

Role of Metal Ion with Different Concentration on Photoassisted Bleaching of Methylene Blue by Nb₂O₅

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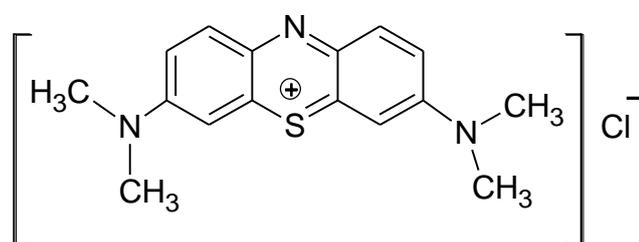
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Abstract: Photo catalytic degradation of Methylene blue has been investigated in the presence of Nb₂O₅ and the progress of reaction was observed spectrophotometrically. The outcome of several operational parameters like concentration of the dye, amount of photo catalyst, pH and nature of photo catalyst has been studied on degradation of malachite green .It was also study that what's effect of addition of common anion with different concentration . It has been found that limited quantity of all metal ions increases the reaction rate to some extent. A tentative reaction and mechanism has been proposed.

Key words: Dye, Photo Degradation, Nb₂O₅, Metal Ions, Methylene Blue.

I. INTRODUCTION

The aim of this work to assess the photocatalytic treatment of azo dye Methylene blue (MF: C₁₆H₁₈N₃SCI, MW: 319.85) selected due to its toxicity, carcinogenic in nature as well as its presence in wastewater of several industries such as textile dyeing, printing, tannery etc. High temperature properties of niobium and tantalum substituted CaMnO₃ system was studied by Xu et al.(1). Ye et al.(2) investigated a novel series of water splitting photocatalysts NiM₂O₆ (M-Nb, Ta) under visible light. The oxidative photodegradation of mercurochrome using TiO₂ as a photocatalyst has been observed by Tennakone et al.(3). Non-linear electrical properties of tantalum doped titania capacitor varistor ceramics was investigated by Li et al.(4) . Modification of TiO₂ ceramic varistor modified with tantalum and barium has been done by Gaikwad et al.(5). New tantalum oxynitride as a photocatalyst has been proposed by Totakenji et al.(6). Ishii et al.(7) observed hydrogen evolution from an aqueous methanol solution of SrTiO₃ photocatalysts co-doped with chromium and tantalum ions under visible light irradiation while M-doped InTaO₄ (M = Mn, Te Co, Ni and Cr) catalyst has been studied by Zou et al.(8). Ibadon et al.(9) studied the photocatalytic activity of TiO₂ foam and surface modified binary oxide titania nanoparticles. Novel Ag₂ZnGeO₄ photocatalyst was used for dye degradation under visible light irradiation by Xiukai Li et al.(10) . An attempt in present work has been made to remove these dyes using semiconductor Nb₂O₅ and light.



II. EXPERIMENTAL SECTION

Stock solutions of Methylene blue 0.01M (0.7996g/250ml) was prepared in purified water and as per desired concentration aqueous solution was ready from stock solution. The desired pH was obtained by H₂SO₄ and NaOH solutions.

III. PHOTOCATALYTIC ACTIVITY TEST

A tungsten lamp (Philips) of 200 W was used as the visible light source and photo catalytic activity of the Nb₂O₅ was investigated by the degradation Methylene blue of in visible light at I_{max} = 663.6 nm .For removal of thermal radiation, cutoff filter was placed outside the beaker (Pyrex). A 50 mL beaker was filled with 40 mL of dye solution containing photo catalyst. The sample of mixture has been taken outside at fixed time interval and optical density measured. The change in the maximum absorption versus irradiation time was obtained. The typical run is presented in Table 1. It is observed that the optical density (O.D.) of Malachite green solution decreases in presence of the semiconductor, metal ions and light. The plot of log OD vs time is found to be linear and hence, this reaction follows pseudo-first order kinetics. The rate constant for this reaction was determined using the expression $k = -2.303 \times \text{slope}$. Attempts have been made to study the effect of addition of common anions such as Na⁺, K⁺, Ca⁺², Ba⁺, Cl⁻, SO₄⁻² and CO₃⁻².

IV. PROCEDURE AND ANALYSIS

In this experiment, known amount of Methylene blue solution and semiconductor (Niobium pent oxide) were taken in beaker and cutoff water filter were placed on beaker to avoid thermal reaction. The solution was irradiating by visible tungsten lamp. Dye sample of about 2-3 ml was taken out at a regular time interval from the solution and optical density (O.D.) was recorded spectrophotometrically (systronics spectrophotometer).Light Intensity was measured by suryamapi (CEL Model SM201).

V. RESULTS AND DISCUSSION

The plot of 1+log O.D. vs. time was found straight line suggesting that bleaching of dye by Nb₂O₅ follows pseudo first order rate law. Rate constant was calculated by graphs as follows

$$K1 = 2.303 \times \text{slope}$$

A typical run is given in Table-1 and Figure-1

Table - 1

A. A Typical Run

[Methylene blue] = 1.0 × 10⁻⁵ M, pH = 8.5

Light intensity = 37.0 mWcm⁻², Nb₂O₅ = 0.10 g

Time	O.D	1+log O.D
0	0.89	0.95
10	0.87	0.94
20	0.85	0.93
30	0.83	0.92
40	0.81	0.91
50	0.8	0.9
60	0.79	0.9
70	0.79	0.9

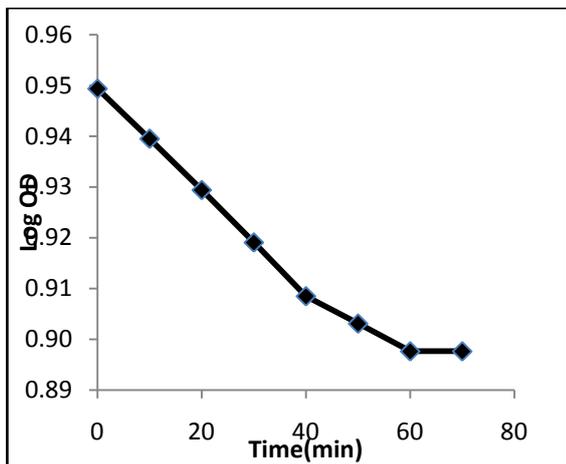


Figure 1: A plot showing a typical run of photochemical degradation of Methylene blue

Rate (k) = 2.303 × Slope

B. Effect of variation in pH

The pH of solution has play important role in dye degradation. pH is directly shows the effect on semiconductor surface property. The outcome of pH on photo catalytic bleaching of Methylene blue with Nb₂O₅ was determine in between 6 to 10 pH under visible light source. When increase the pH from 6.5 to 8.5, It was found that the rate of photo catalytic degradation increases after that increasing in pH reaction rate is going down. Its due to that as pH of reaction mixture increases more OH⁻ ions forms and this ions generate more radical and as per study it's clear that *OH are strong oxidant which can be easily oxidize the chemicals.

As the OH⁻ ions increases this will form the negatively charged surface of Nb₂O₅ and due to this, dye molecule not attract towards the semiconductor surface, because of both are having same charges (anionic dye and semiconductor surface) and due to repulsive force decrease in rate of photo catalytic degradation of dyes.

pH	k x 10 ⁴ (sec ⁻¹)
6	0.17
6.5	0.17
7	0.25
7.5	0.32
8	0.34
8.5	1.14
9	0.36
9.5	0.39
10	0.35
10.5	0.26

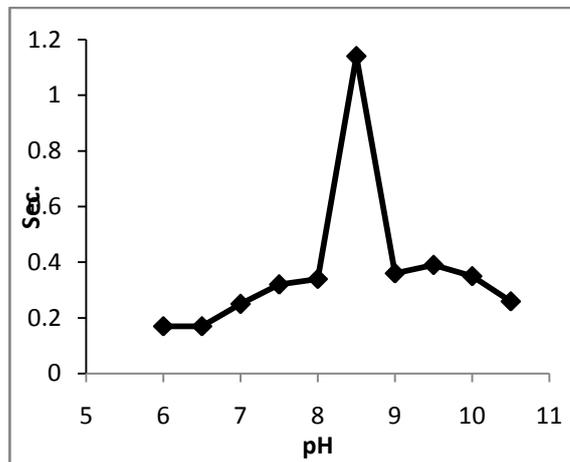


Fig.2: Effect of pH on the photo catalytic bleaching of Methylene blue by Nb₂O₅, Methylene blue = 1x10⁻⁵ M, Nb₂O₅ = 0.10 g, Light intensity = 37.0 mWcm⁻²

C. Effect of amount of catalyst [Nb₂O₅]

At the different amount of Nb₂O₅, dye degradation rate is investigated and its found that it is varying with the amount of semiconductor. The Nb₂O₅ amount was varying from 0.10 to 0.40gm. And it was observed that the rate of dye decolorization increases with increasing catalyst level up to 0.10 g and beyond this, the rate of reaction becomes almost constant (Fig.3).

The reason of this is due to in starting if quantity of semiconductor increases the active sites on semiconductor surface is increase and more radicals form and this radicals are strong oxidant but after some amount ,dye molecule are not available for adsorption. Hence others semiconductor particles not take part in degradation of dyes.

Amount of Semiconductor (gm)	k x 10 ⁴ sec ⁻¹
0.06	0.22
0.08	0.66
0.1	1.14
0.12	0.5
0.14	0.3

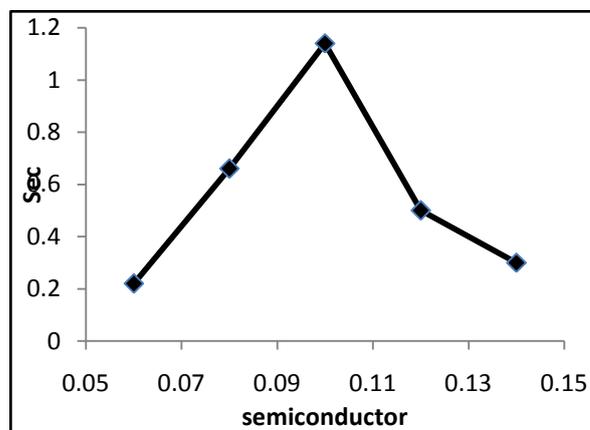


Fig.3: Effect of catalyst concentration [Nb₂O₅] on the photo catalytic bleaching of Methylene blue, Methylene blue =1x10⁻⁵, pH=8.5 Light intensity = 37.0 mWcm⁻²,

D. Effect of concentration of Dye [Methylene blue]

The concentration of dyes varies from 1.0 × 10⁻⁵ M to 4 × 10⁻⁵ M. at fixed concentration of Nb₂O₅=0.10 gm., pH= 8.5, the maximum effectiveness was observed at 8x10⁻⁵

concentration after that if concentration of dye increases adverse effect will be show (Figure-4).

This may be due to the fact that with the increase in initial concentration of the dye, while the irradiation period and catalyst dose are kept constant, more dye molecules are adsorbed onto the surface of Nb₂O₅. Thus, an increase in the number of substrate ions accommodating in inter layer spacing inhibits the action of the catalyst, which thereby decreases the number of reactive [•]OH and O₂^{-•} free radicals attacking the dye molecules and photo degradation efficiency.

[Methylene blue] x 10 ⁵ M	k x 10 ⁴ (sec ⁻¹)
0.6	0.81
0.8	0.92
1	1.14
1.2	0.87
1.4	0.44
1.6	0.3

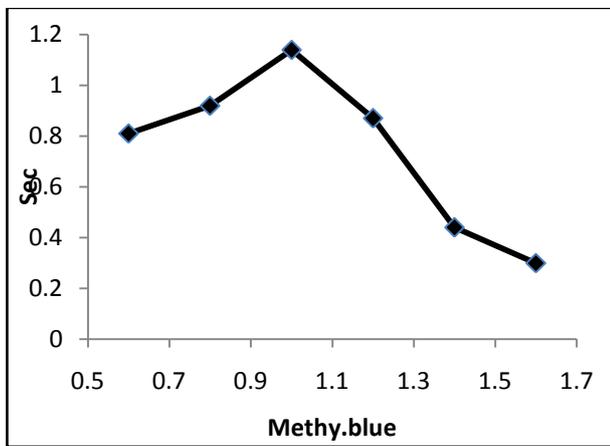


Fig.4: Effect of dye concentration on the photo catalytic bleaching of Methylene blue, Nb₂O₅ = 0.10 g, pH= 8.5, Light intensity = 37.0 mWcm⁻²

E. Effect of light intensity

Light Intensity variation has been done and observation on degradation of Methylene blue are mentioned in given table and according to result it's clear that degradation rate is increases as the intensity of light increase, because if intensity amount increases it will increase the number of photons striking per unit time per unit area of the semiconductor. An almost linear behavior between light intensity and rate of reaction has been observed. However, higher intensities are avoided due to thermal effects.

Intensity of light (mW cm-2)	k x 10 ⁴ (sec ⁻¹)
23	0.08
27	0.11
30	0.34
34	0.72
37	1.14

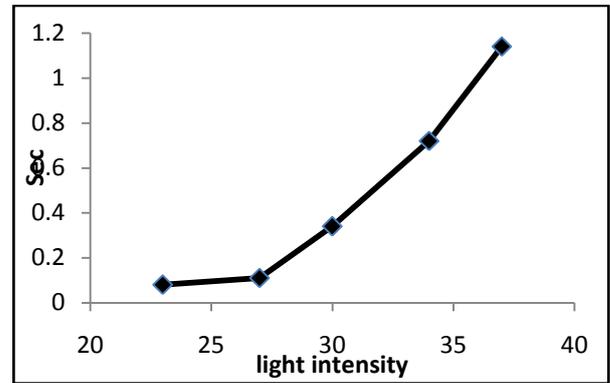


Fig.5: Effect of light intensity on the photocatalytic bleaching of Methylene blue, Nb₂O₅ = 0.10 g, pH= 8.5, Methylene blue = 1 x 10⁻⁵

Effect of common anions (different concentration) on photo catalytic bleaching of Methylene blue by Nb₂O₅. The effect of addition of metal ions (Na⁺, K⁺,Ca²⁺, Ba⁺)on photo degradation efficiency of Nb₂O₅ has been investigated, and results are reported in fig.(6).The result shows that the trace quantities of all the added metal ions enhance the rate of photo catalytic bleaching of Methylene blue to some extent.

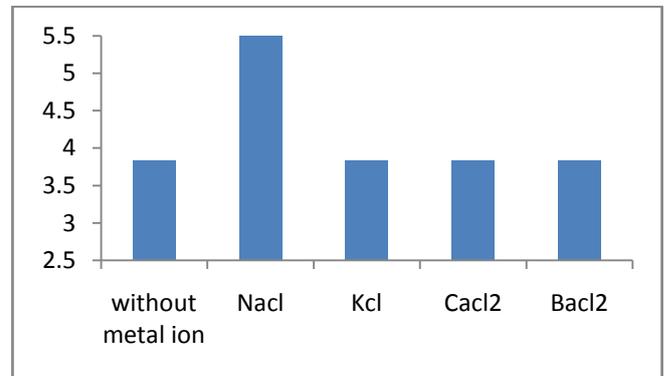
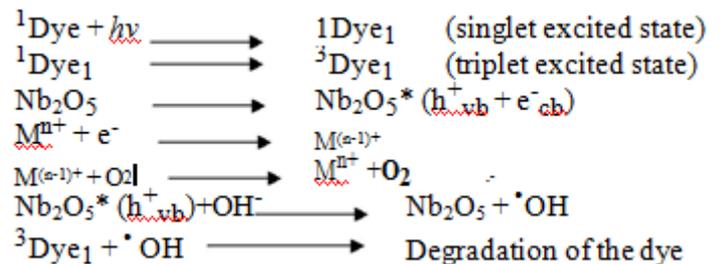


Fig. 6: Effect of common anions on photo catalytic bleaching of Methylene blue by Nb₂O₅, Methylene blue = 1 x 10⁻⁵ M, Nb₂O₅ = 0.10 g, pH= 8.5

The increase in the photo catalytic activity may be due to introduction of new trapping sites by incorporation of transition metal ions. On irradiation, electron migrates on metal where it becomes trapped and electron – hole recombination is suppressed. The hole is then free to diffuse to the semiconductor surface where oxidation of organic species can occur. (Fig.7)

Metal Modification:



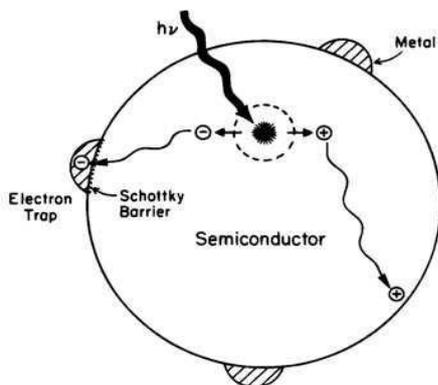
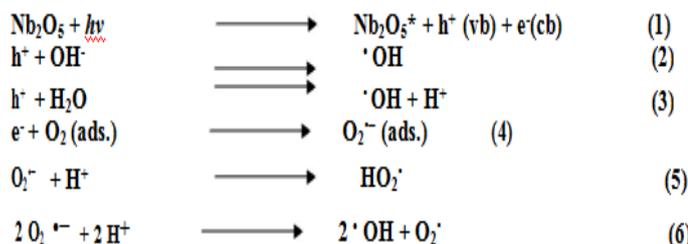


Figure-7: Metal-modified semiconductor photocatalyst particle

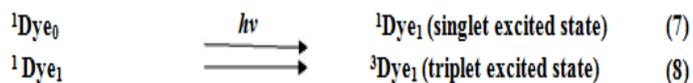
Mechanism:

Photo catalysis over a semiconductor oxide such as Nb₂O₅ is initiated by the absorption of photons with energy equal to, or greater than the band gap energy of the semiconductor (3.2 eV for anatase), producing electron-hole (e-/h+) pairs.



HO₂•, •OH and O₂• are strong oxidizing species and they react with dye molecules to oxidize them.

In the second pathway where a dye absorbs radiation of suitable wavelength and excited to its first singlet state followed by intersystem crossing to triplet state.

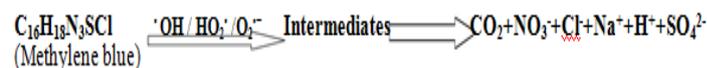


The excited dye may be oxidize to product by highly reactive hydroxyl radical (•OH).



The participation of •OH radical as an active oxidizing species was confirmed using its scavenger, i.e. 2-propanol, where the rate of bleaching was drastically reduced. After continuous irradiation the formation of CO₂, sulphate ions and nitrate ions in bleached dye solution show that there is total destruction of organic compounds in this process. The end products are simple molecules and harmless to the environment.

The whole process can be summarized as:



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