



Photocatalytic Decolorization of Textile dye Methylene blue by photocatalyst WO_3 and SnO_2

K.S. Meena^{1*} and Kanta Meena²

¹Department of Chemistry, M.L.V. Government College, Bhilwara, Rajasthan-311001, India

²Department of Botany, M.L.V. Government College, Bhilwara, Rajasthan-311001, India
kamodsinghlectche@gmail.com

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Abstract

Textile is the largest industry of Bhilwara district in the state of Rajasthan. Bhilwara city is known as "Textile City". The textile industries are most water and chemical intensive industry worldwide and produce large amount of waste water as colored dyes effluents. Colored effluents is toxic in nature and damage to the environment and ecosystem. For the production of 1 kg textile fabric industries consumed 200-400 litres of water. Textile effluent is contains inorganic as well as dissolved organic substances. Dark colour of waste water is due to the presence of residual dyestuffs. The photocatalytic decolorization of textile dye Methylene blue was examined by using photochemical reactor with WO_3 and SnO_2 photo catalyst in presence of U.V. light. The study of the effects of various environmental parameters such as type of catalyst, pH value and catalyst mass were also investigated by using spectrophotometer at different wavelengths.

Keywords: Textile dyes, Methylene blue, WO_3 and SnO_2

Introduction

In textile industries synthetic and colour textile dyes are a major part of water pollution and aquatic life, because they are produces the various bye products as contamination. The side effect of colour dye waste materials which produces during the dyeing process that enters the fresh water bodies and polluted them. The treatment of textile wastewater done by the various biological, physical and chemical methods. But non-biodegradable organic compounds is not possible to degradation by these methods, so that advanced oxidation processes (AOP's) is use with the presence of highly active photocatalysis¹⁻³.

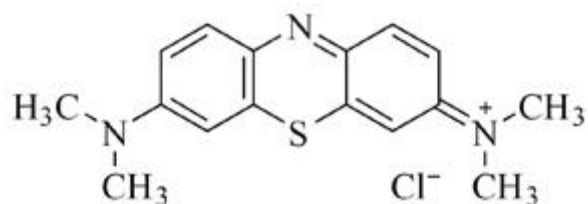
Water is one of the essential resources on our earth. Recycling of waste-water are very important issue today and tomorrow. Today energy-saving green technologies are a demand in our contrary. To develop quantum efficiency of ultraviolet treatment of waste water photochemistry have important role. In environment prospect environment green and nano catalysis were use as photocatalysis. Photochemistry ideal with the study of the physical process of chemical changes which occurs in molecules on absorption of suitable radiation changing from 200 to 800nm⁴⁻⁵.

The textile industries used more than 10,000 dyes every year and generated 280,000 tonnes of discharged waste. Discharged waste mixed in the fresh water and generated textile waste water pollution worldwide. In cloth industry dyeing and finishing process needed large quantity of water and produces highly coloured and large concentration waste water.

This waste water treatment is not possible through classical methods. So that this water is mixed in fresh water and imbalance the photosynthetic activity of aquatic ecosystem system⁶⁻⁸.

Materials and methods

Dyes-Methylene Blue: Formula $C_{16}H_{18}ClN_3S$, Weight 319.86, λ_{max} -664nm.



Structural Formula: Azo tautomeric form of dye.

Photocatalyst: The WO_3 and SnO_2 catalyst used as GR grade chemical of 99% purity^{9,10}.

Instruments: Photochemical degradation¹¹ was carried out in a photochemical reactor instrument. This instrument equipped with UV tubes of 254nm. Magnetic stirrer constant stirring of solution. The wavlenth were obserbed with UV-VIS spectrometer with different concentration. pH meter was used to analysis pH of dye solution. Adjust the pH of the dye solution by measurment of pH meter.

Procedure and Analysis: To experimental perpose the photochemical reaction were carried out by useing of 1000ml of dyes solution of desired concentration. The stock solution (1×10^{-3} M) was prepared in distilled water of methylene blue dyes. Initial absorbance dye solutions was observed by useing of UV-VIS Spectrophotometer. Prior to the runs of experiment, dye solutions were stirred for 10min. After the addition of catalyst WO_3 / SnO_2 expriment to allow the physical adsorption of different dye molecules. The reaction performe on the catalyst surface area, till now to reaction reach the equilibrium level. 3ml sample of suspension was withdrawn with the help of syringe in beaker and reaction mixture was prepared by adding the catalyst (initially 0.01gm). Reaction mixture (2×10^{-5} M) was made up to 100ml by adding double distilled water. The experiments were carried out under UV light 254nm in the photochemical reactor. Absorbance study of dye in each degraded sample was determined with spectrophotometer at λ_{max} 664nm for methylene blue at different time intervals (10 min) after filtration through the centrifugal machine. The color degradation of methylene blue dye with time interval was continuous monitored¹²⁻¹³. Results of photocatalytic degradation (Table-1 and 2) of Methylene blue graphically presented in Figure-1 and 2.

Table-1: Bleaching of Textile dye Methylene blue by WO_3 reagent.

Time (Hour)	Absorbance
0.0	0.495
0.5	0.354
1.0	0.330
1.5	0.210
2.0	0.200
2.5	0.185
3.0	0.155
3.5	0.145
4.0	0.120
4.5	0.100
5.0	0.075

Control Experiments confirmed the requirement of SnO_2 / WO_3 photocatalyst for the active degradation of dye molecules at λ_{max} 664nm.

Results shows that optimum conditions for the removal of dye Methylene Blue Concentration = 2.0×10^{-5} M, pH=7.5, SnO_2 / WO_3 = 0.1gm

The rate of reaction was show that
Rate constant k (Methylene blue) = $2.303 \times \text{slope} = 2.03 \times 10^{-3} \text{ sec}^{-1}$

This degradation Methylene blue dyes by SnO_2 / WO_3 represented a pseudo first order rate law.

Table-2: Bleaching of Textile dye Methylene blue by SnO_2 reagent.

Time (Hour)	Absorbance
0.0	0.490
0.5	0.404
1.0	0.330
1.5	0.210
2.0	0.200
2.5	0.165
3.0	0.155
3.5	0.145
4.0	0.103
4.5	0.280
5.0	0.015

Operational parameters: Photocatalyst Dose: The dose of SnO_2 photocatalyst was reflected the affect the rate of reaction and of dye degradation. In the experiment parameters like initial dye concentration, pH remain constant. The different amount of photocatalyst SnO_2 dose study from 0.01g to 0.12g/100ml. results shows that the rate of dye degradation increases with increasing catalyst contraction up to 0.1g because surface catalytic reaction and after that the rate of reaction becomes almost constant because surface area of catalysis were be used so that surface reaction rate decrease¹⁴⁻¹⁶.

Results shows in Figure-3 the concentration of catalyst increases the number of catalyst active sites and active molecule increase so that rate of reaction was increase on the surface area, resulting that increases the number of OH and O_2^- radicals, that occurs rate of degradation is increased.

After time has sends catalyst active molecule availability with the same concentration of dye was decrease. That time further dye molecules are not available for adsorption reaction purpose. The remaining catalyst particles are not involved in the photocatalytic reaction. Result the degradation of Methylene blue dye molecule were remains constant¹⁷.

Concentration of Dye: The effect of the dye concentrations represented in Figure-4 on the degradation of Methylene blue was observed at various range of concentrations from $0.25 \times 10^{-5} \text{M}$ to $2.5 \times 10^{-5} \text{M}$. The result reflected that initial rate of increase with increase in concentration of dye molecules.

The highest rate of reaction was observed at $2.0 \times 10^{-5} \text{M}$ of Methylene blue dye solution. After this concentration the rate of photo degradation of dyes decreases because the increase in the concentration of active dye molecule. Experiment represented that the increase in initial concentration of dye continually release the hydroxyl radicals concentrations therefore the rate of degradation increase. Dye molecules adsorbed on catalyst surface area and degradation occurs, on the increasing the

concentration of dye keeping catalyst dose constant, catalyst surface get saturated. Simultaneously intense color of dye does not permit light to reach photocatalyst¹⁸.

Effect Hydrogen Ion Concentration: The rate of reaction study with the variation in pH on the rate of decolorisation of dye studied as follows, for Methylene Blue pH from 4 to 8, keeping all other parameters constant (Figure-5) for dye methylene blue proves that optimal pH is 7.5. This may be due to rate of reaction decreases with increase in pH. Increase in pH level resulting increases the number of OH^- ions which max the photocatalyst surface negatively charged. This causes repulsion between negative charge dye and photocatalyst¹⁹⁻²⁰.

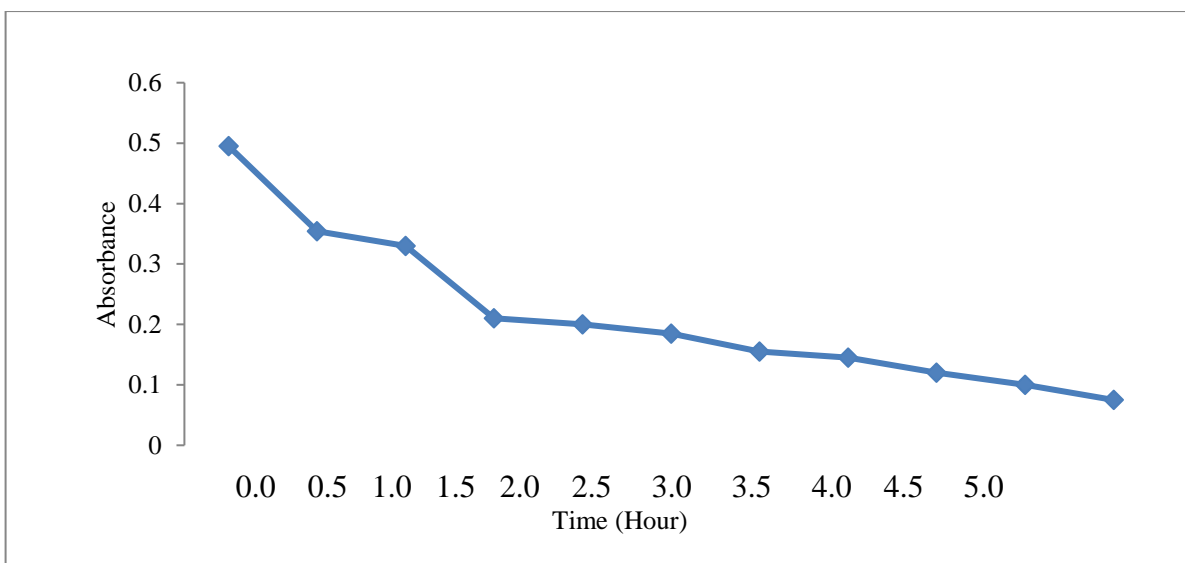


Figure-1: Bleaching of Textile dye Methylene Blue by WO_3 Reagent.

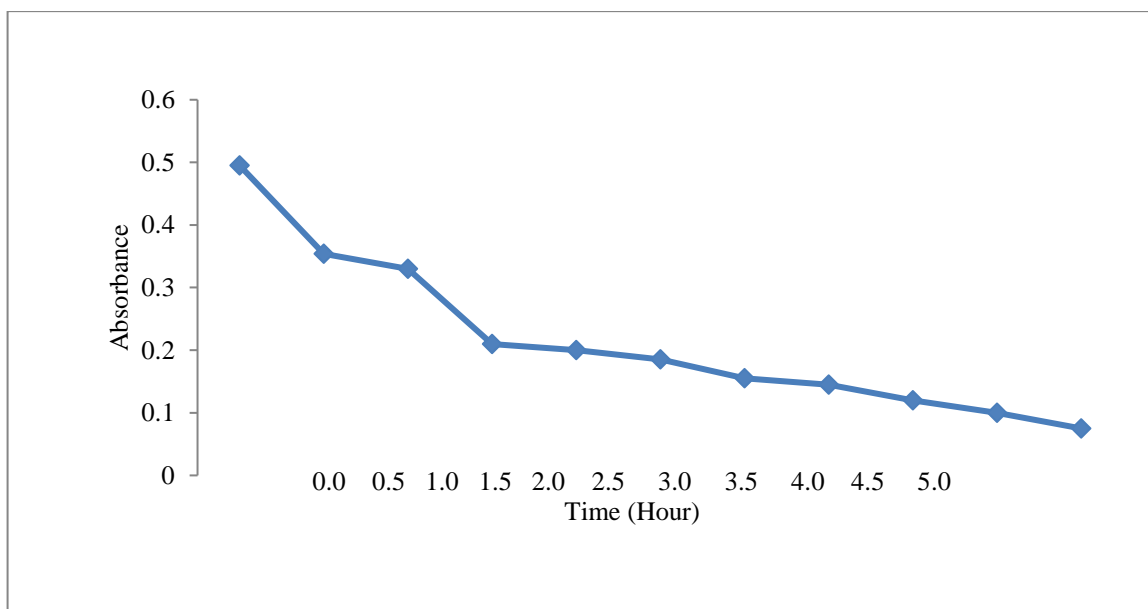


Figure-2: Bleaching of Textile dye Methylene Blue by SnO_2 Reagent.

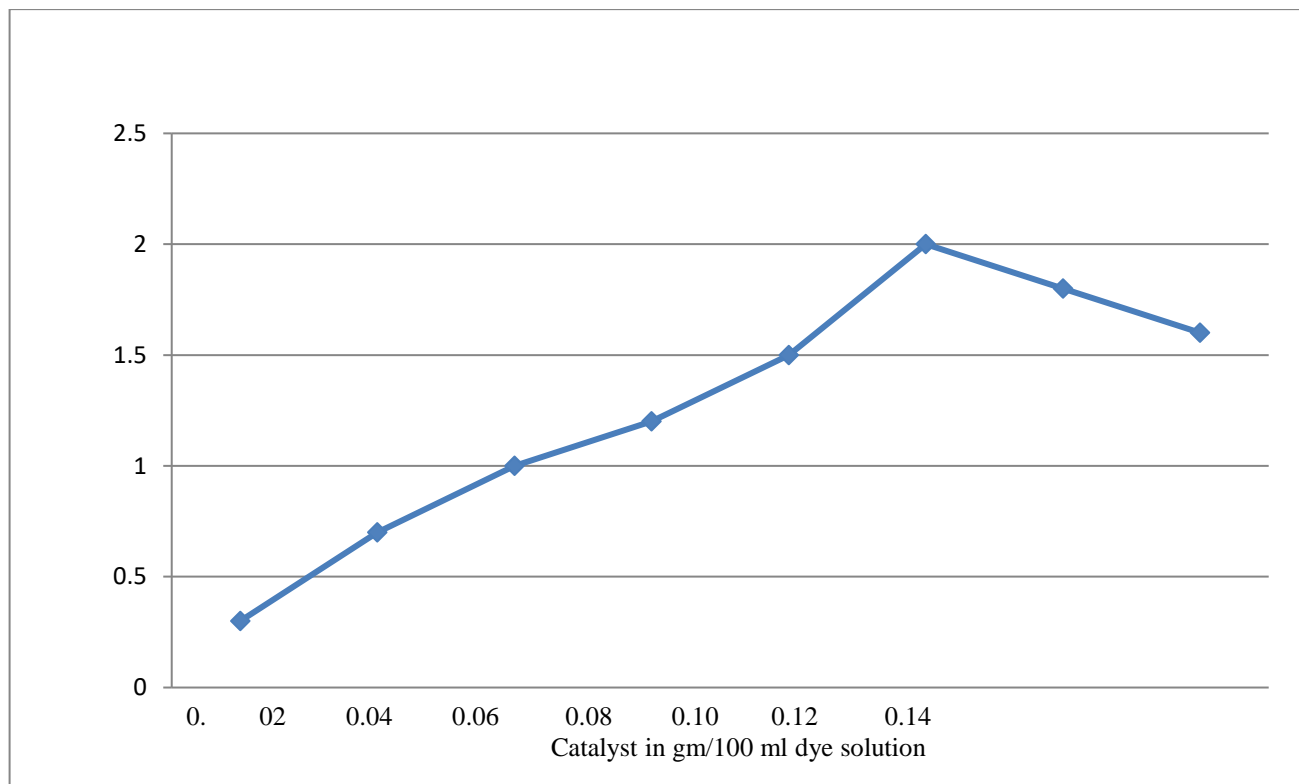


Figure-3: Effect of Catalyst Concentration on photochemical degradation of Methylene Blue (MB) = 2×10^{-5} M, pH=7.5.

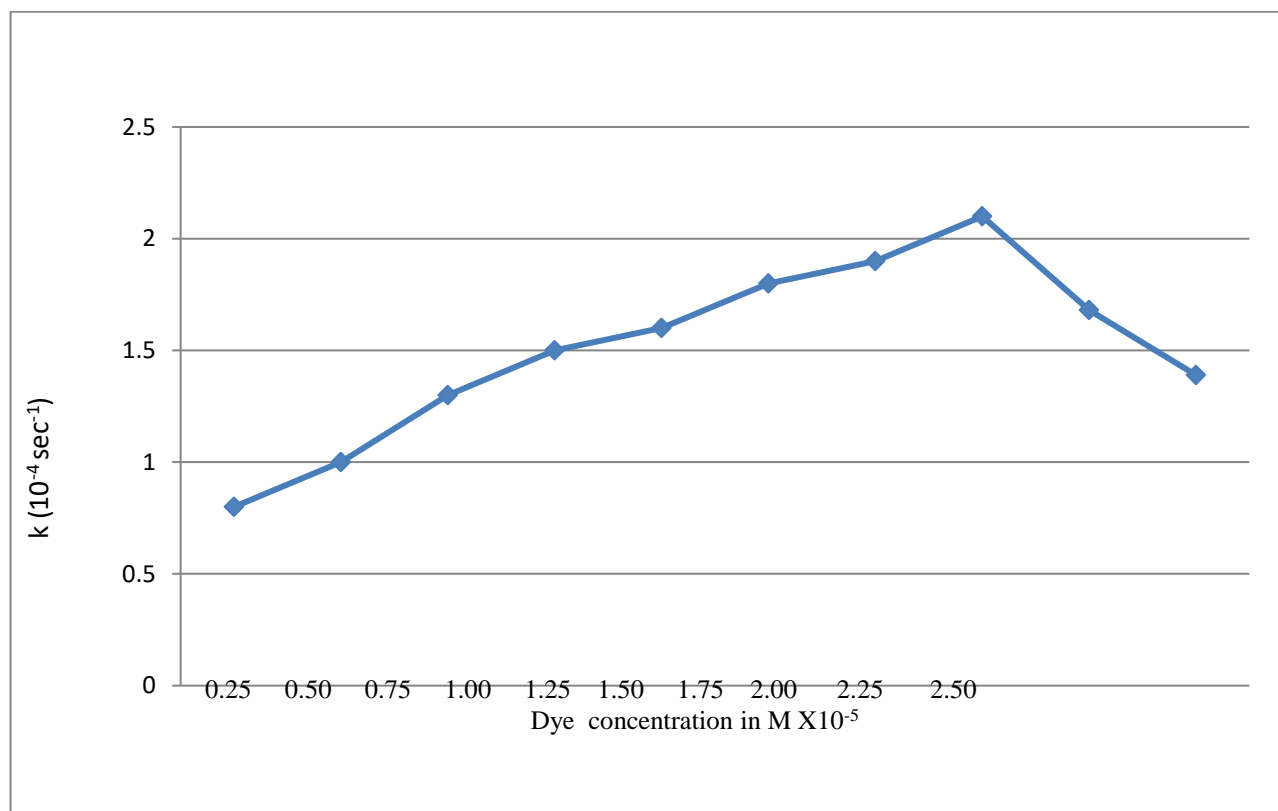


Figure-4: Effect of Dye Concentration on photochemical degradation of Methylene Blue by SnO₂.

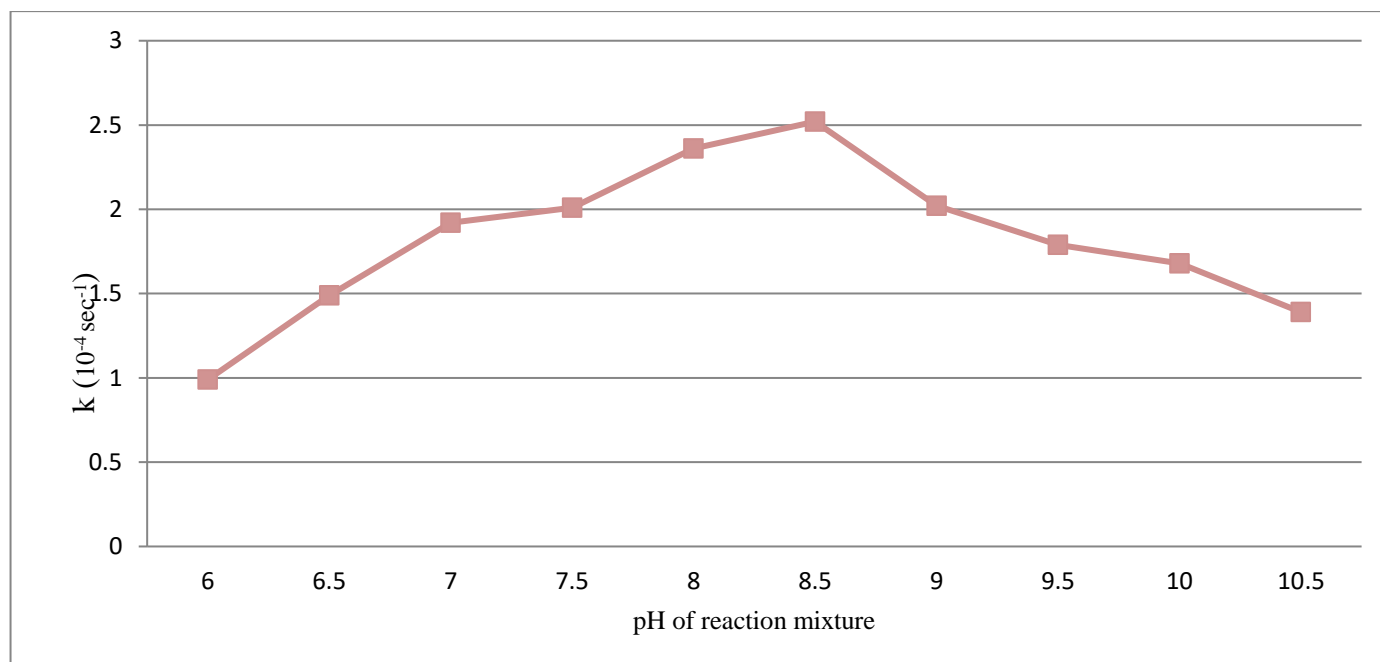


Figure-5: Effect of variation in rate constant with pH for degradation of Methylene Blue by SnO₂.

Conclusion

Photocatalytic degradation of dyes Methylene Blue, were been investigated using SnO₂/WO₃ photocatalyst. Results shows that degradation is dependent upon various operational and environmental parameters. Parameters like amount of catalyst, dye concentration, pH. The optimum conditions presented for degradation of methylene blue are pH 7.5, 0.1gm of SnO₂/WO₃/100ml dye solution and dye concentration 2.0X10⁻⁵M. The photochemical degradation of Methylene Blue by using SnO₂ catalyst was effective for removal of dyes from dye solution. The removal dye colour reaction were also proceed with the partial oxidation and it also completely degrade the toxic dye products.

The photocatalyst efficiency has been found that when increase in catalyst concentration up to a limiting value, decrease in initial concentration, increase in pH. Photochemical degradation shows of the colored effluent has the potential to improve the quality of the textile waste water. The economy and faster rate of reaction may be further improved by using certain modifications like nanosize catalyst.

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References

1. Rauf M.A. (2009). Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution. *Chemical Engineering Journal*, 151(1-3), 1-18.
2. Oviedo A. M., Ray W. and Lee P. N. (2019). Efficient photo-oxidation of NO_x by Sn doped blue TiO₂ nanoparticles. *Journal of Photochemistry and Photobiology A: Chemistry*, 370(1), 18-25.
3. Ameta R. and Ameta S.C. (2016). Photocatalysis: Principles and Applications, *CRC Press Published, Boca Raton, Florida*.
4. Calvert J.G. and Pitts J.N. (1996). *Photochemistry*. Wiley & Sons: New York, US.
5. Tesfay W., Gebres L., Manjunatha P. and Rani M. (2015). Review on the Photocatalytic Degradation of Dyes and Antibacterial Activities of Pure and Doped-ZnO. *International Journal of Science and Research*, 4(5), 2252-2264.
6. Meena K.S. and Dadheech A. (2019). Photocatalytic Degradation of textile dyes Methylene blue and Reactive red 152 by ZnO. *Poll Res.*, 38(1), 221-225.
7. Shanthi S, Manjula R. and Vinulakshmi M. (2014). Studies on the photodegradation of Malachite green dye by the synthesized ZnO nano particles with different sources of energy., *IJRPC*, 4(3), 571-576.
8. Wardell J.L. (1995). *Encyclopedia of Inorganic Chemistry* ed. R. Bruce King. *John Wiley & Son Ltd*.
9. Tungsten trioxide (2006). *The Merck Index*. 14.

10. Pamecha K., Mehta V. and Kabra B.V. (2016). Photocatalytic degradation of commercial textile azo dye Reactive Blue 160 by heterogeneous photocatalysis. *Advances in Applied Science Research*, 7(3), 95-101.
11. Raliya R., Avery C. and Chakrabarti S. (2017). Photocatalytic degradation of Methyl orange dye by pristine titanium dioxide, zinc oxide and graphene oxide nanostructures and their composites under visible light irradiation. *Springer, Applied nanoscience*, 7(5), 253-259.
12. Chen X., Zhansheng W. and Dandan L. (2017). Preparation of ZnO photocatalyst for the efficient and rapid photocatalytic degradation of azo dyes. *Nanoscale research letters*, 143(12).
13. Calvert Yang Y., Wyatt D.T. II. and Bahorshky M. (1998). Decolorization of Dyes Using UV/H₂O₂ Photochemical Oxidation. *Textile Chemist and Colorist.*, 30, 27-35.
14. Shabudeen P.S.S. (2011). Study of the removal of malachite green from aqueous solution by using solid agricultural waste. *Res. J. Chem. Sci.*, 1(1), 88-104.
15. Babu R., Parande A. K., Raghu S. and Kumar T. (2007). Cotton Textile Processing: Waste Generation and Effluent Treatment. *The Journal of Cotton Science* 11, 141–153.
16. Pichat P. (2013). Photocatalysis and Water Purification: From Fundamentals to Recent Applications. *Wiley online Library*.
17. Babu R., Parande A. K., Raghu S. and Kumar T. (2007). Cotton Textile Processing: Waste Generation and Effluent Treatment. *The Journal of Cotton Science*, 11, 141–153
18. Ince N.H. and Gonenc D.T. (1997). Treatability of a Textile Azo Dye by UV/H₂O₂. *Environ. Technol.*, 18, 179-185.
19. Vandevivere P.C., Bianchi R. and Verstraete W. (1998). Treatment and reuse of wastewater from the textile wet processing industry: review of emerging technologies. *J. Chem. Technol. Biotechnol.*, 72, 289-302.
20. Kuo W.G. (1992). Decolorizing dye wastewater with Fenton's reagent. *Water Research.*, 26 (7), 881-886.