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International Journal of Current Research
Vol. 8, Issue, 02, pp.26641-26645 February, 2016

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

EFFECT OF METAL ION (COMMONANIONS WITH SAME CONCENTRATION) ON PHOTOASSISTED BLEACHING OF METHYLENE BLUE BY Nb_2O_5

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ARTICLE INFO

Article History:
Received 24th November, 2015
Received in revised form
26th December, 2015
Accepted 14th January, 2016
Published online 27th February, 2016

Key words:

Azo dye,
Photo degradation,
Semiconductor Nb_2O_5,
Metal ions,
Methylene blue.

ABSTRACT

The photo catalytic bleaching of textile azo dye Methylene blue has been carried out in the presence of semiconductor Nb_2O_5 and the progress of reaction was observed spectrophotometrically. The effect of various operating parameters like pH, concentration of the dye, amount of photo catalyst and nature of photo catalyst on the efficiency of the reaction has been studied. Kinetic analysis of photo degradation reveals that the degradation follows approximately pseudo first order. 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}. It was observed that trace quantities of all the added metal ions increases the reaction rate. The increase in the photo catalytic activity may be due to introduction of new trapping sites by incorporation of transition metal ions on semiconductor surface. A tentative mechanism has been proposed.

Citation: **Lokesh Gurjar and Sharma, B. K, 2016.** "Effect of metal ion (commonanions with same concentration) on photoassisted bleaching of methylene blue by Nb_2O_5", *International Journal of Current Research,* 8, (02), 26641-26645.

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 dying, food, leather, additive, cosmetic, paper, pharmaceutical industries etc. (Dakiky, 2000; Daneshvar *et al.,* 2003). 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 (Brown *et al.,* 1993). It is necessary to find an effective method of wastewater treatment in order to remove color from effluents. A number of physical andchemical techniques has been reported for the removal of dye compounds such as adsorption on activated carbon (Safarik *et al.,* 1997), biodegradation (More, 1989), ozonation (Slokar *et al.,* 1998) and advanced oxidation processes (AOPs) such as Fenton and photo-Fenton catalytic reactions (Kuo, 1993; Morisson *et al.,* 1996), H_2O_2/UV processes (Arslan *et al.,* 1999) and semiconductor photo catalysis (Zhang *et al.,* 1998; Lachheb *et al.,* 2002; Konstantinou *et al.,* 2004). 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 (Muruganandham and Swaminathan, 2007; Lucas and Peres, 2006), so it is able to degrade pollutants effectively (Will and Moraes, 2004; Zheng and Xiang, 2004). Among the AOPs heterogeneous photocatalytic oxidation using TiO_2 as photo catalyst has been extensively studied. TiO_2 is very effective, relatively inexpensive, easily available and chemically stable photo catalyst. 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 (Saien and Khezrianjoo, 2008; Lhomme *et al.,* 2008; Zou, 2008), Bhandari *et al.* (2006) observed photo catalytic degradation of some dyes (erythrosine-B, Rose BengalFCF and eosin Y),with semiconducting zinc oxide in the presence of Fe^{2+}, Ni^{2+}, Ag^+, Cu^{2+}, Co^{2+}, V^{2+} and Mn^{2+} ions as dopent. Main objective of the present study is to enhance the photo catalytic activity of Nb_2O_5 using various metal ions of appropriate

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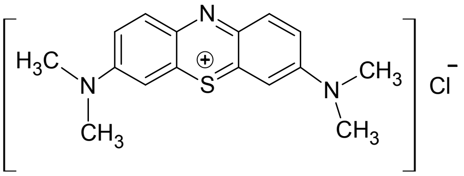
concentration. The aim of this work to assess the photocatalytic treatment of azo dye Methylene blue (MF: $C_{16}H_{18}N_3SCl$, MW: 319.85) selected due to its toxicity, carcinogenic in nature as well as its presence in wastewater of several industries such as textile dying, printing, tannery etc. On 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 cansoccur



Experimental Section

For photocatalytic degradation 0.01M (0.7996g/250ml) stock solution of dye Methylene blue was prepared in double 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.

Photocatalytic activity test

The photocatalytic activity of the Nb_2O_5 under visible lightwas investigatedusingthe photocatalytic degradation of Methylene blue dye at max = 663.6 nm. A 200 W tungsten lamp (Philips) was used as the visible light source. A cutoff filter was placed outside the beaker (Pyrex) to completely remove any thermal radiation just to ensure illumination by visible light. A 50 mL beaker was filled with 40 mL of dye solution containing photocatalyst. The mixture was sampled to assay at given time intervals by recording variation of the absorbance. 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 Methylene blue 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 × slope. 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}

Procedure and Analysis

In photocatalytic experiments, the dye solution and known amount of semiconductor (Nb_2O_5) were taken in a beaker and the beaker was covered with water filter to avoid the 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 test solution and optical density (O.D.) was recorded spectrophotometrically (systronics spectrophotometer). Intensity of light was measured by suryamapi (CEL Model SM201). 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 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 K1= 2.303 x slope A typical run is given in Table-1 and Fig.1

Table 1A. Typical Run

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	0.80	0.90
60	0.79	0.90
70	0.79	0.90

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

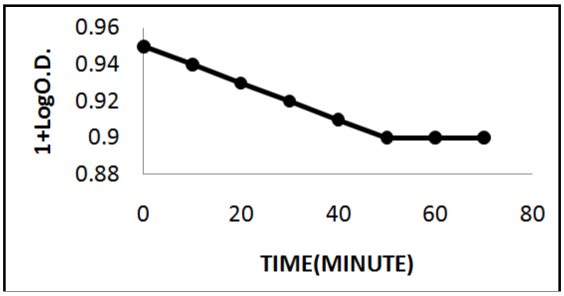


Fig. 1.

Effect of variation in pH

The pH of the reaction medium has a significant effect on the surface properties of Nb_2O_5catalyst. The effect of pH on photo catalytic 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).

Table 2. Effect of variation in pH

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

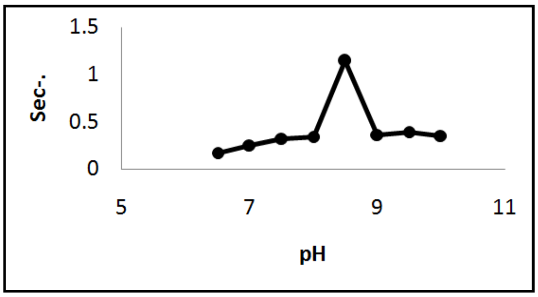


Fig. 2.

It was found that the rate of photo catalytic 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 • OH radicals by combining with the hole of the semiconductor. The hydroxyl radical is an extremely strong, non-selective oxidant [E0= +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 photo catalytic bleaching of dyes.

Effect of amount of catalyst [Nb_2O_5]

The effect of amount of photo catalyst 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 (Table 3, Fig.3).

Table 3. Effect of amount of catalyst

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

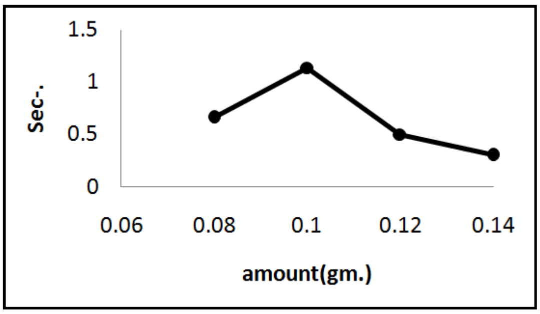


Fig. 3.

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 $^{\bullet}$ OH and $O_2^{\bullet}$ 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 Nb_2O_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 (Table 4, 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 $^{\bullet}$ OH and $O_2^{\bullet}$ free radicals attacking the dye molecules and photo degradation efficiency.

Table 4. Effect of dye concentration

[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

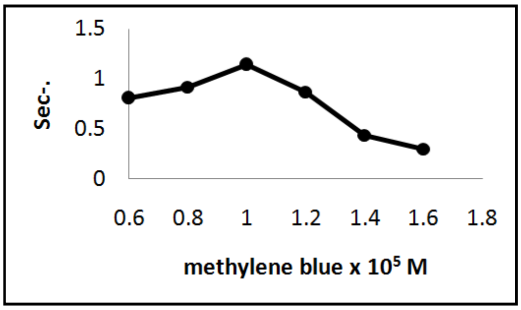


Fig. 4.

Effect of 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 behavior between light intensity and rate of reaction has been observed. However, higher intensities are avoided due to thermal effect (Table 5, Fig 5).

Table 5. Effect of light intensity

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

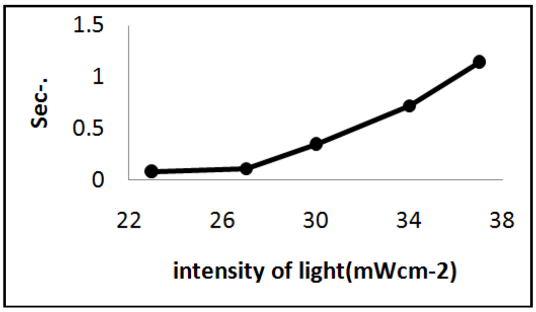


Fig. 5.

Effect of common anions (same concentration) On photo catalytic bleaching of Methylene blue by Nb_2O_5

The effect of addition of metal ions (Na^+, K^+,Ca^{+2},Ba^+, Cl^-)on photo degradation efficiency of Nb_2O_5 has been investigated, and results are reported in Table 6,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. The increase in the photo catalytic activity may be due to introduction of new trapping sites by incorporation of transition metal ions (fig.7) 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.

Table 6. Effect of common anions on photo catalytic bleaching of Methylene blue

Common anion	k x 10^5 (sec^{-1})
without metal ion	3.83
Nacl	7.67
Kcl	3.83
CaCl2	1.91
BaCl2	0

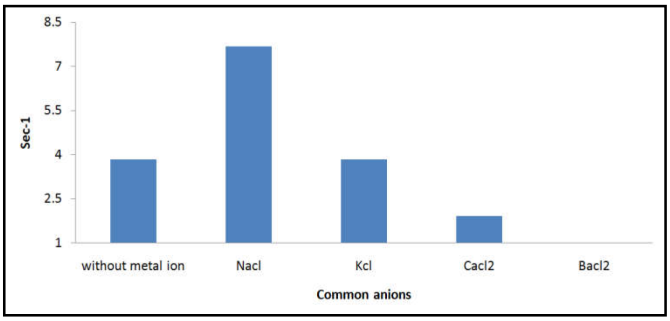


Fig. 6.

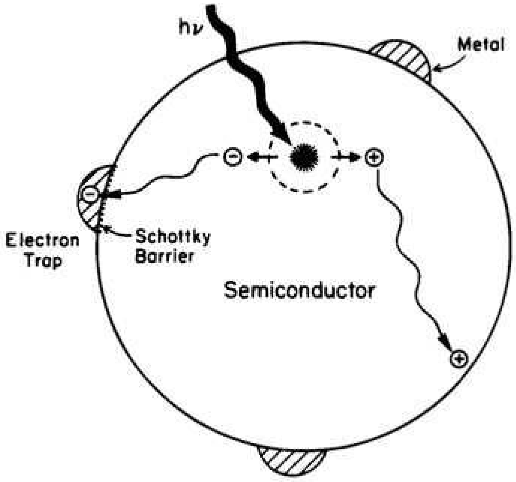


Figure 7. Metal-modified semiconductor photo catalyst particle

As the surface of catalyst particles is negatively charged and hence, it permits more metal ions to get adsorbed on the Nb_2O_5 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 Nb_2O_5 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 Nb_2O_5 can extract electron from hydroxyl ions in the solution to produce the hydroxyl radicals(${}^{\bullet}OH$). These hydroxyl radicals oxidize the dye molecule into colorless products.

$$H^+ + H_2O\,(ads) \longrightarrow {}^{\bullet}OH + H^+$$

$$H^+ + 2OH^- \longrightarrow {}^{\bullet}OH + OH^-$$

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

Metal modification		
${}^1Dye + h\nu \longrightarrow$	${}^1Dye_1$	(singlet excited state)
${}^1Dye_1 \longrightarrow$	${}^3Dye_1$	(triplet excited state)
$Nb_2O_5 \longrightarrow$	$Nb_2O_5{}^*\ (h^+_{vb} + e^-_{cb})$	
$Mn^+ + e^- \longrightarrow$	$M(n-1)+$	
$M(n-1)+ + O^2 \longrightarrow$	$Mn^+ + O^2$	
$Nb_2O_5{}^*\ (h^+_{vb})+OH- \longrightarrow$	$Nb_2O_5 + {}^{\bullet}OH$	
${}^3Dye_1 + {}^{\bullet}OH \longrightarrow$	Degradation of the dye	

Mechanism

Photo catalysis 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.

$$Nb_2O_5 + h\nu \longrightarrow Nb_2O_5{}^* + h^+(vb) + e^-(cb) \quad \ldots\ldots\ldots (1)$$

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 (${}^{\bullet}$ OH).

$$h^+ + OH- \longrightarrow {}^{\bullet}OH \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$h^+ + H_2O \longrightarrow OH + h^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Theelectrons in conduction band react with the Adsorbed oxygen molecules to form super oxide Ions ($O_2^{\bullet}$).

$$e^- + O_2\,(ads.) \longrightarrow O_2^{\bullet}\ (ads.) \quad \ldots\ldots\ldots\ldots (4)$$

Super oxide ions ($O_2^{\bullet}$) is reduced by H+, Accounting for hydroperoxyl radical ($HO^{2\bullet}$) and Hydroxyl radical production.

$$O_2{}^{*-} + H^+ \longrightarrow HO_2{}^* \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$2O_2{}^{*-} + 2H^+ \longrightarrow 2{}^*OH + O_2{}^* \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

$HO_2^{\bullet}$,${}^{\bullet}$ OH and $O_2^{\bullet}$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.

$^{1}Dye_{0} \rightarrow {}^{1}Dye_{1}$(Singlet excited state) …………………… (7)

$^{1}Dye_{1}\,hv \rightarrow {}^{3}Dye_{1}$(Triplet excited state) ………………. (8)

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

$^{3}Dye_{1} + {}^{\bullet}OH\ /\ HO^{2\bullet}\ /O_{2}^{\bullet} \longrightarrow$ Colorless End Products (Degradation) ……………………..… (9)

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:

$$C_{16}H_{18}N_{3}SCl \xrightarrow{\boxed{*OH/OH_{2}*/O_{2}*^{-}}} \text{Intermediate}$$

$$CO_{2}^{+}\ NO_{3}^{-} + SO_{4}^{2-} + H^{+} + Na^{+} + H_{2}O + Cl^{-}$$

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