

## Photo Catalytic water treatment by an eco friendly process- BaO<sub>3</sub>TiO.SrO<sub>3</sub>TiO used in degradation of Malachite green and Crystal violet in aqueous suspension

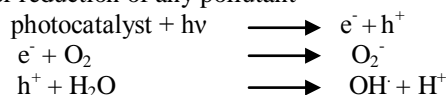
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**Abstract:** Commercially used dyes Malachite green and Crystal violet are toxic for human health. These dyes were removed through photo catalytic degradation using a new semiconductor Barium strontium titanate (Ba<sub>3</sub>TiO.SrO<sub>3</sub>TiO). The maximum degradation conditions were established by varying various factor like pH, intensity of light, concentration of dyes, amount of semiconductor etc. It was observed on kinetic parameters that the process follows pseudo first order rate law. The degraded products formed were NO<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O etc which were nontoxic in nature. The mechanism was confirmed to be a free radical one by use of scavenger.

**Keywords** - Amount of semiconductor, Barium strontium titanate, concentration of dyes, intensity of light, pH, Pseudo first order, scavenger

### I. Introduction

Photo catalysts are widely used in degradation of water soluble organic toxic compounds. It was observed that a majority of organic compounds acting as pollutants can be degraded partially or completely [1][2]. The first use of a semiconductor was made of TiO<sub>2</sub> in UV irradiation to split water[3]. A number of catalysts have been used for the degradation purpose liked TiO<sub>2</sub>, WO<sub>3</sub>, CdS, PbS, Fe<sub>2</sub>O<sub>3</sub> etc. These are used for different studies like in photo voltaic cells, in photo chemical degradation, in bleaching etc. Photocatalysis is caused by formation of holes and electrons at the surface of semiconductor. These holes and electrons are responsible for oxidation or reduction of any pollutant



The photocatalytic activity thus depends on surface and bulk property of any photocatalyst[4]. Further the photo catalytic activity of any semiconductor can be increased by improving method of synthesis, metallization, making alloy or many more[5]. The most commonly used semiconductor is rutile form of TiO<sub>2</sub> [6].

In new era some ternary and quaternary semiconductors are also used like BaWO<sub>4</sub>, CeCrO<sub>3</sub>[7], Ba<sub>3</sub>Li<sub>2</sub>Ti<sub>8</sub>O<sub>20</sub>[8], modified and loaded semiconductors like silica titania[9] etc. ZnO based ternary transparent semiconductor was used by Angelika et al[10]. Dielectric properties of sol gel derived barium strontium titanate. [Ba<sub>0.4</sub> Sr<sub>0.6</sub> TiO<sub>3</sub>] thin film was studied by Gupta et al[11].

Various techniques are involved in discoloration process of water[12] like ozonation which degrades almost all pollutants, electrochemical coagulation which is a proven technology for discoloration, bio- sorbents which cause valorization of bio waste as adsorbent, white rot fungi which mineralizes almost all dyes with no by-products and photo catalysis which degrades a number of dyes.

Photo sensitive degradation of a textile azo dye Acid orange on TiO<sub>2</sub> particles using visible light was studied by K.Vinidgopal et al[13] while Ameta[14] used semiconducting iron (III) oxide in bleaching of some dyes. Photosensitization studies in selected dyestuffs was studied by shukla et al[15] while phenol photodegradation on platinized TiO<sub>2</sub> photocatalysts related to charge carrier dynamics was carried out by Emilio et al[16].

Photo removal of Malachite green (MG) using advanced oxidation was carried out by Mohamed et al[17] while effect of factors on decolorization of azo dye Methyl orange was studied by Liu et al[18]. photocatalytic degradation of textile dye X<sub>3</sub>B by heteropolyoxometalate acids was carried out by Meiqin et al[19] where as bleaching of X<sub>3</sub>B dye with TiO<sub>2</sub> and photo fenton reagent[20] gives promising results.

Azo dye photocatalytic degradation in aqueous suspension of TiO<sub>2</sub> under solar irradiation was carried out by Augugliaro et al[21] with various influencing factors like pH, substrate concentration, catalyst amount etc. They also studied the influence of strong oxidant species like H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> etc and of some ions like Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> etc. Visible light induced photo catalytic degradation of some Xanthene dyes using immobilized anthracene was studied by Punjabi et al[22]. A photo assisted bleaching of dyes utilizing TiO<sub>2</sub> and visible light was carried out by Epling et al[23] while photocatalytic oxidation of organophosphorous pesticides using ZnO

was carried out by Fadaei et al[24]. Adsorption of Amido black 10 B onto cross linked chitosan (a polysaccharide) was studied by Yang et al[25].

Malachite green and crystal violet dyes are widely used in color industries, leather industries, yarn and plastic industries, in cosmetics ,detergents etc. the structure of these two dyes is given in figure-1 and figure-2. Malachite green is a triarylmethane dye and has  $\lambda_{\max}$  621 nm. It is used as a biological stain for microscopic analysis of cell biology and tissue samples. It is also used as an absorber in dye lasers and as pH indicator between pH 0.2 – 1.8. the intake of Malachite green causes carcinogenic symptoms and lung adenomas. Crystal violet is a triaryl methane dye having following structure. It has  $\lambda_{\max}$  590nm. It is used to dye paper and for printing, in ball pens and inkjet printers but it is found toxic and may cause human bladder cancer, renal, hepatic and lung tumor.

These dyes while use are added to water polluting it. An attempt in present work is made to degrade these dyes which will help the environment keep clean. The treated water may be used for various purposes like in agriculture, as coolant, in washing etc.

## II. Experimental

Stock solutions of dyes (Malachite green 0.0957g/250 ml= $1 \times 10^{-3}$ M and Crystal violet 1.0175g/250ml =  $1 \times 10^{-2}$  M) were prepared in doubly distilled water. These were then diluted as required. Optical density of the solutions were recorded by systronics 0.66. To 50 ml of the solution, 0.1 gm of the photocatalyst ( Barium Strontium Titanate) was added and it was exposed to a 200 watt tungsten lamp. The O.D. of the solution was recorded at different time intervals and graph was plotted between time and  $1 + \log$  O.D.. It was found to be a straight line suggesting the reaction to follow pseudo first order kinetics. The rate constant was determined by –  $K = 2.303 \times \text{slope}$

A water filter was used to cut off the heat reaction. Use of scavenger suggested the participation of OH<sup>-</sup> free radical in the reaction which is found to be strong enough to break the different bond of dye (N=N, C=N, C-N, C=C, C-C etc). Controlled experiments proved the reaction neither to be photo degradation nor to be catalytic degradation rather it was a photo catalytic degrading process.

## III. Result And Discussion

### “3.1. Effect of irradiation time”

The relation between time and percentage degradation is given in figure-3 for Malachite green and Crystal violet. It is observed that percent degradation increases with irradiation time. The process slows down with time because it stands difficult to convert N-atoms into nitrogen compounds[26]. The difficulty in break down of C-N bond has been given by Maillard et al[27]. The dye is degraded by formation of OH<sup>-</sup> free radical whose formation increases with increase in irradiation time and so increases the percentage degradation.

### “3.2. Effect of dye concentration”

The concentration of pollutant is a major parameter to be considered in water treatment. Thus the effect Malachite green and Crystal violet was studied by varying their concentrations from  $1.5 \text{ mgL}^{-1}$  to  $30 \text{ mgL}^{-1}$ . and  $16 \text{ mgL}^{-1}$  to  $162 \text{ mgL}^{-1}$  respectively. All other factors were kept constant. The results are given in figure 4 and 5. It is observed that the rate of degradation increases up to a certain concentration ( $23 \text{ mgL}^{-1}$  for Malachite green and  $81 \text{ mgL}^{-1}$  for Crystal violet) because more surface area of dyes is available for OH<sup>-</sup> free radical to abstract an electron. Then decreases in degradation is explained that after a certain value, the rise in concentration of dye imparts a darker color to the solution which do not allow larger number of photons to reach the surface of photo catalyst. As a result lesser amount of OH free radicals are produce reducing the rate of photo degradation.

### “3.3. Effect of catalyst loading”

Amount of catalyst affects the degradation of dyes. Thus the effect is studied by varying the amount of catalyst ( $0.8 \text{ gL}^{-1}$  to  $4.0 \text{ gL}^{-1}$  for Malachite green and from  $0.8 \text{ gL}^{-1}$  to  $3.2 \text{ gL}^{-1}$  for Crystal violet) and all other factors were kept constant. The results are given in figure 6 and 7. It was observed in both cases that up to certain loading, ( $3.2 \text{ gL}^{-1}$  for Malachite green and  $2.8 \text{ gL}^{-1}$  for Crystal violet) photo catalytic degradation rate increases and then with further increase in loading, the rate decreases. It may be explained as that with increase in amount more area of photocatalyst is exposed to the photons to generate OH free radicals resulting in increased rate. Further increases in amount, produces greater amount of free radical thus crowding forces them to recombine resulting in decrease in the rate of degradation.

### “3.4. Effect of light intensity”

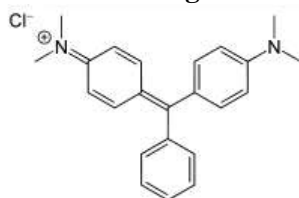
Variation of light intensity is one of the major factor affecting the degradation. Thus the experiments were performed by varying it from  $23 \text{ mW cm}^{-2}$  to  $37 \text{ mW cm}^{-2}$  with keeping all other factors constant. The results are reported in figure 8 and 9. It was observed that increase in light intensity increases the rate of

degradation [28][29]. It is due to increase in number of photons striking per unit area of the photo catalyst. Higher intensities were not studied as increase in intensity may cause thermal reaction instead of photo catalytic one.

### “3.5.Effect of pH”

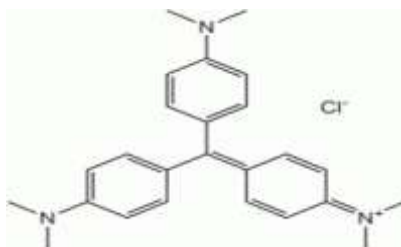
The most important factor affecting degradation is pH. The effect of pH on the photo catalytic degradation of Malachite green and Crystal violet is reported in figure 10 and 11. All other factors were kept constant. It is observed that rate of degradation increases with varying pH from 6.5 to 8.2 for Malachite green and from 5.3 to 8.9 for Crystal violet. It may be explained that as the pH rises, concentration of OH<sup>-</sup> ions rises which may support increase in number of OH<sup>-</sup> free radicals. Beyond a particular pH for both the dyes, if pH is increased further, the rate decreases. This is because of repulsion between excessive OH<sup>-</sup> ions on photocatalyst surface and electron rich dye surface.

#### IV. Figures



**Fig. 1 : Structure of Malachite green**

(IUPAC Name – 4- [(4-dimethylaminophenyl) phenyl-methyl] – N, N-dimethylaniline.



**Fig. 2 : Structure of crystal violet**

(IUPAC Name – Tris (4-(dimethyl amino) phenyl) methylum chloride.

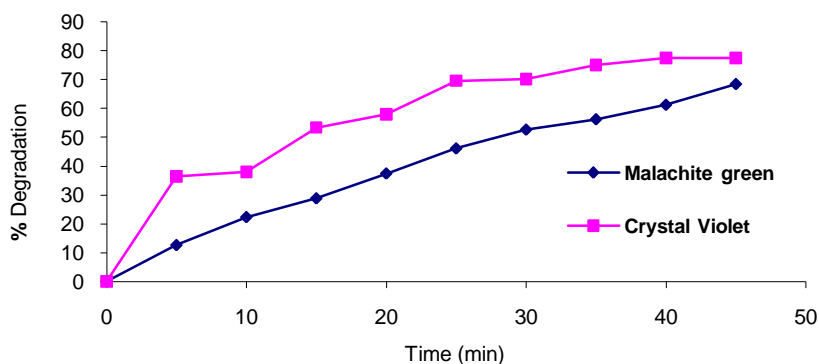


Fig. 3 : Effect of irradiation time for Malachite green and crystal violet

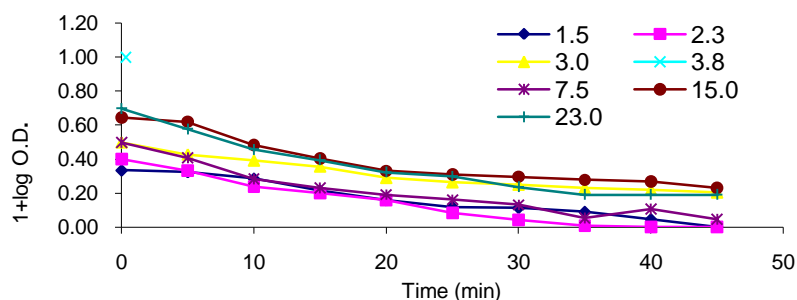


Fig. 4 : Effect of variation in dye concentration for Malachite Green-photo catalyst system (catalyst loading 3.2 gmL<sup>-1</sup>, pH = 8.2 and light intensity 37mWcm<sup>-2</sup>).

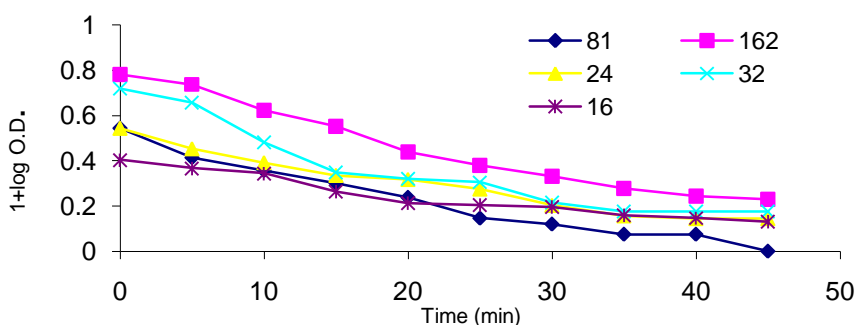


Fig. 5 : Effect of variation in dye concentration in mg/L for crystal violet - photo catalyst system (catalyst loading 2.8 gmL<sup>-1</sup>, pH = 8.9 and light intensity 37mWcm<sup>-2</sup>).

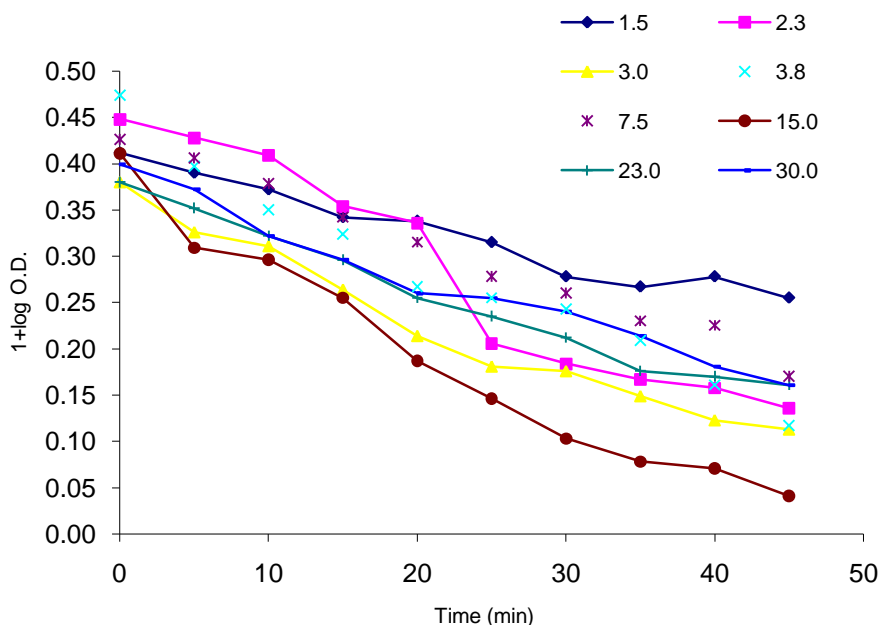


Fig. 6: Effect of variation in catalyst loading in g/L for Malachite green photo catalyst system (initial dye concentration: 23 mgL<sup>-1</sup>, pH : 8.2 and light intensity 37mWcm<sup>-2</sup>).

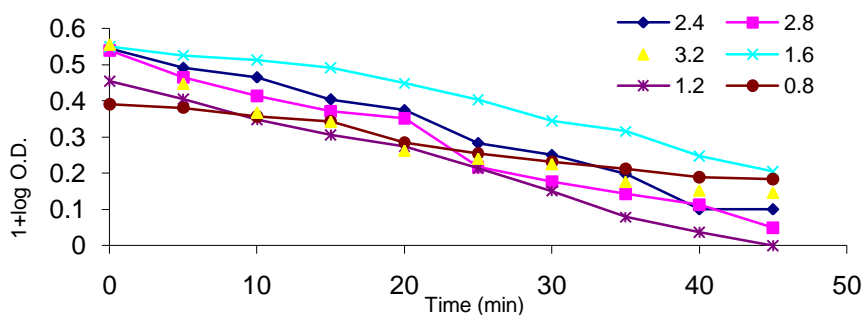


Fig. 7: Effect of variation in catalyst loading in g/L for crystal violet photo catalyst system (initial dye concentration:  $2.8 \text{ gmL}^{-1}$ , pH : 8.9 and light intensity  $37 \text{ mWcm}^{-2}$ ).

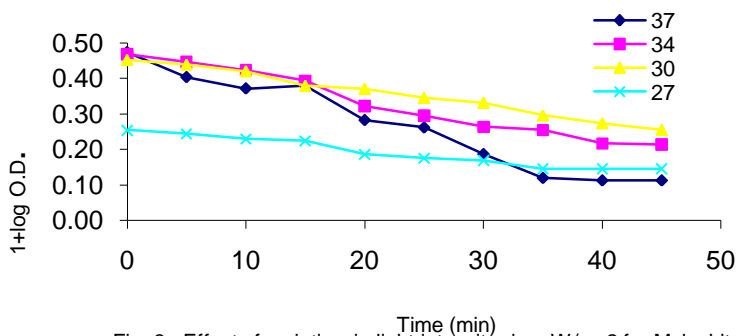


Fig. 8 : Effect of variation in light intensity in  $\text{mW/cm}^2$  for Malachite green - photo catalyst system initial dye concentration  $23 \text{ mgL}^{-1}$ : crystal loading  $3.2 \text{ gmL}^{-1}$  and pH: 8.2

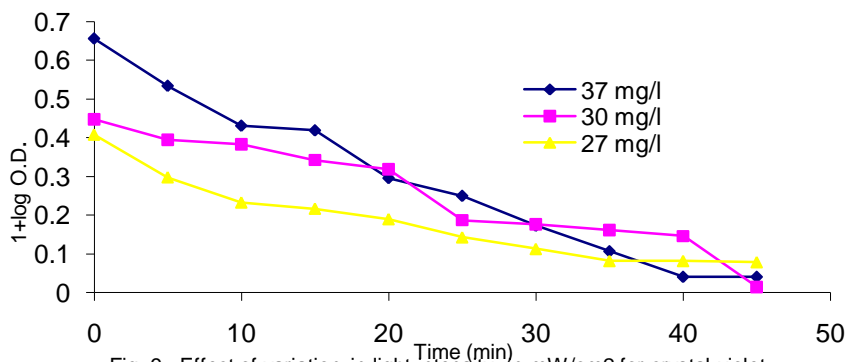


Fig. 9 : Effect of variation in light intensity in  $\text{mW/cm}^2$  for crystal violet - photo catalyst system, initial dye concentration  $81 \text{ mgL}^{-1}$ : crystal loading  $2.8 \text{ gmL}^{-1}$  and pH: 8.9

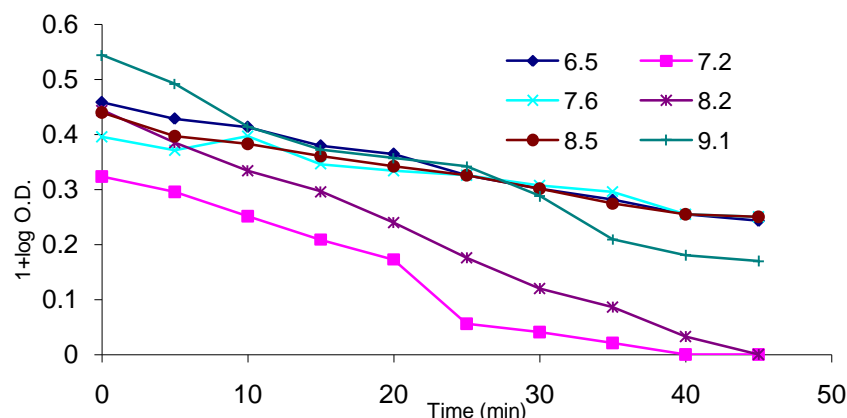


Fig. 10: Effect of variation in pH for Malachite green photo catalyst system (initial dye concentration  $23\text{mgL}^{-1}$ , catalyst loading  $3.2\text{gmL}^{-1}$  and light intensity  $37\text{mWcm}^{-2}$ ).

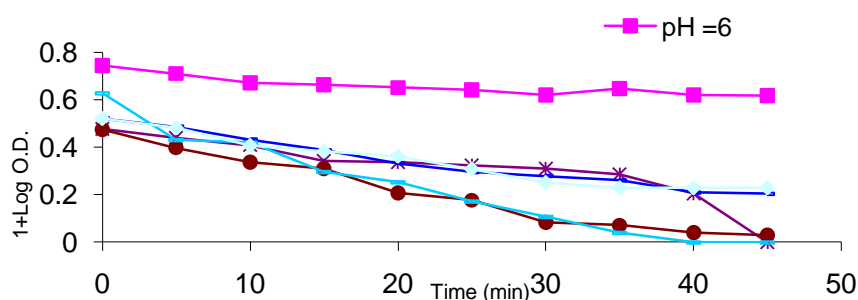
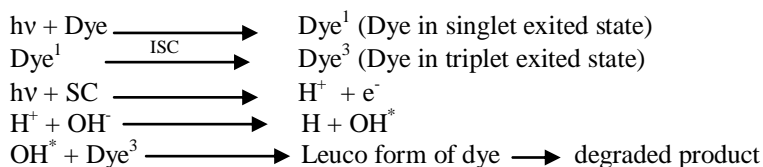


Fig. 11: Effect of variation in pH for Malachite green photo catalyst system (initial dye concentration  $81\text{mgL}^{-1}$  catalyst loading  $2.8\text{gmL}^{-1}$  and light intensity  $37\text{mWcm}^{-2}$ ).

## V. Conclusion

It is concluded here by that dyes are being degraded, with the help of photocatalyst and in presence of visible light, into fragments and no harmful products are formed. The proposed mechanism is



Here ISC = Inter system crossing

SC = Semiconductor or photocatalyst

$\text{h}^+$  = Hole generated at the surface of photocatalyst

$\text{e}^-$  = Electron generated at the surface of photocatalyst

Thus an eco-friendly and environmental protecting process is proposed which utilizes solar energy and may be used to make the planet clean and pollution free.

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