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USE OF ZINC FERRITE AS A PHOTOCATALYST FOR DEGRADATION OF TOLUIDINE BLUE

PRIYA PARSOYA* and SURESH C. AMETA

Department of Chemistry, PAHER University, UDAIPUR – 313003 (Raj.) INDIA

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ABSTRACT

The photocatalytic activity of $ZnFe_2O_4$ was investigated by carrying out the photocatalytic degradation of toluidine blue dye under visible light. $ZnFe_2O_4$ was synthesized by precipitation method. The dye solution was exposed to a 200 W tungsten lamp. The degradation rate of the dye was observed by measuring its absorbance at regular time intervals at 630 nm. Effect of various parameters like pH, concentration of dye, amount of semiconductor and intensity of light on rate of degradation was observed. The optimum rate was observed at pH = 9.5; toluidine blue = 2.10 x 10^{-5} M; zinc ferrite = 0.06 g and light intensity = 60.0 $mWcm^{-2}$. The rate constant for a typical run was observed as 2.67 x 10^{-4} sec^{-1}. A tentative mechanism has been proposed for the photocatalytic degradation of toluidine blue in presence of zinc ferrite involving superoxide anion radical as the active oxidizing species.

Key words: Ternary oxide, Photocatalyst, Toluidine blue, Zinc ferrite.

INTROUCTION

Nowadays, the world is facing a major problem of environmental pollution. Organic chemicals pollutants are present in effluents from industrial and domestic sources. These must be removed or destroyed before these are discharged to the nearby water resouress. The disposal of a large amount of waste water from textile, dyeing, printing, cosmetic, food, photography, pharmaceuticals indrustries creates environmental pollution. These effluents are hazardous in nature, because they normally contain appreciable quantities of different organic compounds, which are not biodegradable.

Photocatalysis has emerged as a promising technology for waste water treatment, because it is an efficient, cost-effective, and eco-friendly method to solve problems of environmental pollutions. Efforts have been made to develop a newer, fast, convenient and green chemical method for the degradation of toluidine blue using 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 involves such reactions, where light is utilized to activate a substance; thus, modifiying the rate of a chemical reaction without being involved itself. The substrate absorbing light and acting as a catalyst for a chemical reaction, is known as photocatalyst. Basically all photocatalysts are semiconductors, but semiconductors may not be necessarily a photocatalyst.

Available online at www.sadgurupublications.com
*Author for correspondence; E-mail: priyapp1987@gmail.com

Sang et al.[1] observed that photocatalysis is extremely effective to overcome environmental and energy crisis problems under light irradiations starting from UV/Vis to near-infrared (NIR) regions and finally the full solar light spectrum. Photocatalytic activity of nanoparticles semiconductor has been studied by Kamat and Meisel[2]. Photocatalytic elimination of sulphur hexafluoride and nitrogen trifluoride have been observed by Richter and Caillol[3]. It was also concluded that photocatalytic reactors with combination of solar chimney power plants (SCPPs) and semiconductor photocatalysis can be used for photocatalytic reduction of CO_2.[4]

Schiavello[5] reported some working principles of photocatalysis by semiconductor. Kamat and Vinodgopal[6] has used heterogeneous semiconductor photocatalysis as a promising approach for degradation of a large number of organic pollutants, as it is found to be cost effective also. Hasnat et al.[7] made a comparative study of photocatalytic degradation of cationic and anionic dyes. It has been used in some a clean-up processes[8,9] degradation of some dyes. Ameta et al.[10,11] have reported photocatalytic.

Li et al.[12] reported that $ZnFe_2O_4$ has much potential applications in gas sensing, magnetic behavior, electrical characteristics and photocatalysis. Chen et al.[13] reported that zinc ferrite has high photocatalytic activity under visible light irradiation due to its narrow band gap. Maletin et al.[14] observed that the preparation condition, partical size, various dopant's and processing on the structure effects physical properties of spinel ferrite nanoparticales. Bangale and Bamane[15] synthesized zinc ferrite by sol-gel combustion method having high specific surface area.

EXPERIMENTAL

Zinc ferrite was prepared by…… method as described earlier[16]. 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 λ_{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 keeping these beakers for 3-4 hrs, the absorbance of each solution was measured with the help of a spectrophotometer (Systronics Model 106). It was observed that the absorbance of toluidine blue solutions of first three beakers remained virtually constant, while there was a significant decrease absorbance. This decrease suggests that this reaction requires both; the presence of light as well as zinc ferrite. Hence, justifying that this reaction is a photocatalytic reaction in nature and it is not 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 observed that there was a decrease in absorbance of toluidine blue solution with increasing

time of exposure. A linear plot between 1 + log A (Absorbance) v/s time was obtained, which indicates that the photocatalytic degradation of toluidine blue follows pseudo-first order kinetics.

The data of typical run have been presented in Table 1 and represented graphically in Fig 1.

Table: 1 A typical run

pH = 9.5		$ZnFe_2O_4$ = 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}

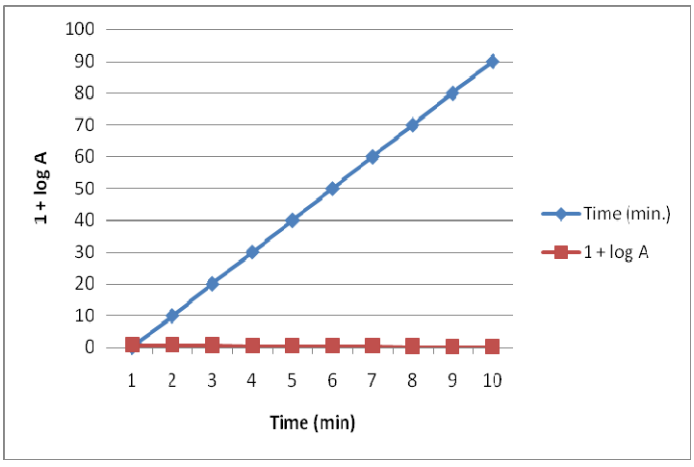

Fig 1: A typical run

The effect of different rate affecting parameters were studied to get the optimum rate for photocatalytic degradation of dye like pH, concentration of dye, amount of semiconductor and light intensity.

Effect of pH

The effect of pH on photocatalytic degradation was also investigated. The reaction rates were determined in pH range from 5.0-10.0. The results are tabulated in Table 2.

Table 2: Effect of pH

[Toluidine blue] = 2.10×10^{-5} M $ZnFe_2O_4$ = 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

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 ($O_2^{-\bullet}$), which are produced by the reaction between O_2 molecule and electron (e^-) of the semiconductor. With the formation of more $O_2^{-\bullet}$, 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 absoption of ^-OH ions.

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.

Table 3: Effect of toluidine blue concentration

pH = 9.5 Light intensity = 60.0 $mWcm^{-2}$
$ZnFe_2O_4$ = 0.06 g

[Toluidine blue] × 10^5 M	Rate constant (k) × 10^4 (s^{-1})
1.50	1.27
1.60	1.56
1.70	1.73
1.80	2.12

Cont…

[Toluidine blue] × 10^5 M	Rate constant (k) × 10^4 (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

It was observed that the rate of photocatalytic degradation of dye increases with increasing concentration of toluidine blue up to 2.10×10^{-5} M. It may be attributed to the fact that as the concentration of the toluidine blue was increased, more dye molecules were available for excitation followed by consecutive energy/electron transfer and hence, there was an increase in the rate. The rate of degradation was found to decrease with an increase in the concentration of dye above 2.10×10^{-5} M. This may be due to the fact that after a particular concentration, the dye may start acting as an internal filter itself and will not permit the sufficient light intensity to reach the surface of the photocatalyst at the bottom of reaction vessel and thus, decreasing the rate of photocatalytic degradation of toluidine blue.

Effect of amount of semiconductor

The effect of amount of semiconductor on the rate of photocatalytic removal of toluidine blue was also observed by taking different amounts of zinc ferrite. The results are tabulated in Table 4.

Table 4: Effect of amount of zinc ferrite

pH = 9.5 [Toluidine blue] = 2.10×10^{-5} M	Light intensity = 60.0 $mWcm^{-2}$
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

It was observed that the rate of reaction was found to increase on increasing the amount of semiconductor, zinc ferrite. The rate of degradation reached to its optimum value at 0.06 g of the photocatalyst. Beyond 0.06 g, the rate of reaction become almost constant. This may be due to fact that as the amount of semiconductor was increased, the exposed surface area of zinc ferrite also increases. However, after a particular value (0.06 g), an increase in the amount of semiconductor will only increase the thickness of layer of the semiconductor and not its exposed surface area. This was confirmed by taking reaction vessels of different sizes. It was observed that this point of saturation was shifted to a higher value for vessels of larger volumes while a reverse trend was observed for vessels of smaller capacities.

Effect of light intensity

The effect of variation of light intensity on the photocatalytic degradation of toluidine blue was also investigated. The light intensity was varied by changing the distance between the light source and the exposed surface area of semiconductor. The results are tabulated in Table 5.

Table 5: Effect of light intensity

pH = 9.5 $ZnFe_2O_4$ = 0.06 g
[Toluidine blue] = 2.10×10^{-5} M

Light intensity ($mWcm^{-2}$)	Rate constant (k) $\times 10^4$ (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 indicate that photocatalytic degradation of toluidine blue was enhanced with the increase in intensity of light, because an increase in the light intensity will increase the number of photons striking per unit area per unit time of photocatalyst surface. There was a slight decrease in the rate of reaction as the intensity of light was increased beyond 60.0 $mWcm^{-2}$. It may be due to some side thermal reactions. Therefore, light intensity of medium order was used throughout the experiments.

Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation of Toluidine blue dye has been proposed as follows:

$$^1TB_0 \xrightarrow{h\nu} {}^1TB_1 \quad ...(1)$$

$$^1TB_1 \xrightarrow{ISC} {}^3TB_1 \quad ...(2)$$

$$SC \longrightarrow e^- (CB) + h^+ (VB) \text{ or } SC^* \quad ...(3)$$

$$e^- + O_2 \text{ (Dissolved oxygen)} \longrightarrow O_2^{-\bullet} \quad ...(4)$$

$$^3TB_1 + O_2^{-\bullet} \longrightarrow \text{Leuco TB} \quad ...(5)$$

$$\text{Leuco TB} + O_2 \longrightarrow \text{Products} \quad ...(6)$$

Toluidine blue (TB) absorbs radiations of suitable wavelength and it is excited giving its first excited singlet state followed by intersystem crossing (ISC) to give its more stable triplet state. Along with this, the semiconductor $ZnFe_2O_4$ (SC) also utilizes this energy to excite its electron from valence band to the conduction band. The electron in conduction band is abstracted by dissolved oxygen to generate $O_2^{-\bullet}$, which

will convert dye to its leuco form, ultimately degrading to products. It was confirmed that the •OH radical does not participate as an active oxidizing species in the degradation of toluidine blue as the rate of degradation was not affected in presence of hydroxyl radical scavenger (2-propanol).

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