Remediation of textile effluents by membrane based treatment techniques: A state of the art review. *J. Environ. Manag.* (2015) 147, 55–72.
3. C. Galindo, P. Jacques, A. Kalt, Photochemical and photocatalytic degradation of an indigoid dye: a case study of acid blue 74, *J. Photochem. Photobiol. A: Chem.* 141 (2001) 47–56.
4. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Hermann, Photocatalytic degradation pathway of methylene blue in water, *Appl. Catal. B: Environ.* 31 (2001) 45–157.
5. A. Bianco-Prevot, C. Baiocchi, M.C. Brussino, E. Pramauro, P. Savarino, V. Augugliaro, G. Marci, L. Palmisano, Photocatalytic degradation of acid blue 80 in aqueous solutions containing TiO_2 suspensions, *Environ. Sci. Technol.* 35 (2001) 971–976.
6. S.S. Patil, V.M. Shinde, Biodegradation studies of aniline and nitrobenzene in aniline plant waste water by gas chromatography, *Environ. Sci. Technol.* 22 (1988) 1160–1165.
7. A.T.More, A.Vira, S. Fogel, Biodegradation of trans-1,2-dichloroethylene by methane utilizing bacteria in an aquifer simulator, *Environ. Sci. Technol.* 23 (1989) 403–406.
8. I. Arslan, I.A. Balcioglu, T. Tuhkanen, D. Bahnemann, H_2O_2 /UV-C and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ /UV-C versus TiO_2 /UV-A treatment for reactive dyewastewater, *J. Environ. Engg.* 126 (2000) 903–911.
9. N. Stock, J. Peller, K. Vinodgopal, P.V. Kamat, Combinative sonolysis and photocatalysis for textile dye degradation, *Environ. Sci. Technol.* 34 (2000) 1747–1750.
10. A. Uygur, An overview of oxidative and photooxidative decolorisation treatments of textile waste-waters, *J. Soc. Dyers Colour.* 113 (1997) 211–217.
11. S. Das, P. V. Kamat, S. Padmaja, V. Au and S. A. Madison, Free radical induced oxidation of the azo dye Acid Yellow 9, *J. Chem. Soc., Perkins Trans.* 2(1999) 1219-1224.
12. Y. Yang, D. Wyatt and M. Bahorsky, Decolorization of dyes using UV/ H_2O_2 photochemical oxidation *Textile, Chem. Colorist*, 30, 27-35 (1998).
13. C. Galindo, P. Jacques and A. Kalt, Photochemical and Photocatalytic Degradation of an Indigoid Dye, *J. Photochem. Photobiol. A: Chem.*, 141 (2001) 47-56.
14. N. Serpone and E. Pelizzetti (Eds.), *Photocatalysis: fundamentals and applications*, Book, Wiley Interscience, New York (1989).
15. M. A. Fox and M. T. Dulay, Heterogeneous photocatalysis, *Chem. Rev.*, 93 (1993) 341-357.
16. V. K. Meena and R. C. Meena, *J. Ind. Council Chem.*, 27(2010) 180-184.
17. V. Kumar and R. C. Meena, Studies on photodegradation of Tropaeolin O in aqueous solution using immobilized Dowex-11 photocatalyst, *J. Ind. Chem. Soc.*, (2011) 257-264.
18. R. B. Pachwarya and R. C. Meena, Degradation of Azo Dyes Ponceau S, S-IV from the Wastewater of Textile Industries in a New Photocatalytic Reactor with High Efficiency Using Recently Developed Photocatalyst MBIRD-11, *Energy Source Part A*, 33(2011), 1651-1660.
19. R. C. Meena and M. Meena, Solar photocatalytic degradation of azo dye ponceau BS through applying alternative developed photocatalyst MBIR Dowex 11, *Environ. Sci.*, 7 (2012) 199-204.
20. V.K. Meena, Photo catalytic degradation of textile Azo dye using newly developed photo catalyst, *Int. J. Adv. Sci. and Res.*, 1(2016) 58-62.
21. S. Murmat, Optimization of azo-dyes to reduce environmental impact of textile industries, *Int. J. Adv. Res.* 5(11) (2017) 1519-1528.