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Nb_2O_5 USED AS PHOTOCATALYST FOR DEGRADATION OF METHYLENE BLUE USING SOLAR ENERGY

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ABSTRACT

The photocatalytic degradation of Methylene Blue was studied using Nb_2O_5 as semiconductor. Visible light was used as the source of energy. The effect of various parameters like amount of semiconductor, pH, light intensity, dye concentration etc. on the photodegradation were investigated. A tentative mechanism is proposed.

Keywords:*Semiconductor, Sunlight, Pseudo first order rate law, pH, Concentration of dye, bleaching of dye, Methylene Blue, Nb_2O_5 etc.*

INTRODUCTION

In recent years, array of industrial activities have been disturbing the water quality by release of various contaminants like dyestuff, heavy metal ions and many other organic substances. Due to the high concentration of organics in the effluents and the higher stability of modern synthetic dyes, the conventional biological methods are ineffective for

the complete colour removal and degradation of organics and dyes. Heterogeneous photocatalysis by semiconductor particles is a promising technology for water treatment. Photocatalytic degradation of methyl orange in aqueous TiO_2 under different solar irradiation sources was carried out by Rashed and El-Amin[1]. Photocatalytic degradation of Rhodamine B dye using hydrothermally synthesized ZnO was reported by Byrappa et al.[2]. Poulious et al.[3] observed the photodegradation of textile dye reactive black S in the presence of semiconducting oxides. Relationships between physicochemical properties and photoreactivity of four biorecalitrant phenylurea herbicides in aqueous TiO_2 suspension was studied by Parra et al.[4] whereas Mills et al.[5] reported photooxidation of water using WO_3 powder in presence of Fe^{+3} ions. Zang et al.[6] reported photocatalytic reduction of methyl yellow on CdS nanoparticles mediated in reverse micelles. Adsorption of triphenyl methane dyes on to jack fruit peel carbon was reported by Inbaraj et al.[7]. Recently nanotechnology is used via CdS/TiO_2 nanocomposite materials by Sesha et al.[8]. Therefore an attempt has been made to remove these dyes using semiconductor Nb_2O_5 and light.

EXPERIMENTAL

The stock solution of dye was prepared in doubly distilled water and diluted as required. The pH of the solution was adjusted by adding Prestandarized NaOH and HCl solutions and was determined by pH meter (Hena imported pen type).

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 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 (O.D.) was recorded spectrophotometrically (systronics spectrophotometer). Intensity of light was measured by suryamapi (CEL Model SM201).

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

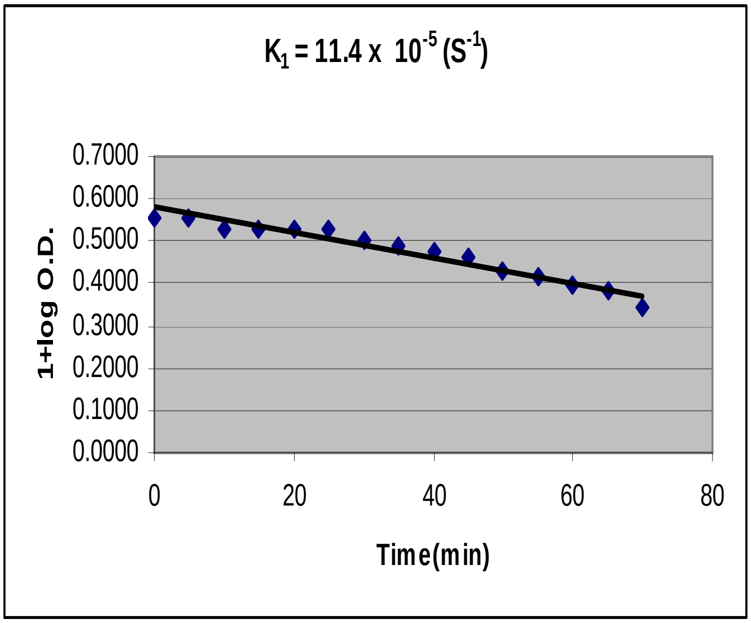
$$K_1 = 2.303 \text{ x slope}$$

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

Table-1 and Fig.1

[Dye]= $1.0 \text{x} 10^{-6}$ M; Nb_2O_5=0.10g;
pH=9.0; Intensity= 37.0 mW cm^{-2}

Time(min)	O.D.	1+log O.D.
0	0.36	0.5563
5	0.36	0.5563
10	0.34	0.5315
15	0.34	0.5315
20	0.34	0.5315
25	0.34	0.5315
30	0.32	0.5051
35	0.31	0.4914
40	0.3	0.4771
45	0.29	0.4624
50	0.27	0.4314
55	0.26	0.4150
60	0.25	0.3979
65	0.24	0.3802
70	0.22	0.3424



Effect of pH:

The effect of pH variation on rate of the photodegradation of methylene blue is given in Table 1 and Fig.1. It was found that as pH of the reaction mixture is raised, the rate of photocatalytic bleaching increases. It attains maximum value at pH 9.0. After this, if pH is raised further, the rate decreases. The pH affects not only the surface properties of Nb_2O_5 but also the dissociation of dye molecules and the formation of hydroxyl radicals. Increase in pH will increase the number of OH^- ions. A hole is generated in semiconductor, which abstracts an electron from OH^- ions converting it into $OH^\cdot$ free radical. This free radical is responsible for the bleaching of dye as confirmed by use of scavenger.

Effect of concentration of dye:

Experiments were carried out by keeping the pH constant and it was found that up to an optimum concentration ($1.0 \text{x} 10^{-6}$ M); the rate of photocatalytic bleaching increases as the rate of reaction is directly proportional to the molar concentration of reacting species. After this limit, if more concentration of dye is taken, it imparts a dark colour to the solution so it may act as filter to the incident light reaching to the semiconductor surface. Thereby only fewer photons reach the catalyst surface and therefore, generation of $OH^\cdot$ free radical on the catalyst surface is reduced since the active site of semiconductor gets covered by dye ions. This results in the decrease of the rate of bleaching. The data are given in Table-3 and Fig.3.

Effect of amount of Nb_2O_5:

Experiments were carried out by taking different amount of Nb_2O_5 and keeping other factors constant. It was found that up to a particular amount (0.10g), the rate of photocatalytic bleaching increases. It may due to the increase in the active site available on the catalyst surface for the reaction; which in turn increases the rate of radical formation. After this, the rate of bleaching decreases when the catalyst amount is increased. With a higher catalyst loading the deactivation of activated molecules by collision with ground state molecules dominates, thus reducing the rate of reaction. The data are summarized in Table-4 and Fig.4

Effect of light intensity:

The effect of intensity of light on rate of bleaching was studied and the data are given in Table-5 and Fig.5.

The rate of photocatalytic bleaching increases as the light intensity was increased. It may be explained on the basis of number of excited molecules. As more intensity of light falls on Nb_2O_5 molecules, more number of molecules get excited which in turn may bleach more dye molecules and thus the rate of bleaching was found to increase with increase in intensity of light.

Photocatalytic degradation mechanism:

On the basis of above studies, a tentative mechanism has been proposed for the bleaching of dye by Nb_2O_5 particles.

$$^1Dye_0 \rightarrow {}^1Dye_1 \text{ (Singlet excited state)}$$
$$^1Dye_1 \rightarrow {}^3Dye_1 \text{ (Triplet excited state)}$$
$$Sc \rightarrow e^- + h^+ \text{ or } Sc^+$$
$$h^+ + OH^- \text{ (from base)} \rightarrow OH^\cdot$$
$$^3Dye_1 + OH^\cdot \rightarrow \text{Products}$$

Dye absorbs the light and gets excited to its first singlet state. This gets converted to triplet state through intersystem crossing. On the other hand, the semiconductor gets excited by absorbing light and an electron is excited from its valence band to conduction band leaving behind a hole. This hole abstracts an electron from OH^- ion generating $OH^\cdot$ free radical. The dye is now being bleached by this free radical. The participation of $OH^\cdot$ radical was confirmed by using scavenger, which almost stops the bleaching reaction.

CONCLUSIONS

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. Colour change from Blue to colourless is irreversible and degradation rate of the dye follows the pseudo-first order kinetics.

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Table-2 and Fig.2

[Dye]=1.0x10^{-6} M; Intensity=37.0 mW cm^{-2};
Nb_2O_5=0.10g

pH	K_1 x 10^5 (S^{-1})
6	1.7
6.5	1.7
7	2.5
7.5	3.2
8	3.4
8.5	4.1
9	11.4
9.5	3.9
10	3.5
10.5	2.6

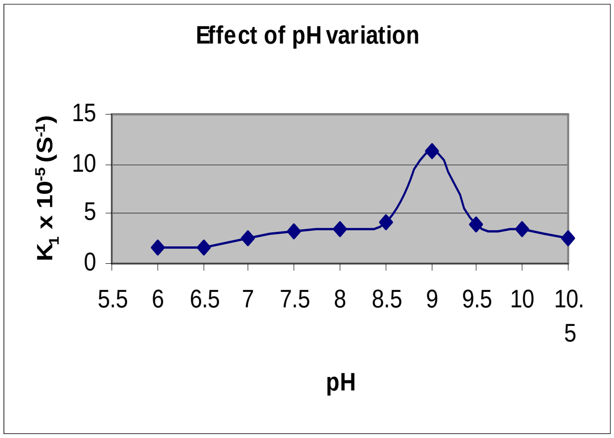


Table-3 and Fig. 3

pH=9.0; Nb_2O_5=0.10g; Intensity= 37.0 mW cm^{-2}

[Dye]x10^{-6} M	K_1x10^5 (S^{-1})
0.6	8.1
0.8	9.2
1	**11.4**
1.2	8.7
1.4	4.4
1.6	3

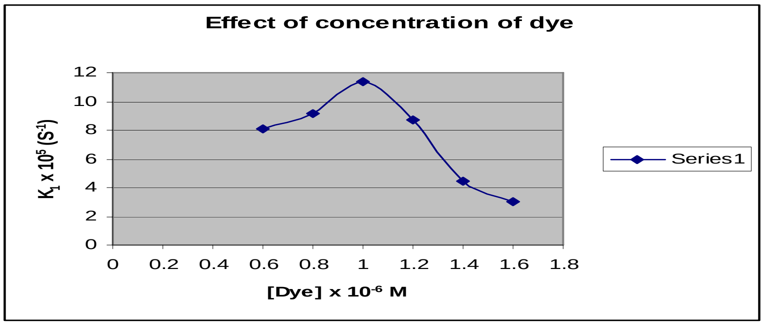


Table-4 and Fig. 4

[Dye]=1.0x10^{-6} M; pH=9.0; Intensity= 37.0 mW cm^{-2}

Amount of Semiconductor(g)	K_1x10^5 (S^{-1})
0.06	2.2
0.08	6.6
0.1	**11.4**
0.12	5
0.14	3

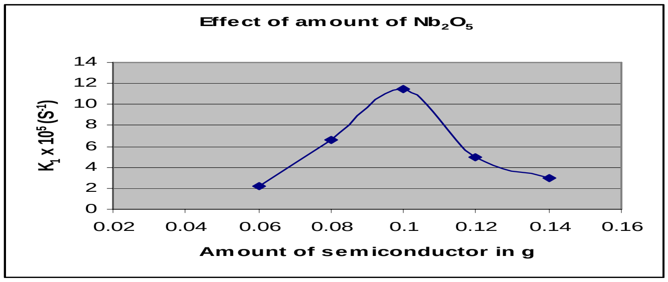
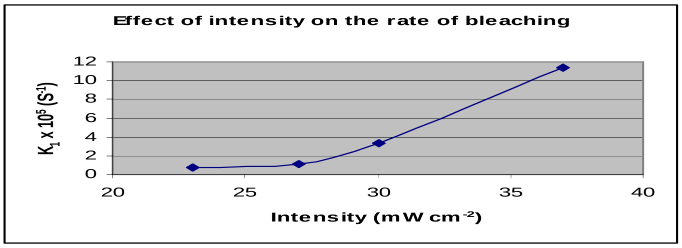


Table-5 and Fig.5

[Dye]=1.0×10^{-6} M; pH=9.0; Nb_2O_5=0.10g

Intensity(mW cm^{-2})	**$K_1\times10^5$ (S^{-1})**
23	0.8
27	1.1
30	3.4
37	**11.4**

[redacted]



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