



PHOTOCATALYTIC DEGRADATION OF ROSE BENGAL BY Ni-DOPED TITANIUM DIOXIDE

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ABSTRACT

The present investigation deals with the photocatalytic degradation of Rose Bengal by using Ni (0.5, 1.0, 1.5 and 2.0 % by weight) doped titanium dioxide. The progress of the reaction was observed spectrophotometrically at 550 nm. The effect of various operating parameters like pH, concentration of dye, dose of semiconductor and light intensity has been studied to achieve optimal reaction conditions. A tentative mechanism has been proposed for the photocatalytic degradation of Rose Bengal, involving hydroxyl radical as an active oxidizing species. It was observed that the adsorption of Rose Bengal dye using Ni doped TiO₂ follows pseudo-first order kinetics. This was observed that the degradation is more effective and fast for 0.5% Ni-TiO₂.

Key words: Photocatalytic degradation, Nickel doped TiO₂, Rose Bengal.

INTRODUCTION

Environmental pollution and industrialization on a global scale has drawn much attention to the crucial need for developing advance, hygienic and environment friendly purification technology. The most common purification processes has limitations due to the use of electricity and/or other energy sources. To address such problems, advance oxidation process like heterogeneous catalysis via metal oxide semiconductor like TiO₂, has been established that are capable to operate effectively under visible and UV light. Wide band gap of semiconductor are unable to absorb visible light. Hence, various efforts have been made to increase the photocatalytic activity by various methods like, doping it with metal and/or non-metal. Efficiency of advanced oxidation processes for the degradation of recalcitrant compounds has been broadly studied¹⁻⁶. Photocatalytic processes, utilizing TiO₂ semiconductor as a photocatalyst has received increasing attention because of its low cost, non-toxicity, relatively high chemical stability, and the advantage of using sunlight as a source of irradiation^{7,8}.

Zhang⁹ synthesised Ni/TiO₂ nanoparticles with different Ni dopant content by a modified sol-gel method and the photocatalytic efficiency of these catalysts was tested using an organic dye. It was observed that Ni doping greatly enhanced the photocatalytic efficiency of these catalysts with photodegradation of methyl orange as a model reaction. Shahina et al.¹⁰ studied the effects of Ni doping on photocatalytic activity of TiO₂ thin films (uniformly and non-uniformly) prepared by liquid phase deposition technique on glass substrate from an aqueous solution of ammonium hexafluorotitanate and NiF₂.

Lu et al.¹¹ used a low cost zeolite fly ash bead/TiO₂ composite materials with various surface structure features and their importance on TiO₂ coating, adsorbability and photocatalytic performances. Yang et al.¹² prepared Pt/TiO₂ hollow nanofibers with highly visible light photocatalytic activity by a uniaxial electrospinning method combined with photo-deposition and observed an enhanced photocatalytic performance under visible light towards the degradation of Orange II.

Li et al.¹³ studied the effect of rutile TiO₂ on the photocatalytic performance of novel g-C₃N₄/brookite-TiO_{2-x}N_y composite photocatalyst for NO decomposition under visible and UV light irradiation. Jo et al.¹⁴ synthesized cobalt promoted TiO₂/GO As-synthesized nanocomposites, via sol-gel and hydrothermal routes, which showed extraordinary photocatalytic activity towards the degradation of oxytetracycline and Congo red.

Natercia et al.¹⁵ synthesised a new composite of TiO₂ (P25) and N-doped carbon quantum dots (P25/NCQD) by a hydrothermal method and used as catalyst of the photooxidation of NO under UV and visible light irradiation. Rauf et al.¹⁶ reported the degradation of azo dyes using transition metal doped TiO₂ as photocatalysts in aqueous solutions. It was observed that such dopants reduce the recombination of e⁻_{CB} and h⁺_{VB} and decrease the band gap or create intra-band gap states, which enhances light absorption.

EXPERIMENTAL

Titanium(IV)oxide (Merck), nickel(II) hexahydrate (HiMEDIA), and Rose Bengal (HiMEDIA) were used. Systronic spectrophotometer-106 was used for measuring absorbance.

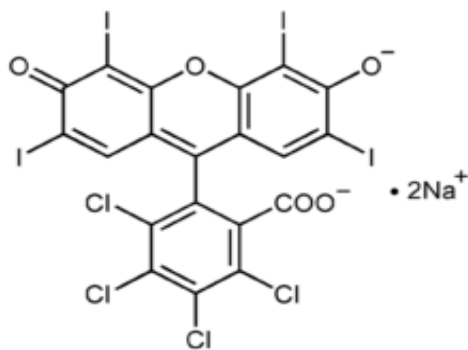


Fig. 1: Structure of Rose Bengal

Preparation of Ni-doped TiO₂

Undoped and Ni-doped titania (with different concentration of dopants) were prepared by the procedure described earlier¹⁷.

Photocatalytic degradation

1.0×10^{-3} M stock solution of Rose Bengal (RB) was prepared. The absorbance of Rose Bengal solution was determined at $\lambda_{\text{max}} = 550$ nm.

The dye solution was divided into four beakers. These beakers were kept under four different experimental conditions and initial and final absorbances (A) were observed after 4 hrs for solution of each beaker.

- Beaker 1 - Rose Bengal solution was kept in dark. Same initial and final absorbances were observed even after 4 hrs.
- Beaker 2 - Rose Bengal was kept in light. Same initial and final absorbances were observed after 4 hrs.
- Beaker 3 - Rose Bengal solution + 0.10 g titanium dioxide was kept in dark. Same initial and final absorbances were observed after 4 hrs.
- Beaker 4 - Rose Bengal solution + 0.10 g titanium dioxide kept in light. Absorbance decreased significantly after 4 hrs.

Thus, it is revealed that this reaction requires the presence of both; light and the semiconductor titanium dioxide. Hence, this reaction is photocatalytic in nature.

The photocatalytic activity of 0.5, 1.0, 1.5 and 2.0% Ni doped TiO₂ particles towards the degradation of Rose Bengal was investigated under visible light, and most kinetic measurements were performed at room temperature (300 K). The concentration of dye in the form of absorbance before and after photocatalytic degradation was measured at 550 nm (λ_{max}). A 200 W tungsten lamp was used as the visible light source. A water filter was placed on the beaker to completely cut off any thermal radiation just to ensure illumination by visible light only. The progress of the photocatalytic reaction was observed by taking absorbance at regular time intervals.

The change in absorbance at the λ_{max} value versus the irradiation time was measured. A typical run is presented in Table 1. It was observed that the absorbance of Rose Bengal solution decreased in presence of the photocatalyst and light. The plot of $1 + \log A$ versus time was linear and hence, this reaction followed pseudo-first order kinetics. The rate constant (k) for this reaction was determined from the expression $k = 2.303 \times \text{slope}$. A value of $k = 1.48 \times 10^{-4} \text{ s}^{-1}$ was determined for this reaction in its optimum conditions.

Table 1: A typical run

pH = 8.5		0.5% Ni-TiO ₂ = 0.11 g
[Rose Bengal] = 8.00×10^{-6} M		Light intensity = 60.0 mWcm ⁻²
Time (min.)	Absorbance (A)	1 + log A
0.0	0.609	0.7852
10.0	0.582	0.7649
20.0	0.524	0.7193
30.0	0.474	0.6757
40.0	0.481	0.6821
50.0	0.426	0.6294
60.0	0.402	0.6042
70.0	0.351	0.5453
80.0	0.303	0.4814
Rate constant (k) = $1.48 \times 10^{-4} \text{ sec}^{-1}$		

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on the rate of degradation of dye was investigated in the pH range (5.0-10.0) and results are reported in Table 2.

Table 2: Effect of pH

pH	0.5 % Ni-TiO ₂	1.0% Ni-TiO ₂	1.5% Ni-TiO ₂	2.0% Ni-TiO ₂
	[RB] = 8.00 × 10 ⁻⁶ M	[RB] = 1.30 × 10 ⁻⁵ M	[RB] = 1.30 × 10 ⁻⁵ M	[RB] = 1.30 × 10 ⁻⁵ M
	Light intensity = 60.0 mW cm ⁻²	Light intensity = 60.0 mW cm ⁻²	Light intensity = 70.0 mW cm ⁻²	Light intensity = 60.0 mW cm ⁻²
	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹
6.0	0.57	0.43	0.43	0.69
7.0	0.86	0.67	0.53	0.73
7.5	0.98	0.84	0.66	0.76
8.0	1.04	1.19	0.73	0.79
8.5	1.48	1.43	0.79	0.82
9.0	0.84	1.13	0.82	0.88
9.5	0.74	0.89	1.03	1.17
10.0	0.79	0.76	0.83	0.74

It has been observed that the rate of degradation increases with increase in pH upto a certain pH; further increase in pH resulted in a decrease in the rate of reaction. An increase in the rate of photocatalytic degradation with increase in pH may be due to generation of more [•]OH radicals, which are produced from the interaction of OH⁻ and hole (h⁺) of the semiconductor. These [•]OH radicals are responsible for the oxidative degradation of dye. The rate decreases after certain pH because more OH⁻ ions are available at higher pH and these will be adsorbed on the surface of the semiconductor making it negatively charged so that the approach of anionic form of Rose Bengal towards semiconductor surface will be retarded due to repulsion. This will result into a decrease in the rate of degradation.

Effect of concentration of rose Bengal

The effect of concentration of Rose Bengal on the rate of degradation was observed in range of 0.30 × 10⁻⁵ M to 3.8 × 10⁻⁵ M and results are summarized in Table 3.

Table 3: Effect of concentration of rose Bengal

[RB] × 10 ⁵ M	0.5% Ni-TiO ₂	1.0% Ni-TiO ₂	1.5% Ni-TiO ₂	2.0% Ni-TiO ₂
	Light intensity = 60.0 mW cm ⁻²	Light intensity = 60.0 mW cm ⁻²	Light intensity = 70.0 mW cm ⁻²	Light intensity = 60.0 mW cm ⁻²
	pH = 8.5	pH = 8.5	pH = 9.5	pH = 9.5
	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹
0.30	1.27	0.49	0.67	0.65
0.80	1.48	0.83	0.80	0.76

Cont...

[RB] × 10 ⁵ M	0.5% Ni-TiO ₂	1.0% Ni-TiO ₂	1.5% Ni-TiO ₂	2.0% Ni-TiO ₂
	Light intensity = 60.0 mW cm ⁻² pH = 8.5	Light intensity = 60.0 mW cm ⁻² pH = 8.5	Light intensity = 70.0 mW cm ⁻² pH = 9.5	Light intensity = 60.0 mW cm ⁻² pH = 9.5
	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹
1.30	1.15	1.43	1.03	1.17
1.80	0.87	0.71	0.85	0.88
2.30	0.71	0.29	0.80	0.76
2.80	0.65	0.21	0.67	0.61
3.30	0.25	0.07	0.48	0.51
3.80	0.19	0.02	0.22	0.31

It has been observed that the rate of photocatalytic degradation increases with increase in concentration of dye upto certain concentration. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of dye further. This may be attributed to the fact that as the concentration of dye was increased, more dye molecules were available for excitation and hence, there was an increase in the rate. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of dye further. Here, the dye starts acting as a filter for the incident light and it does not permit the desired light intensity to reach the semiconducting particles and thus, decreasing the rate of the photocatalytic degradation of dye.

Effect of amount of catalyst

The effect of amount of catalyst was also investigated by taking different amounts of catalyst in range of 0.02 to 0.14 g and results are given in Table 4.

Table: 4: Effect of amount of catalyst

Amount of Ni-TiO ₂ (g)	0.5%Ni-TiO ₂	1.0% Ni-TiO ₂	1.5%Ni-TiO ₂	2.0% Ni-TiO ₂
	[RB]= 0.80 × 10 ⁻⁵ M Light intensity = 60.0 mW cm ⁻² pH = 8.5	[RB] = 1.30 × 10 ⁻⁵ M Light intensity = 60.0 mW cm ⁻² pH = 8.5	[RB] = 1.30 × 10 ⁻⁵ M Light intensity = 70.0 mW cm ⁻² pH = 9.5	[RB] = 1.3 × 10 ⁻⁵ M Light intensity = 60.0 mW cm ⁻² pH = 9.5
	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹
0.02	1.09	0.84	0.64	0.81
0.04	1.41	1.03	0.80	0.88
0.06	1.42	1.43	0.86	1.17
0.08	1.16	1.33	1.03	0.96
0.10	1.39	1.29	0.99	0.98
0.11	1.48	1.06	0.95	1.17
0.12	1.21	0.72	0.89	0.86
0.13	1.13	0.54	0.86	0.76
0.14	1.07	0.43	0.72	0.67

Here, the data indicate that as the amount of photocatalyst was increased, the rate of degradation also increases in all cases but after a particular amount of photocatalyst, it shows saturation like behavior followed by slight decrease in rate constant. It may be due to fact that as the amount of semiconductor was increased, the exposed surface area of the semiconductor was also increased. After this, the rate of degradation started decreasing on increasing the amount of catalyst, because it only increases the thickness of the layer of semiconductor, and not the exposed surface area.

Effect of light intensity

The effect of light intensity towards the degradation of rose Bengal was observed by altering the light intensity in the range of 20.0-70.0 mWcm⁻². The results are given in Table 5.

Table 5: Effect of light intensity

Light intensity (mWcm ⁻²)	0.5% Ni-TiO ₂	1.0% Ni-TiO ₂	1.5% Ni-TiO ₂	2.0% Ni-TiO ₂
	[RB] = 0.80 × 10 ⁻⁵ M	[RB] = 1.30 × 10 ⁻⁵ M	[RB] = 1.20 × 10 ⁻⁵ M	[RB] = 1.30 × 10 ⁻⁵ M
	pH = 8.5	pH = 8.5	pH = 9.5	pH = 9.0
	TiO ₂ = 0.11 g	TiO ₂ = 0.06 g	TiO ₂ = 0.08 g	TiO ₂ = 0.06 g
	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹
20.0	0.63	0.24	0.39	0.25
30.0	0.66	0.56	0.40	0.37
40.0	0.68	0.59	0.46	0.46
50.0	1.30	0.69	0.48	0.48
60.0	1.48	1.43	0.95	1.17
70.0	1.34	0.88	1.03	0.79

An increasing relationship between light intensity and the rate of reaction was observed. It was found that degradation of dye was enhanced on increasing the intensity of light. This may be due to an increase in the number of photon striking per unit area of titanium dioxide powder on increasing the intensity of light. However, higher intensities were avoided due to thermal effects.

Activity of undoped TiO₂

Photocatalytic activity of undoped TiO₂ was observed for degradation of Rose Bengal to compare the efficiency of undoped with that of Ni-doped TiO₂. The results are reported in Table 6.

Table 6: Typical run with undoped TiO₂

[Rose Bengal] = 8.00 × 10 ⁻⁶ M		TiO ₂ = 0.11 g
Light intensity = 60.0 mWcm ⁻²		pH = 8.5
Time (min.)	Absorbance (A)	1 + log A
0.0	0.767	0.8852
10.0	0.703	0.8469
20.0	0.677	0.8305

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Time (min.)	Absorbance (A)	1 + log A
30.0	0.646	0.8102
40.0	0.621	0.7930
50.0	0.569	0.7551
60.0	0.542	0.7338

Rate constant (k) = $1.08 \times 10^{-4} \text{ sec}^{-1}$

Effect of change of anion

Counter anion of Ni-source in Ni-doped TiO₂ was also changed to observe the change in efficiency of nickel doped TiO₂ towards the degradation of rose Bengal. The results are given in Table 7.

Table 7: Typical run

pH = 8.5
 [Rose Bengal] = $8.00 \times 10^{-6} \text{ M}$

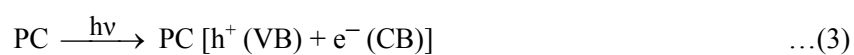
0.5%Ni-TiO₂ = 0.08 g
 Light intensity = 70.0 mWcm^{-2}

Time (min.)	Absorbance (A)	1 + log A
0.0	0.376	0.5752
10.0	0.337	0.5276
20.0	0.335	0.5250
30.0	0.312	0.4941
40.0	0.290	0.4623
50.0	0.277	0.4424
60.0	0.266	0.4248

Rate constant (k) = $1.15 \times 10^{-5} \text{ s}^{-1}$

Mechanism

On the basis of experimental observations, a tentative mechanism for photocatalytic degradation (mineralization) of rose Bengal may be proposed as:



Rose Bengal molecules absorb radiations of suitable wavelength and give rise to the singlet excited state. Then it may undergo an intersystem crossing (ISC) process to yield the more stable triplet excited state of the dye. Photocatalyst (PC) also utilizes the radiant energy to excite its electron from the valence band (VB) to the conduction band (CB); thus, leaving behind a hole (h^+) in the VB. This hole may abstract an electron from hydroxyl ions to generate hydroxyl radicals. These hydroxyl radicals will then oxidize the dye to its leuco form, which may ultimately degrade to products.

The participation of $\cdot\text{OH}$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavengers (isopropanol), where the rate of degradation was drastically reduced.

- Doping with nickel enhanced the photocatalytic activity of TiO_2 significantly.
- Dopant concentration also affects the efficiency of a photocatalyst.
- Among all the four different semiconductors (0.5, 1.0, 1.5, 2.0%), 0.5% Ni- TiO_2 gives most efficient photocatalytic degradation of Rose Bengal.
- Rate constant increased from $1.08 \times 10^{-4} \text{ sec}^{-1}$ to $1.48 \times 10^{-4} \text{ sec}^{-1}$ (i.e. by 37%) after doping with 0.5% Ni (by weight) in TiO_2 under same experimental conditions.
- Change of anion in nickel source (dopant) also affect the efficiency of Ni-doped TiO_2 .

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