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TRANSFORMATION OF HETEROCYCLIC DYE METHYLENE BLUE THROUGH ZNO NANO PARTICLE CATALYST

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Abstract -
Transformation of Methylene Blue Dye (MB) using ZnO nano particle as catalyst into simpler basic molecules in 3 hour time duration. It has been found that ZnO nano particles have good potential to transform heterocyclic compounds into basic smaller molecules in very short duration. we also observed the influence of different operating regulators on rate of transformation - lamp light intensity, temperature, catalyst, pH,. ZnO is capable to transform all MB molecules in simpler form like CO_2, NO_x. Due to light-catalytic action and we can recover 99.9 % transparent water in 3 hour. We can reuse same catalyst many times. This technique of transformation of heterocyclic molecules will prove more economical.

Key Words: ZnO, Photocatalyst, Methylene Blue, Transformation, Non-Biodegradable, Organic Pollutants

1. Introduction

Transformation of heterocyclic dyes (MB) in eco-friendly and sustainable way is very difficult and challenging for chemists. We know that 7 to 10 % unfixed heterocyclic dyes, azo dyes, metallic dyes are present in textile effluent and most of them are hazardous and have carcinogenic properties and reduces soil fertility.The conventional treatment methods like physical and chemical, biological cannot transform this dye completely in short duration. These traditional degradation methods requires huge amount of electricity and chemicals. We used ZnO Photo catalytic for oxidative transformation of MB and we observed that after 3 hour treatment we can get 99-99.99% transparent water.

Ever since 1977, when Frank and bard[i-ii] firstly used TiO_2 to decompose cyanide. Many researchers agree that transition metal oxide such as TiO_2, ZnO, CdS and WO_3 etc. are excellent photo catalysts to transform heterocyclic organic pollutants. Zhongbiao Wu et al [iii] worked on newly developed photo catalyst and alkaline earth tantalates TiO_2 and some other photo catalyst in different application. These new techniques have arisen as a new group of photo catalyst materials for water splitting into basic molecules H_2, O_2 and organic molecular degradation under ultra-violet/visible light irradiation. Some recent years published research work on transformation of azo dyes of textile effluent and photocatalyst.i[v-xii]. Wang C., at al. [xiii] reported enhanced photo catalytic activity for Methyle orange transformation or degredation using $SO_4^{2-}/ZnO/TiO_2$ and ZnO as photo catalysts respectively. M. K. Seery et al[xiv] examined the effect of doping on photocatalysis, silver doped titanium dioxide nanomaterials to enhanced activity of visible light photocatalysis. I. K. Konstantinou[xv] worked on photocatalytic transformation of pesticides in aqueous titanium diox-ide suspensions using artificial light and solar light: inter-mediates and degradation pathways. A. L. Ahmad and S. W. Puasa[xvi] worked reactive dyes degradation from an aqueous solution by comb ined coagulation/micellar-enhanced ultrafiltration process. Guittonneau et al [xvi] studied the oxidation of many volatile polychlorinated hydrocarbons, such as chloromethanes($CHCl_3$, CCb) and chloroethanes in different comb inations in diluted aqueous solutions. X. Wang etal [xvii] enhanced photocatalytic hydrogen evolution by prolonging the lifetime of carriers in ZnO/CdS heterostructure. Heller [xviii] pointed out that, all the extensive Knowledge that was gained during the development of semiconductor photo electrochemistry during he 1970s and 1980s has greatly assisted the development of photo catalysis process. I.Poulios and Tsachpinis[xix] investigated the Photo catalytic degradation of Reactive Black 5, and used different semi conducting oxides, TiO_2, UV-100 TiO_2, ZnO, and TiO_2/WO_3. Four parallel black light blue fluorescent tubes were used as the UV-light source. It received much attention in the transformation and complete mineralization of environmental pollutants. Many more scientist also studies photo catalytic degradation and influencing factors.[xx-xl]

ZnO based techniques have good potential of transformation of heterocyclic organic dye MB and we can recover 99-99.99% transparent water in 3 hour treatment. We also observe effect of different parameters on rate of degradation. These parameters are (i) Amount of catalyst (ii) pH (iii) Light intensity (iv) Dissolve Oxygen; all the sets were observed for 3 hour in UV/Vis lamplight.

2. Materials and Methods:

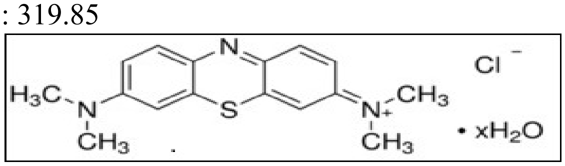
2.1 Methylene Blue Dye:: *Methylene Blue* Dye (Sigma-Aldrich)

Colour Index Number : 52016

CAS Number : 122965-43-9

Molecular Formula : $C_{16}H_{18}ClN_3S \cdot xH_2O$

Molecular Weight : 319.85



IUPAC Name: 3,7-bis(Dimethylamino)phenazathionium chloride,Basic Blue 9,Tetramethylthionine chloride

2.2 Catalyst: ZnO nano particles used as photocatalyst,

ZnO were synthesized by mixing equal volume of 0.01 M zinc nitrate hexahydrate and 0.01M hexamethylenetetramine solutions in deionised water. we put this mixture for six hours with continues stirring at 100^oC . after completion of this process we separate ZnO nano particles from the solution. Separated ZnO nanoparticle was calcined at 300^oC for 3 hours.

2.3 Experimental set up and Experimental procedure

The photo reaction is carried out in glass beakers which contains MB samples and ZnO catalysts with continues stirring by magnetic stirrer.

We followed following protocols for monitoring the experimental process.

(i) Without catalyst 3 days: - No change in OD/dye concentration
(ii) With catalyst in dark 3 days : - No change in dye concentration/OD.
(iii) ZnO-MB : - We observed that highly coloured sample solution transform in to 99.9 %transparent.

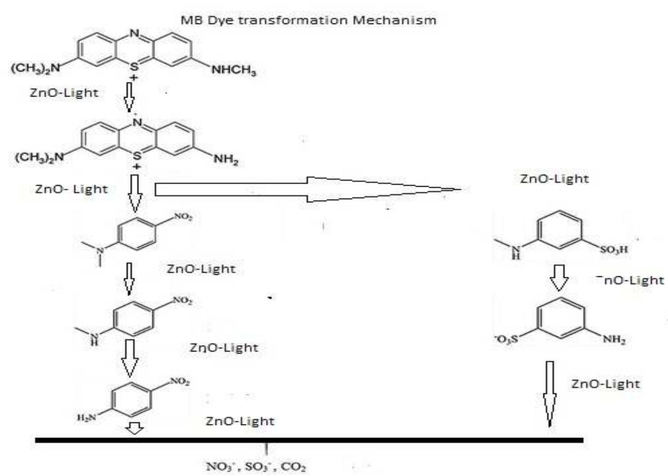
2.4 Analytical methods:

The change in MB concentration is observed by Shimadzu1800 UV/Visible spectrophotometer. Pipette out 10 mL sample at the time interval of 30 minutes to analyse change in OD (optical density) of MB solution. We also monitored pH during the experiments. Irradiation intensity was measured using a radiometer/photometer IL 1400A.

3. Result and discussion

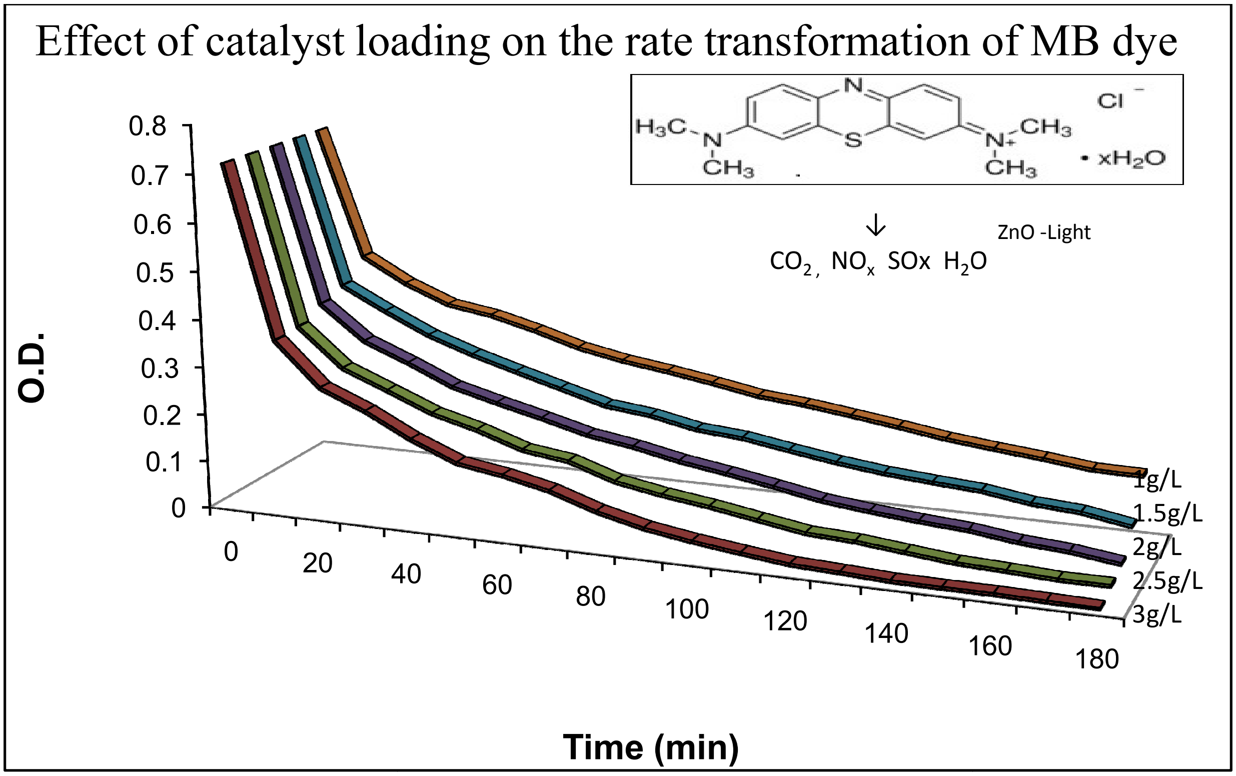
3.1 Probable Chemical Reaction of This Transformation:

Oxidative transformation of MB by ZnO nano-particles. Due to action of solar radiations of UV-Visible range on catalyst, the electronic migration starts from balance band VB (holes form) to conduction band -CB. due to this migration electrons production of ^{o}OH radicals starts. These ^{o}OH radicals have potential to transform MB into simpler molecules CO_2, NO_X , SOx etc. The main factors which influence the activity of the Photo catalytic reactor are catalyst loading, concentration of pollutant, pH, Dissolve oxygen, light intensity. The generation of holes, hydroxyl radicals and Supra oxide ions (o^-) can explain better with the help of proposed diagram. This proposed diagram shows the action of photo catalyst and process of generation of oxidative intermediates.



3.2 Effect of catalyst.

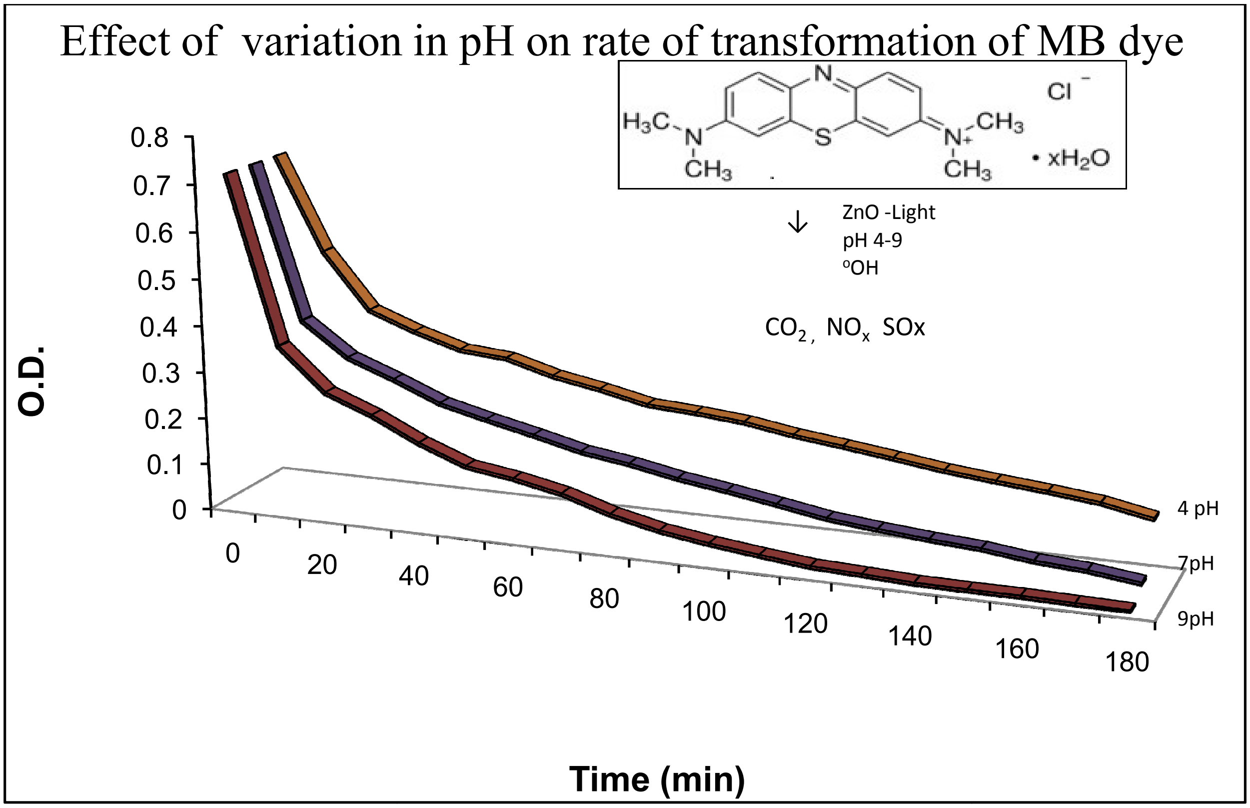
It has been observed that photocatalytic rate of transformation of MB increases with increase the amount of the photo catalyst. This may be due to more availability of active sites at the catalyst surface to generate ^{o}OH radicals & supra oxide ions (O^-). These are principle oxidizing intermediate in advance oxidation process resultant rate of transformation increases.



Graph -i Effect of catalyst loading on the rate of transformation (Solution volume: 1L, Light intensity UV-Visible lamp 10.4 mW/cm^2 , pH 7, Aeration from bottom 3L/Minute, Temperature 303K)

3.3 Effect of pH.

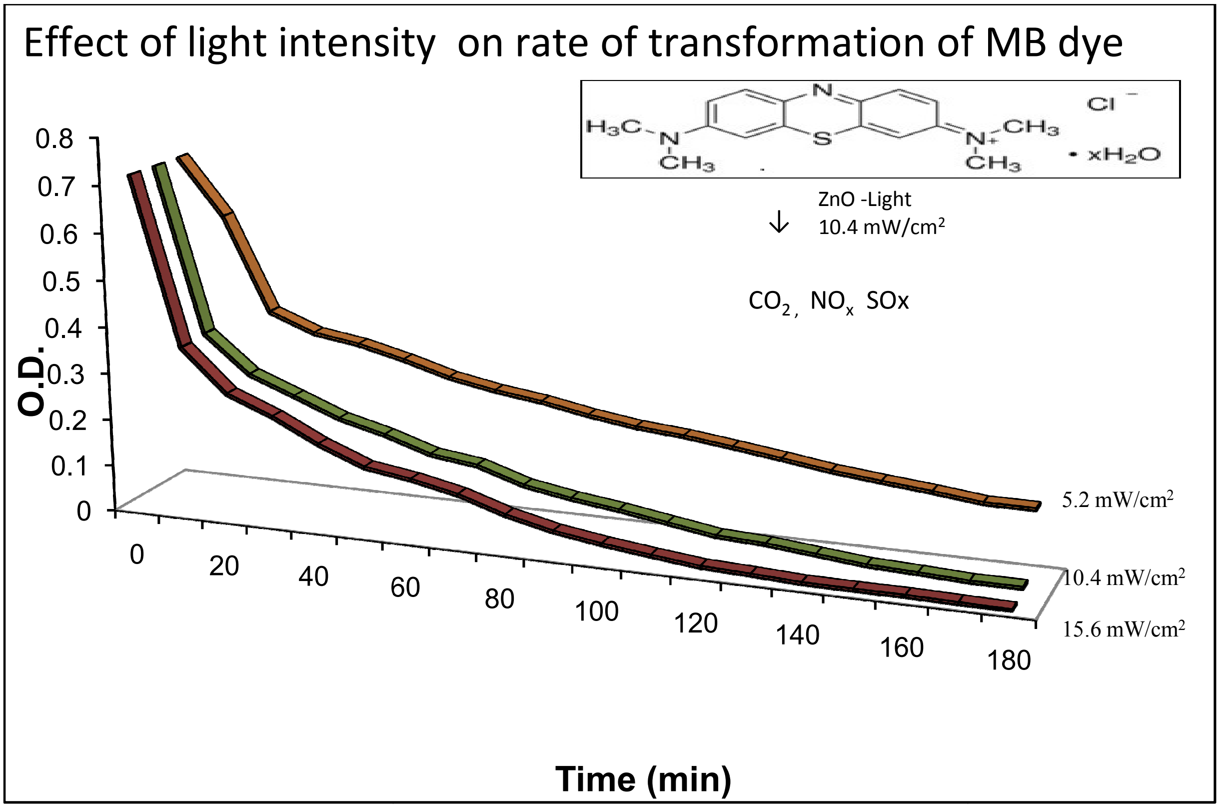
The results shows that rate of transformation is very low in high acidic pH range. The rate of transformation of MB increases fast, in pH range 7 to 9. The rate of photocatalytic transformation enhanced in basic range pH may be due to more availability of ^{-}OH ions in basic pH range 7.5 to 10. This basic range pH helps to generate more ^{o}OH radicals by interacting with holes (Develops due to VB TO CB through ISC) . Formation of hydroxyl radicals are more responsible for the photo catalytic transformation than supra oxide (^{-}O)shown in the graph.



Graph - ii Effect of pH on rate of transformation (Solution volume: 1 L ,Catalyst 2 g/L, Light intensity 10.4 mW/cm^2, Aeration from bottom 3L/Minute, Temperature 303K)

3.4 Effect of light intensity

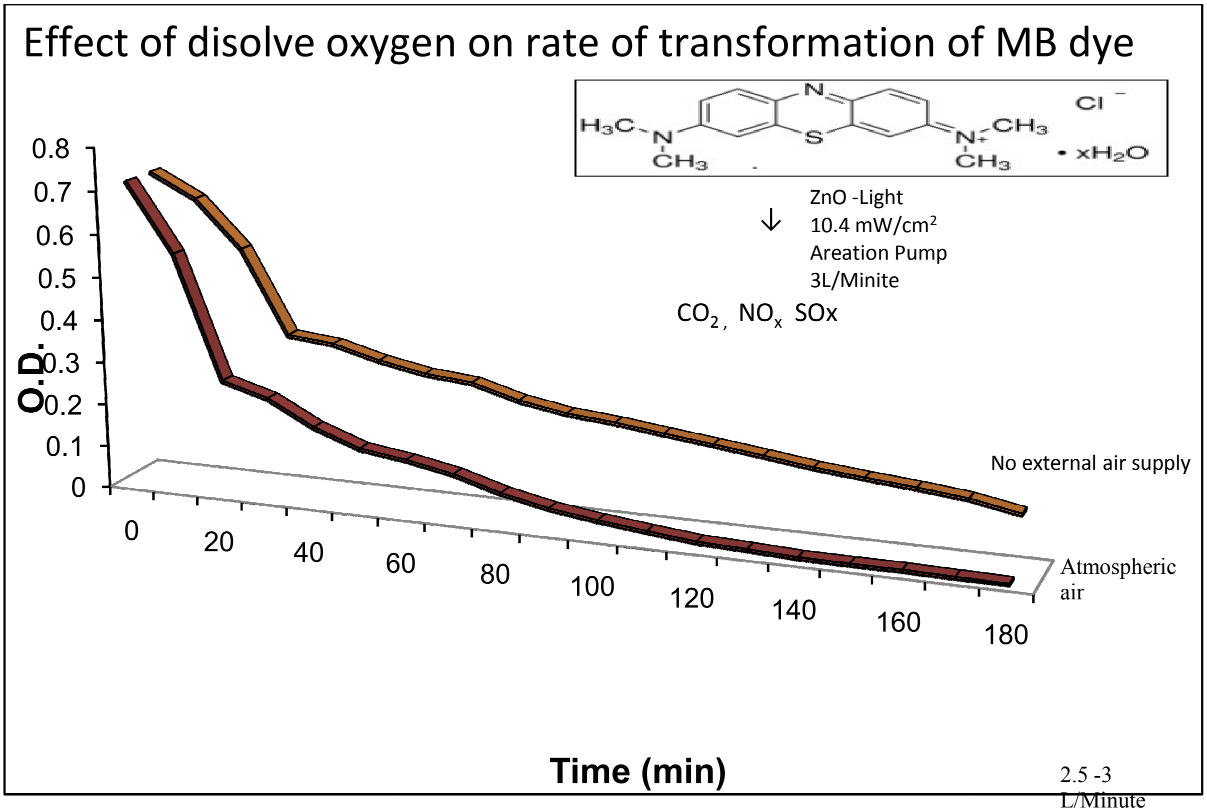
We observed that rate of transformation of MB increases with higher light intensity. This enhancement in rate of transformation of MB may be due to higher rate of generation of holes, hydroxyl radicals and supra oxide ions (o^-) .



Graph-iii Effect of variation of light intensity on transformation (Solution volume: 1L, Amount of Catalyst 2 g/L, pH 7, Aeration from bottom 3L/Minute, Temperature 303K)

3.5 Effect of dissolved oxygen on rate of transformation

We supplied atmospheric air from the bottom of the reaction system the rate of transformation enhanced. During AOP hydroxyl radicals (^{o}OH) and superoxide ion (O^{-}) produces. The amount of dissolve oxygen increases the rate of production of radicals (^{o}OH) and superoxide ion (O^{-}).



Graph-iv Effect of supply of atmospheric air on transformation rate (Solution volume: 1L, Amount of Catalyst 2 g/L, pH 7 , Light intensity 10.4 mW/cm^2, Temperature 303K)

4. Conclusion

After observation we conclude that ZnO nano-particles have very good potential to transformation MB in to simple basic molecules. No chemical sludge production, Cost efficient because we can reuse the catalyst.

We observe the effect of different parameters given in order as amount of catalyst, light intensity,pH, atmospheric air supply increase the rate of transformation of MB increases. We also observe that rate of transformation between pH range 7 to 10 rate of transformation is found good.

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