

The Photocatalytic Degradation of Toluidine Blue Utilizing Zinc Ferrite as a Catalyst

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Abstract

The photocatalytic activity of ZnFe_2O_4 was studied by photocatalytically degrading toluidine blue dye in visible light. Precipitation was used to create ZnFe_2O_4 . A 200 W tungsten lamp was used to illuminate the dye solution. The dye's degradation rate was determined by measuring its absorbance at 630 nm at regular intervals. The rate of deterioration was discovered to be affected by many characteristics such as pH, dye concentration, semiconductor quantity, and light intensity. The optimum rate was observed at pH = 9.5; toluidine blue 2.10×10^{-5} zinc ferrite = 0.06 g and light intensity = 60.0 mWcm^{-2} . The rate constant for a typical run was observed as $2.67 \times 10^{-4} \text{ sec}^{-1}$. A preliminary process for the photocatalytic degradation of toluidine blue in the presence of zinc ferrite has been proposed, employing superoxide anion radical as the active oxidising species.

Keywords: Photocatalyst, Ternary oxide, Toluidine blue, Zinc ferrite

INTRODUCTION

The globe is currently dealing with a huge problem of environmental contamination. Organic chemical pollutants can be found in industrial and domestic effluents. These must be removed or destroyed before being released into a neighbouring water

reservoir. The discharge of significant amounts of waste water from the textile, dyeing, printing, cosmetic, food, photography, and pharmaceutical industries pollutes the environment. These effluents are dangerous in nature because they often contain significant amounts of

diverse organic chemicals that are not biodegradable.

Photocatalysis has emerged as a viable technique for waste water treatment since it is an efficient, cost-effective, and environmentally friendly way to tackle pollution problems. Attempts have been made to produce a newer, faster, more convenient, and environmentally friendly chemical technique for the breakdown of toluidine blue utilising zinc ferrite. ZnFe_2O_4 is an efficient photocatalyst as it has a high quantum yield. It is a safe and inexpensive material, stable to photocorrosion, and insoluble in water.

Photocatalysis refers to processes in which light is used to activate a material, hence altering the pace of a chemical reaction without being engaged itself. A photocatalyst is a substrate that absorbs light and acts as a catalyst for a chemical process. Although all photocatalysts are semiconductors, not all semiconductors are photocatalysts.

According to Sang et al.¹, photocatalysis is particularly successful in overcoming environmental and energy crisis concerns when exposed to light irradiations ranging from UV/Vis to near-infrared (NIR)

regions and eventually the entire solar light spectrum. Kamat and Meisel² investigated the photocatalytic activity of nanoparticles semiconductor. Richter and Caillol³ discovered photocatalytic removal of sulphur hexafluoride and nitrogen trifluoride. It was also determined that photocatalytic reactors utilising a combination of solar chimney power plants (SCPPs) and semiconductor photocatalysis may be employed for photocatalytic CO_2 reduction.

Schiavello described some of the operating principles of semiconductor photocatalysis. Kamat and Vinodgopal⁶ discovered heterogeneous semiconductor photocatalysis to be a viable strategy for the degradation of a wide range of organic contaminants, as well as cost effective. Hasnat et al. investigated the photocatalytic degradation of cationic and anionic dyes. It has been employed in several cleaning processes^{8,9} as well as the degradation of some colours. Photocatalytic activity has been reported by Ameta et al.⁷

According to Li et al., ZnFe_2O_4 offers a wide range of possible applications in gas sensing, magnetic behaviour, electrical properties, and photocatalysis. Because of its small band gap, zinc

ferrite exhibits strong photocatalytic activity when exposed to visible light, according to Chen et al. Maletin et al. discovered that the preparation condition, particle size, different dopants, and processing on the structure all had an influence on the physical characteristics of spinel ferrite nanoparticles. Bangale and Bamane¹⁵ used a sol-gel combustion process to create zinc ferrite with a high specific surface area.

EXPERIMENTAL

Zinc ferrite was prepared by..... method as described earlier¹⁶. 0.0306 g of toluidine blue was dissolved in 100.0 mL of doubly distilled water so that the concentration of dye solution was 1.0×10^{-3} M. It was used as a stock solution. This stock solution was further diluted. The absorbance of toluidine blue solution was determined with the help of a spectrophotometer at $\lambda_{\max} = 630$ nm. 50.0 mL of dye solution was placed in four separate beakers.

- The first beaker containing toluidine blue solution was kept in dark.
- The second beaker containing toluidine blue solution was exposed to light.

- The third beaker containing toluidine blue solution and 0.06 g ZnFe_2O_4 was kept in dark, and
- The fourth beaker containing toluidine blue solution and 0.06 g ZnFe_2O_4 was exposed to light.

After three to four hours, the absorbance of each solution was measured using a spectrophotometer (Systronics Model 106). The absorbance of toluidine blue solutions in the first three beakers remained nearly constant, whereas there was a considerable reduction in absorbance. This reduction implies that the presence of both light and zinc ferrite is required for this reaction. As a result, this reaction in nature is a photocatalytic reaction rather than a chemical (thermal) or photochemical reaction.

A solution of 2.10×10^{-5} M toluidine blue was prepared in doubly distilled water and 0.06 g of ZnFe_2O_4 was added to it. The pH of the reaction mixture was adjusted to 9.5 and then this solution was exposed to a 200 W tungsten lamp (60.0 mWcm^{-2}).

RESULTS AND DISCUSSION

It was discovered that the absorbance of toluidine blue solution decreased with

increasing exposure duration. A linear curve was produced between $1 + \log A$ (Absorbance) v/s time, indicating that

the photocatalytic degradation of toluidine blue follows pseudo-first order kinetics.

Table: 1 A typical run

pH = 9.5		ZnFe ₂ O ₄ = 0.06 g
[Toluidine blue] = 2.10×10^{-5} M		Light intensity = 60.0 mWcm ⁻²
Time (min.)	Absorbance (A)	1 + log A
0.0	0.522	0.7176
10.0	0.457	0.6599
20.0	0.383	0.5832
30.0	0.335	0.5250
40.0	0.285	0.4548
50.0	0.251	0.3994
60.0	0.216	0.3346
70.0	0.190	0.2787
80.0	0.162	0.2095
90.0	0.140	0.1461
Rate constant (k) = 2.44×10^{-4} s ⁻¹		

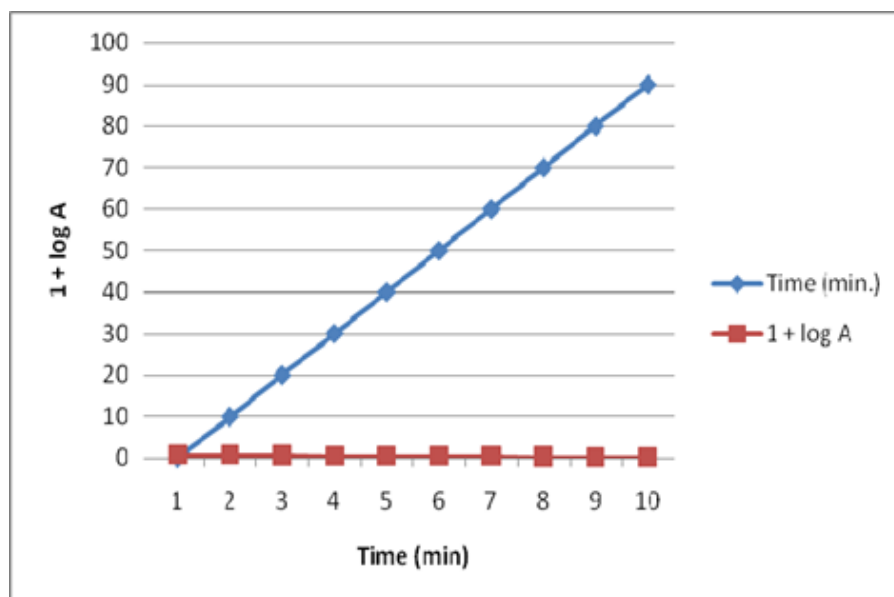


Fig 1: A typical run

The influence of several rate-affecting factors such as pH, dye concentration, semiconductor quantity, and light intensity on the optimal rate for photocatalytic dye degradation was investigated.

Effect of pH

The influence of pH on photocatalytic degradation was also studied. The reaction rates were measured in the pH range of 5.0-10.0. Table 2 summarises the findings.

It has been observed that the rate of photocatalytic degradation of toluidine blue increases as pH was increased and it attained optimum value at pH 9.5. On

further increasing pH, the rate of the reaction was decreased. This behavior may be explained on the basis that as pH was increased, there is greater probability for the formation of oxygen anion radical ($O_2^{\cdot-}$), which are produced by the reaction between O_2 molecule and electron (e^-) of the semiconductor. With the formation of more $O_2^{\cdot-}$ radicals, the rate of photocatalytic degradation of the dye increases. Above pH 9.5, a decrease in the rate of photocatalytic degradation of the dye was observed, which may be due to the fact that cationic form of dye is converted to its neutral form, which faces on attraction towards the negatively charged semiconductor surface due to the absorption of ^-OH .

Table 2: Effect of pH

[Toluidine blue] = 2.10×10^{-5} M

ZnFe₂O₄ = 0.06 g

Light intensity = 60.0 mWcm⁻²

pH	Rate constant (k) × 10 ⁴ (s ⁻¹)
5.0	0.21
5.5	0.22
6.0	0.30
6.5	0.36
7.0	0.520
7.5	0.80
8.0	0.93
8.5	1.28
9.0	2.37
9.5	2.44
10.0	2.20

Effect of toluidine blue concentration

The effect of dye concentration was studied by taking different concentrations of toluidine blue. The results are tabulated in Table 3.

The rate of photocatalytic dye degradation increased with increasing concentration of toluidine blue up to 2.10×10^{-5} M. It is possible that as the concentration of toluidine blue grew, more dye molecules were accessible for excitation, followed by sequential

energy/electron transfer, and thus the rate increased. The rate of degradation was shown to decrease when the dye concentration increased over 2.10×10^{-5} M. This might be because, beyond a certain concentration, the dye acts as an internal filter, preventing sufficient light intensity from reaching the surface of the photocatalyst at the bottom of the reaction vessel, slowing the rate of photocatalytic degradation of toluidine blue.

Table 3: Effect of toluidine blue concentration

pH = 9.5	Light intensity = 60.0 mWcm^{-2}
ZnFe ₂ O ₄ = 0.06 g	
[Toluidine blue] $\times 10^5 \text{ M}$	Rate constant (k) $\times 10^4 (\text{s}^{-1})$
1.50	1.27
1.60	1.56
1.70	1.73
1.80	2.12
[Toluidine blue] $\times 10^5 \text{ M}$	Rate constant (k) $\times 10^4 (\text{s}^{-1})$
1.90	2.22
2.00	2.37
2.10	2.44
2.20	1.94
2.30	1.62
2.40	1.57

By using varying quantities of zinc ferrite, the influence of semiconductor quantity on the rate of photocatalytic elimination of toluidine blue was also noticed. Table 4 summarises the findings.

The rate of reaction was found to rise when the amount of semiconductor, zinc ferrite, was increased. At 0.06 g of photocatalyst, the rate of degradation reached its maximum. Beyond 0.06 g, the response rate becomes almost constant. This might be because as the amount of semiconductor rose, so did the exposed surface area of zinc ferrite. However, at a certain value (0.06 g), increasing the amount of semiconductor increases just the

thickness of the layer of the semiconductor and not its exposed surface area. This was demonstrated by using reaction containers of various diameters. This point of saturation was shown to be greater for vessels with bigger volumes, whereas it was found to be lower for vessels with smaller capacity.

Effect of light intensity

The effect of light intensity variation on the photocatalytic degradation of toluidine blue was also studied. The light intensity was adjusted by moving the light source closer to the exposed surface area of the semiconductor. Table 5 summarises the findings.

Table 4: Effect of amount of zinc ferrite

pH = 9.5		Light intensity = 60.0 mWcm ⁻²	
[Toluidine blue] = 2.10 × 10 ⁻⁵ M			
Amount of semiconductor (g)		Rate constant (k) × 10 ⁴ (s ⁻¹)	
0.02		2.12	
0.04		2.25	
0.06		2.44	
0.08		2.40	
0.10		1.82	
0.12		1.48	
0.14		1.38	
0.16		1.28	

Table 5: Effect of light intensity

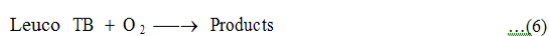
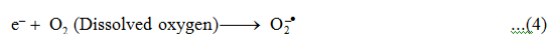
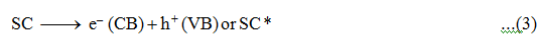
pH = 9.5 [Toluidine blue] = 2.10×10^{-5} M	ZnFe ₂ O ₄ = 0.06 g
Light intensity (mWcm ⁻²)	Rate constant (k) × 10 ⁴ (s ⁻¹)
20.0	1.23
30.0	1.38
40.0	1.53
50.0	2.09
60.0	2.44
70.0	2.18

The results show that increasing the light intensity improves photocatalytic degradation of toluidine blue because it increases the number of photons impacting per unit area per unit time on the photocatalyst surface.

As the light intensity was raised over 60.0 mWcm⁻², the rate of response decreased somewhat. It might be caused to some unintended heat reactions. As a result, middle order light intensity was applied throughout the studies.

Mechanism

Based on these findings, the following possible mechanism for photocatalytic degradation of Toluidine blue dye has been proposed:



Toluidine blue (TB) absorbs appropriate wavelength radiations and is excited, producing its initial excited singlet state, which is followed by intersystem crossover (ISC) to produce its more stable triplet state. This energy is also used by the semiconductor ZnFe₂O₄ (SC) to excite its electron from the valence band to the conduction band. The electron in conduction band is abstracted by dissolved oxygen to generate O₂^{•-} which convert dye to its leuco form, ultimately degrading to products. The addition of a hydroxyl radical scavenger did not impact the rate of degradation, indicating that the •OH radical does not participate as an

active oxidising species in the degradation of toluidine blue (2-propanol).

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