$MnWO_4$ USED AS SEMICONDUCTOR IN PHOTOCATALYTIC BLEACHING OF METHYLENE BLUE.

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ABSTRACT
The bleaching of Methylene Blue was carried out in presence of semiconductor $MnWO_4$. The source used for energy was visible light. Various parameters like amount of semiconductor, pH, light intensity, dye concentration etc. were varied suggesting the bleaching done by $MnWO_4$. A tentative mechanism is proposed.
Key Words: *pH, Methylene Blue, bleaching, $MnWO_4$.*

INTRODUCTION

Life is made colourful by colours. These colours can be natural or artificial. Now a days these colours in form of dyes are used by industries on a vast scale. When not consumed completely these dyes are released in the environment polluting it as well as life. An attempt is made to remove these dyes by use of semiconductor $MnWO_4$ and light.
Spectrophotometric study of adsorption of bromo thymol blue on charcoal and phosphates of Fe^{3+}, Al^{3+}, Cr^{3+} and Zn^{2+} was carried out by Budhraja *et al* [1]. Modification of photocatalytic activity of SbS_3 in presence of $NaHCO_3$ was reported by Ameta *et al* [2]. Mills *et al* [3] reported photooxidation of water using WO_3 poeder in presence of Fe^{3+} ions. Sharma *et al* [4] observed the catalytic activity of transition metal oxides and mixed metal oxides. Photochemical oxidation of metanil yellow with fenton and other reagents are reported by Vaidya *et al* [5]. Adsorption of triphenyl methane dyes on to jackfruit peel carbon was reported by Inbaraj *et al* [6].

EXPERIMENTAL

The stock solution of dye was prepared in distilled water and diluted as required. The pH of the solutions was determined using pH meter (Hena imported pen type). Solution of dye was taken in a beaker; known amount of $MnWO_4$ was added and covered with water filter to avoid the heat reaction. The solution was irradiated by visible tungsten lamp and the O.D. was recorded spectrophotometrically (Systronics Spectrophotometer).

RESULTS AND DISCUSSION

The plot of 1 + log O.D. was found straight line suggesting that bleaching of dye by $MnWO_4$ follows pseudo first order rate law. Rate constant were calculated by graphs as follows:-K_1 = 2.303 x Slope.A typical run is given in *Table-1* and *Graph –1*.
Effect of variation of pH: Effect of variation of pH was studied. It was found that as pH of the reaction mixture is raised, the rate of photocatalytic bleaching increases.It attains a maximum value. After it, if pH is raised, the rate decreases. Increase in pH increases the number of OH^- ions. When a hole is generated by semiconductor, an electron is abstracted from OH^- ion converting it into $OH^\bullet$ free radical. This free radical is responsible for the bleaching of dye as proved by use of scavanger. The effect of pH variation is given in*Table-2* and *Graph-2*.

Effect of concentration of Methylene Blue: The rate of photocatalytic bleaching increases as the intensity increases. It may be explained on basis of number of excited molecules. As more intensity of light falls on $MnWO_4$ molecules, more number of molecules get excited which in turn may bleach more dye molecules, thus the rate of bleaching was found increasing with increase in intensity of light. On the basis of above studies carried out, mechanism is proposed of bleaching of the dye through its degradation by $MnWO_4$ particles.
Keeping all other factors constant, the concentration of dye was changed and its effect on rate of bleaching was studied. The data are summarized in*Table-3* and *Graph-3*.

$$^1Dye_0 \rightarrow {}^1Dye_1 \text{ (Singlet excited state)}$$

$$^1Dye_1 \xrightarrow{ICS} {}^3Dye_1 \text{ (Triplet excited state)}$$

$$Sc \longrightarrow e^- + h^+ \text{ or } Sc^+$$

$$h^+ + OH^- \text{ (from base)} \longrightarrow {}^\bullet OH$$

$$^3Dye_1 + {}^\bullet OH \longrightarrow \text{Products}$$

Dye absorbs the light and gets excited to singlet state. This through intersystem crossing, gets converted to triplet state. On the other hand the semiconductor gets excited by absorbing light and an electron is excited from valance band to conduction band leaving behind a hole. The hole abstracts an electron from OH^- ions generating $^\bullet OH$ free radical. The dye is now being bleached from this free radical producing luco base.
The rate of photocatalytic bleaching was found to increase with increase in the concentration of Methylene Blue (Table-3). This may be explained that rate of reaction is directly proportional to the molar concen-tration of reacting species and it will be up to optimum concentration of Methylene Blue (Concentration 2.00 x 10-5 M). If more concentration of dye is taken, it imparts a darker colour to the solution and it may act as filter to the incident light reaching the semiconductor surface. As a consequence, the rate of photocatalytic bleaching of Methylene Blue decreases.
Effect of Amount of $MnWO_4$: The weight of MnWO4 was varied and its effect on bleaching was studied whose results are summarised in *Table- 4* and *Graph- 4*. It was found that up to a limited weight, the rate of photo-bleaching increases. It may be due to more surface area available of semiconductor to catch hold the light and generate the excited states. After a limit, rate of bleaching may decrease due to the interference of molecules of $MnWO_4$. The abundance of molecules interferes in the pathway of other molecules gaining the excited state, thus resulting decrease in bleaching.
Effect of intensity on rate of bleaching: The effect of intensity of light on rate of bleaching was studied by keeping the reaction mixture at different places below the lamp. The data are given in *Table- 5*and *Graph-5*. The participation of $^\bullet OH$ radical is confirmed by the use of scavanger, which stops the bleaching reaction completely.

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REFERENCES

1. Jyoti Budhraja and Mukhtar Singh, *J. Indian Chem. Soc.*, **81**, 573 (2004).
2. Rakshit Ameta, Aryamitra Panday, P. B. Punjabi and Suresh C. Ameta, *J. Indian Chem. Soc.*, **82**, 807 (2005).
3. A. Mills and J. R. Darwent, *J. Chem. Soc. Faraday Trans 2*, **78**, 359 (1982).

4. R. R. Sharma, A. Venkatachalam and S. J. Garg, *Samyak J. Chem.*, **2**, 16 (1998).
5. Pramila Saraswat, Rekha Chandak and V. K. Vaidya, *Ind. Council of Chemists*, **21,** 23 (2004).
6. B. Stephen Inbaraj and N. Sulochana, *J. Indian Chem. Soc.*, **82,** 232 (2005).

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