



Effect of metal ion (common cations with same concentration) on photoassisted bleaching of methylene blue by Nb₂O₅

Lokesh Gurjar and B. K. Sharma*

Department of Chemistry, Mewar University, Chittorgarh (Rajasthan)

**Department of Chemistry, S. G. G. Govt. College, Banswara (Rajasthan)*

ABSTRACT

The photocatalytic bleaching of textile azo dye Methylene blue has been carried out in the presence of semiconductor Nb₂O₅ and the progress of reaction was observed spectrophotometrically. The effect of various operating parameters like pH, concentration of the dye, amount of photocatalyst and nature of photocatalyst on the efficiency of the reaction has been studied. Attempts have been made to study the effect of addition of common cations and common ions such as Na⁺, K⁺, Ca⁺², Ba⁺, Cl⁻, SO₄⁻² and CO₃⁻². It was observed that trace quantities of all the added metal ions increases the reaction rate to some extent. A tentative mechanism has been proposed.

Key words: Photocatalytic degradation, Methylene blue Semiconductor Nb₂O₅, metal ions.

INTRODUCTION

Azo dyes are versatile class of colored organic compounds, which are characterized by the presence of one or more azo bonds (-N=N-). These are widely used in number of industries such as textile dyeing, food, leather, additive, cosmetic, paper, pharmaceutical industries etc.[1-2].

During dye production and textile manufacturing processes, a large quantity of waste water containing dyestuffs with intensive color and toxicity are introduced into the aquatic systems [3]. The azo linkage is reduced to aromatic amines under anaerobic conditions that can be toxic and potentially carcinogenic [4-6].

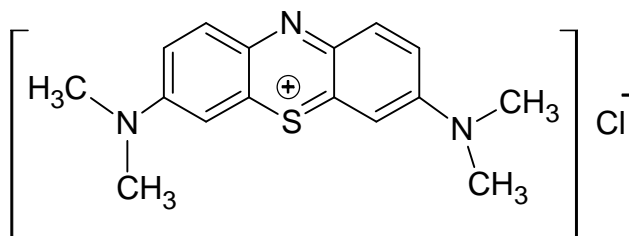
It is necessary to find an effective method of waste water treatment in order to remove color from effluents. A number of physical and chemical techniques has been reported for the removal of dye compounds such as adsorption on activated carbon [7], biodegradation [8], ozonation [9] and advanced oxidation processes (AOPs) such as Fenton and photo-Fenton catalytic reactions [10,11], H₂O₂/UV processes [12] and semiconductor photocatalysis [13-15].

Advance oxidation processes are the methods in which very reactive species such as hydroxyl radicals (·OH) are produced. The hydroxyl radical is a powerful oxidant that can rapidly and non-selectively oxidize organic contaminants into carbon dioxide and water [16,17], so it is able to degrade pollutants effectively[18,19]. Among the AOPs heterogeneous photocatalytic oxidation using TiO₂ as photocatalyst has been extensively studied. TiO₂ is very effective, relatively inexpensive, easily available and chemically stable photocatalyst. The appropriate illumination of these particles produces excited-state high energetic electron and hole pairs (e⁻/h⁺). These pairs are able to initiate a wide range of chemical reactions that may lead to complete mineralization of organic and inorganic pollutants [20-22], Bhandari *et al.*[23] observed photocatalytic degradation of some dyes (erythrosin-B, Rose Bengal FCF and eosin Y), with semiconducting zinc oxide in the presence of Fe²⁺, Ni²⁺, Ag⁺, Cu²⁺, Co²⁺, V²⁺ and Mn²⁺ ions as

dopent. Main objective of the present study is to enhance the photocatalytic activity of Nb_2O_5 using various metal ions of appropriate concentration.

The aim of this work to asses the photocatalytic treatment of azo dye Methylene blue (MF: $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}$, 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.[scheme.1]

On irradiation, electron migrates on metal where it becomes trapped and electron-hole recombination is suppressed. The hole is then free to diffuse on the semiconductor surface where oxidation of organic species can occur.



MATERIALS AND METHODS

The stock solution of dye Methylene blue 0.01M (0.7996g/250ml) was prepared in doubly distilled water. Aqueous solutions of desired concentrations were prepared from the stock solution. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. All laboratory reagents were of analytical grade.

In photocatalytic experiment, the dye solution and known amount of semiconductor (Nb_2O_5) and metal ions were taken in a beaker and cutoff filter was placed outside the beaker (Pyrex) to completely remove any thermal radiation. The solution was irradiate by visible tungsten lamp. Dye sample of about 2-3 ml was taken out at a regular time interval from the test solution and optical density was recorded spectrophotometrically (systronics spectrophotometer). It is observed that the optical density (O.D.) of Methylene blue solution decreases in presence of the semiconductor, metal ions and light. Attempts have been made to study the effect of addition of common cations and common anions such as Na^+ , K^+ , Ca^{+2} , Ba^+ , Cl^- , SO_4^{-2} and CO_3^{-2} .

RESULTS AND DISCUSSION

The plot of $1+\log \text{O.D.}$ vs. time was found straight line suggesting that bleaching of dye by Nb_2O_5 follows pseudo first order rate law. Rate constant was calculated by graphs as follows

$$K_1 = 2.303 \times \text{slope}$$

A typical run is given in Table-1 and Fig.1

Table 1
A Typical Run

[Methylene blue] = 1.0×10^{-5} M, pH = 8.5
Light intensity = 37.0 mWcm^{-2} , Nb_2O_5 = 0.10 g

Time(min.)	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	0.90
60	0.79	0.90
70	0.79	0.90

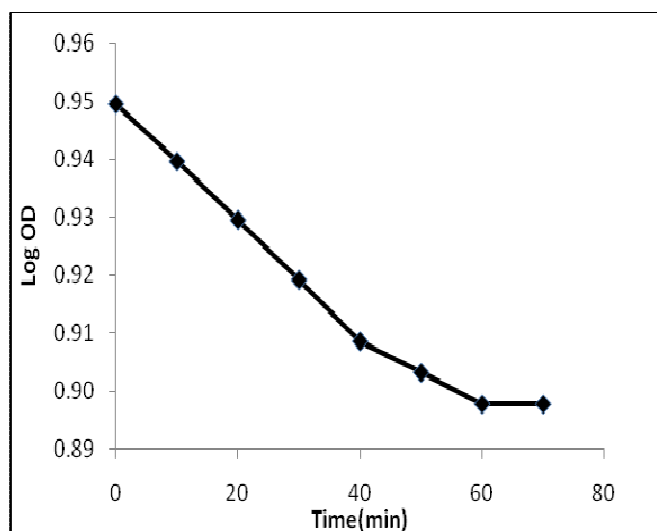


Fig.1- A typical run

Effect of variation in pH:

The effect of pH on photocatalytic bleaching of Methylene blue with Nb_2O_5 was investigated in the pH range of 6.0 to 9.0 under visible light source, reported in Fig -2. It was found that the rate of photocatalytic bleaching increases with an increase in pH up to 7.5. Thereafter there is an adverse effect on the rate of reaction on increasing pH further. This observation can be explained on the basis that as the pH of solution increases, more OH^- ions are available. These OH^- ions will generate more $\cdot\text{OH}$ radicals by combining with the hole of the semiconductor. The hydroxyl radical is an extremely strong, non-selective oxidant [$E^0 = +3.06$], which leads to the partial or complete mineralization of several organic chemicals.

After a certain pH value, more OH^- ions will make the surface of semiconductor negatively charged and is retarded the approach of dye molecules toward the semiconductor surface due to repulsive force between semiconductor surface and anionic dye molecule. This will result into a decrease in rate of photocatalytic bleaching of dyes.

Effect of amount of catalyst [Nb_2O_5]:

The effect of amount of photocatalyst on the degradation kinetics of Methylene blue was investigated employing different concentrations of the Nb_2O_5 varying from 0.10 to 0.40g/ 100ml. It was observed that the rate of dye decolourization increases with increasing catalyst level up to 0.10 g and beyond this, the rate of reaction becomes almost constant (Fig.3).

This may be due to the fact that, initially the increase in the amount of catalyst increases the number of active sites on the Nb_2O_5 surface that in turn increases the number of $\cdot\text{OH}$ and $\text{O}_2\cdot^-$ radicals. After a certain level of catalyst availability with the same concentration of dye, further dye molecules are not available for adsorption. The additional catalyst particles therefore are not involved in the catalytic activity. Hence the degradation remains constant.

Effect of concentration of Dye [Methylene blue]:

The effect of substrate concentration on the degradation of Methylene blue was studied at different concentrations varying from 1.0×10^{-5} M to 4.0×10^{-5} M at fixed concentration of $\text{Nb}_2\text{O}_5 = 0.10$ g, pH=8.5. The highest efficiency was observed at lower concentration, which decreases with the increase in substrate concentration from 1.0×10^{-5} M to 4.0×10^{-5} M (Fig-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 Nb_2O_5 . Thus, an increase in the number of substrate ions accommodating in interlayer spacing inhibits the action of the catalyst, which thereby decreases the number of reactive $\cdot\text{OH}$ and $\text{O}_2\cdot^-$ free radicals attacking the dye molecules and photodegradation efficiency.

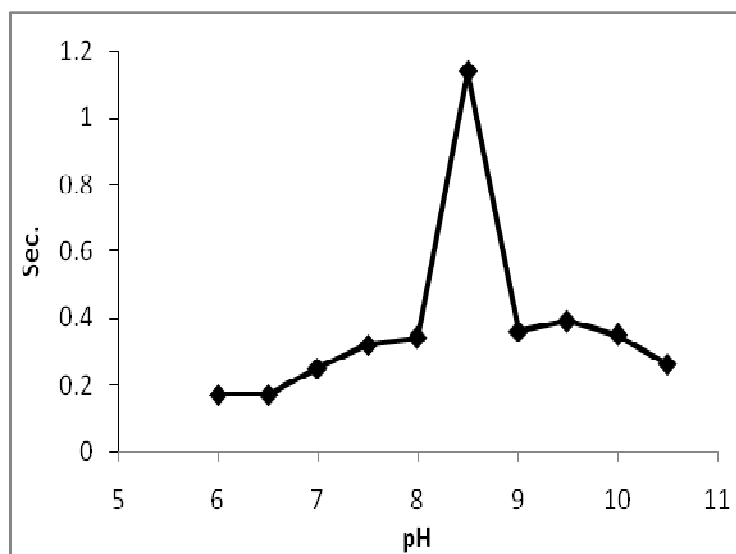
Effect of light intensity

The effect of variation in light intensity on the rate was also investigated and the observations are reported in Table. The data indicate that the degradation action is accelerated as the intensity of light increases, because any increase in the light intensity will increase the number of photons striking per unit time per unit area of the semiconductor powder. An almost linear behaviour between light intensity and rate of reaction has been observed. However, higher intensities are avoided due to thermal effects.

Table -2

[Methylene blue] = 1.0×10^{-5} M
Light intensity = 37.0 mWcm⁻², Nb₂O₅ = 0.10 g

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****Table-3**

[Methylene blue] = 1.0×10^{-5} M, pH = 8.5
Light intensity = 37.0 mWcm⁻²

Amount of Semiconductor (g)	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

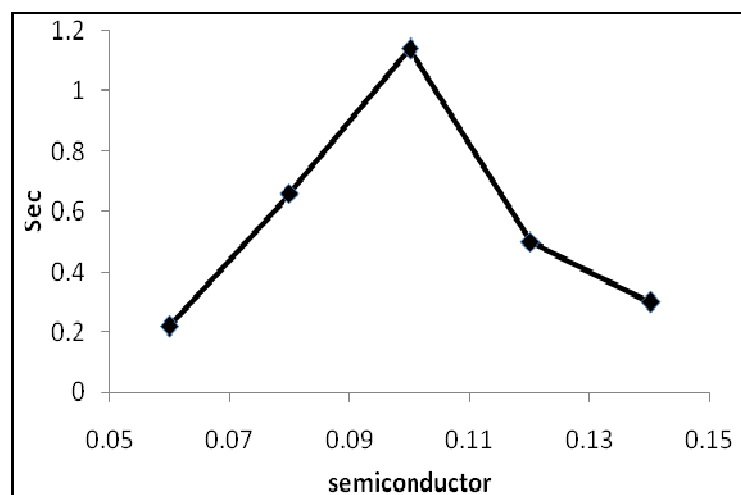


Fig.3: Effect of catalyst concentration

Table-4

pH = 8.5

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

[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

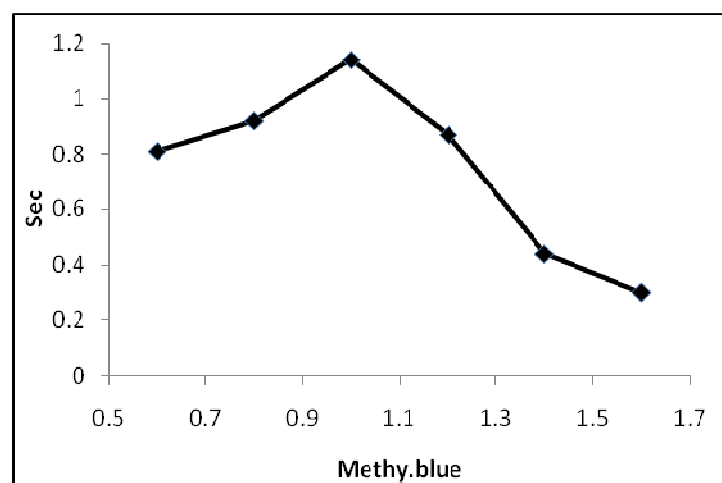


Fig.4: Effect of dye concentration

Table-5

[Methylene blue] = 1.0 x 10⁻⁵ M, pH = 8.5, Nb₂O₅ = 0.10 g

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

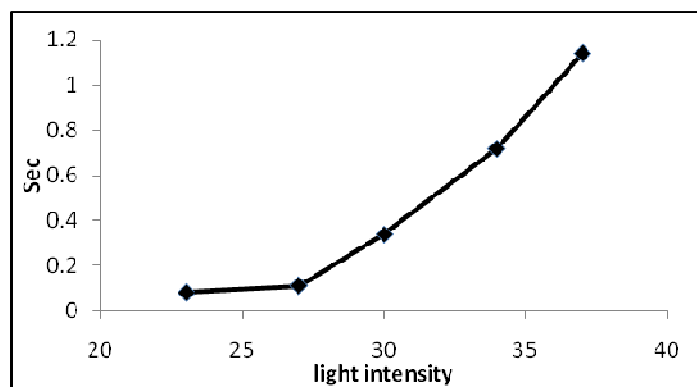


Fig.5: Effect of light intensity

Effect of common cations (with same concentration) on photocatalytic bleaching of Methylene blue by Nb₂O₅

The effect of addition of metal ions (Na⁺, K⁺, Ca²⁺, Ba⁺, Cl⁻, SO₄²⁻ and CO₃²⁻) 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 photocatalytic bleaching of Methylene blue to some extent.

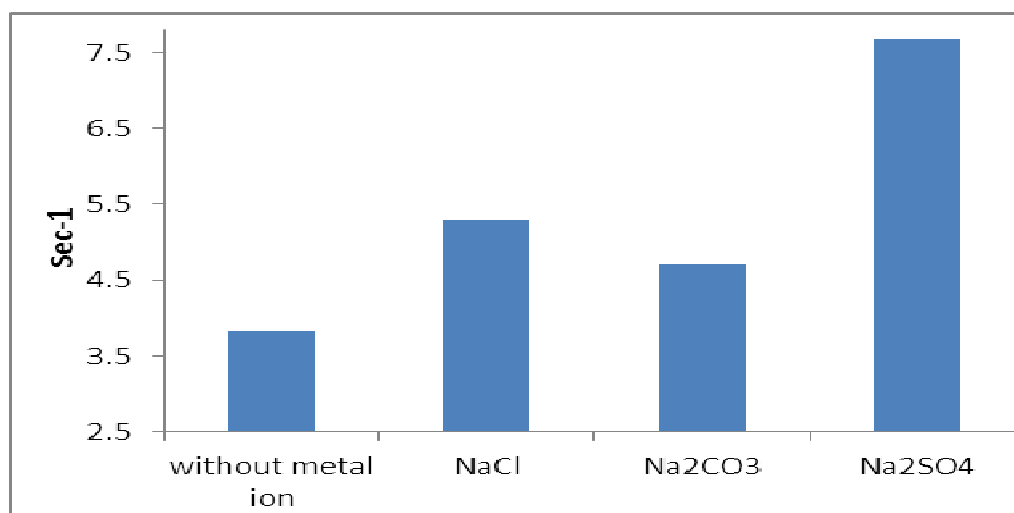
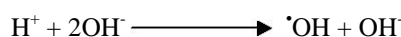
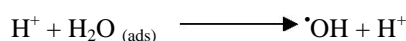


Fig. 6: Effect of common cations on photo catalytic bleaching of Methylene blue

The increase in the photocatalytic 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. (Scheme 2)

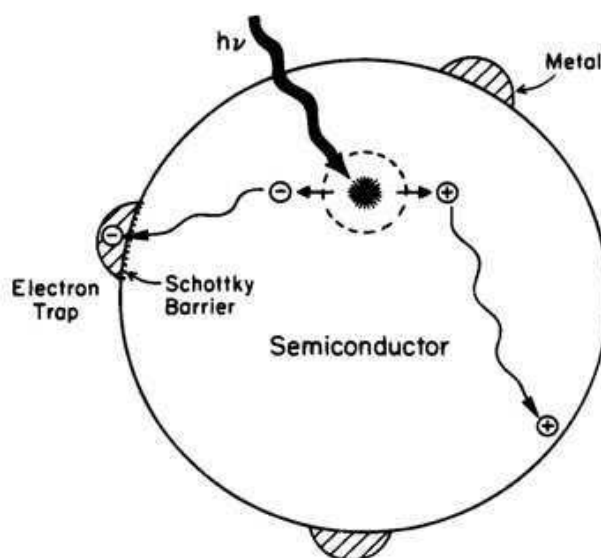
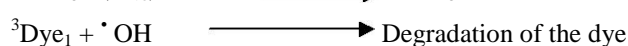
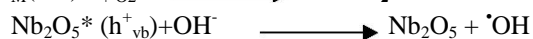
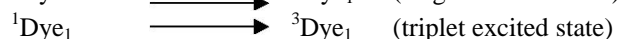
As the surface of catalyst particles is negatively charged and hence, it permits more metal ions to get adsorbed on the Nb₂O₅ particles surface and as consequence, the surface of semiconductor will become positively charged. As methylene blue dye is anionic dye, so it will face more Electrostatic attraction with cations (Mn⁺) adsorbed on the semiconductor surface.

The electron from Nb₂O₅ conduction band is transferred to metal ion to convert it into its lower oxidation state, in turn transfer this electron to oxygen molecule. Thus prevent electron-hole recombination. At the same time, the positively charged vacancies(h⁺) remaining in the valence band of Nb₂O₅ can extract electron from hydroxyl ions in the solution to produce the hydroxyl radicals((• OH). These hydroxyl radicals oxidize the dye molecule into colorless products.



The concentration of transition metal ions is very small and large concentrations are detrimental.

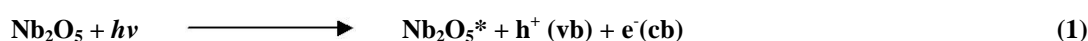
Metal modification



Scheme 2. Metal-modified semiconductor photocatalyst particle

MECHANISM

Photocatalysis over a semiconductor oxide such as Nb_2O_5 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.



Where cb is conduction band and vb is valence band.

The photo produced holes and electrons may migrate to the particle surface, where the holes can

React with surface-bound hydroxyl groups (OH^-) and water molecules to form hydroxyl radicals ($\cdot\text{OH}$).



The electrons in conduction band react with the adsorbed oxygen molecules to form super oxide ions ($\text{O}_2^{\cdot-}$).

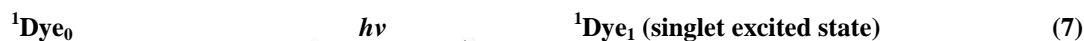


Super oxide ions ($\text{O}_2^{\cdot-}$) is reduced by H^+ , accounting for hydroperoxyl radical ($\text{HO}_2\cdot$) and hydroxyl radical production.



HO_2^{\cdot} , OH^{\cdot} and $\text{O}_2^{\cdot-}$ 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.



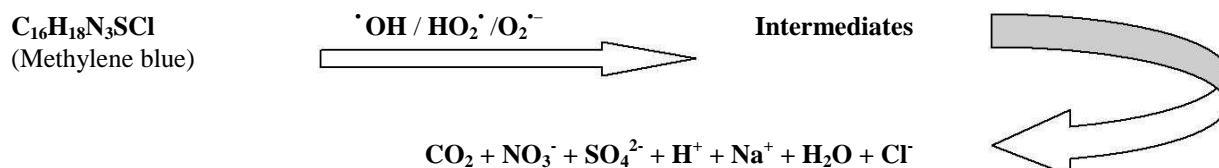
The excited dye may be oxidized to product by highly reactive hydroxyl radical (OH^{\cdot}).



The participation of OH^{\cdot} 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 CO_2 , 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:



CONCLUSION

The photocatalytic degradation of Methylene blue dye was found to be dependent on various kinetic parameters like concentration of dye, pH, amount of semiconductor, intensity of light etc. And also degradation is fast when small amount of metal ions add. Colour change is irreversible and degradation rate of the dye follows the pseudo-first order kinetics.

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