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ZINC FERRITE: AN EFFICIENT PHOTOCATALYST FOR DEGRADATION OF ROSE BENGAL

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ABSTRACT

$ZnFe_2O_4$ was synthesised by precipitation method. The photocatalytic activity of $ZnFe_2O_4$ was investigated by carrying out the photocatalytic degradation of rose Bengal dye under visible light. The degradation rate of the dye was observed by measuring its absorbance at regular time intervals at 540 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 = 7.0; rose Bengal = 5.0×10^{-6} M; zinc ferrite = 0.1 g and light intensity = 60.0 $mWcm^{-2}$. The rate constant for a typical run was observed as 2.45×10^{-4} sec^{-1}. A tentative mechanism has been proposed for the photocatalytic degradation of rose Bengal in presence of zinc ferrite involving hydroxyl radical as an active oxidizing species.

Key words: Ternary oxide, Photocatalyst, Rose Bengal, Zinc ferrite.

INTRODUCTION

Presently, the world is facing a major problem of environmental pollution. Organic chemicals are common pollutants, which are found in waste water effluents from industrial and domestic sources. These must be removed or destroyed before discharge in to the environment. The disposal of a large amount of waste water from industries like textile, dyeing, printing, cosmetic, food, photography, pharmaceuticals etc. create environmental pollution. These effluents are hazardous in nature, because they normally contain appreciable quantities of different toxic organic compounds, which cannot be easily degraded.

Although, some conventional waste water treatment methods such as adsorption, biological treatment, coagulation etc. are available, but these are associated with some or the other demerits. Therefore, efforts should be made to develop efficient, cost-effective, and eco-friendly new methods to solve these environmental problems.

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In this context, photocatalysis has been considered as a promising technology for waste water treatment. In the proposed investigation, efforts have been made to develop a newer, fast, convenient and green chemical method for the degradation of rose Bengal using zinc ferrite $ZnFe_2O_4$. It is an efficient photocatalyst, and has a high quantum yield. It is a safe and inexpensive material, stable to photocorrosion and insoluble in water, and above all, it may provide an eco-friendly pathway for degradation of some pollutant. Treated water can be recycled and may be used for some useful purposes.

Photocatalysis includes such reactions, which utilize light to activate a substance, modifiying the rate of a chemical reaction without being involved itself. A substrate, which absorbs light and acts as a catalyst for a chemical reaction, is known as photocatalyst. Basically, photocatalysts are semiconductors, but all semiconductors are not necessarily photocatalysts.

Schiavello[1] reported some working principles of photocatalysis by semiconductor. Heterogeneous semiconductor photocatalysis has been used as a promising approach for degradation of a large number of organic pollutants, as it is found to be cost effective also[2]. Hasnat et al.[3] made a comparative study of photocatalytic degradation of cationic and anionic dyes. Photocatalysis has many environmental applications and it has been demonstrated to be an asset for a clean-up process[4,5]. Ameta et al.[6,7] have used this process for removal of some dyes.

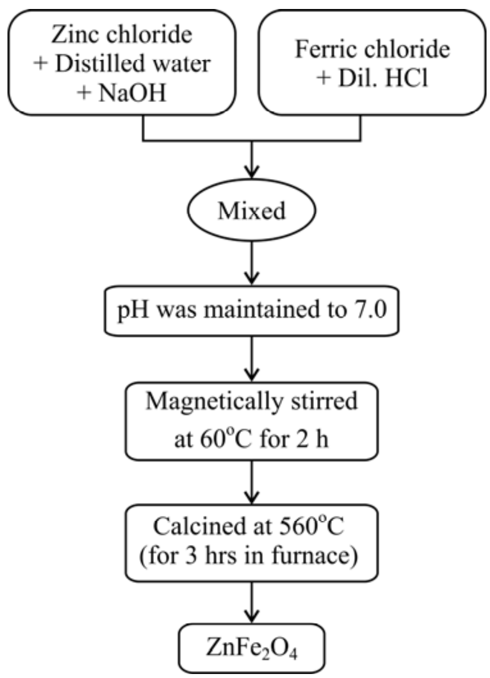
Li et al.[8] reported that $ZnFe_2O_4$ has much potential applications like gas sensing, magnetic behavior, electrical characteristics and photocatalysis. Chen et al.[9] reported that zinc ferrite has high photocatalytic activity under visible light irradiation due to its narrow band gap. Maletin et al.[10] observed the effect of preparation condition, partical size, various dopant's and processing on the structure and physical properties of spinel ferrite nanoparticales. Bangale and Bamane[11] synthesized zinc ferrite by sol-gel combustion method with high specific surface area. Jang et al.[12] described the fabrication of nanocrystalline zinc ferrite, n-type photocatalyst having a spinel structure, by polymerized complex (PC) method and characterized its optical properties. Deraz and Aliarifi[13] indicated that the combustion method provides a promising option for synthesis of high quality nano-sized zinc ferrite.

Caruntu et al.[14] reported the synthesis of highly uniform single phase zinc ferrite through a single step low temperature reaction by the liquid phase deposition (LPD) method. Band gap of zinc ferrite is relatively small so necessary to absorb a large portion of the visible light from solar spectrum and as such, this is potentiatlly useful in solar light and shows higher activity for the photocatalytic oxidation of water under visible light irradiation (420 nm).

EXPERIMENTAL

A stock solution of rose Bengal of concentration 1.0×10^{-3}M was prepared in doubly distilled water. Working solution of 1.0×10^{-5}M solution of rose Bengal was prepared by diluting the stock solution and 0.10 g of $ZnFe_2O_4$ was added to it. The pH of the reaction mixture was kept to 7.0 and then this solution was exposed to a 200 W tungsten lamp. The absorbance of rose Bengal solution was determined with the help of spectrophotometer (Systronics Model 106) at λ_{max} = 540 nm. A decrease in absorbance of rose Bengal solution was observed with increasing time of exposure.

Preparation of $ZnFe_2O_4$



RESULTS AND DISCUSSION

Effect of pH

The pH of the rose Bengal solution was varied from 5.0 to 9.0. It was observed that rate of reaction increases with increasing pH and maximum rate was found at 7.0. Above this pH, the rate of reaction decreases with increasing pH.

It was observed that rate of degradation increases on increasing pH of the medium because more $^{\bullet}OH$ radical are generated on increasing pH, due to availability of more ^{-}OH ions. At higher pH than 7.0, the reaction rate is retarded. It may be due to the fact that at pH 7.0, surface of the zinc ferrite is negatively charged, due to adsorption of ^{-}OH ions and anionic dye rose Bengal will face a force of repulsion and as a result, the reaction rate is retarded.

Table 1: Effect of pH

[Rose Bengal] = 5.0×10^{-6} M ZnFe$_2$O$_4$ = 0.10 g

Light intensity = 60.0 mW cm^{-2}

pH	k x 10^4 (sec^{-1})
5.0	0.61
5.5	0.82
6.0	1.02
6.5	1.60
7.0	**2.45**
7.5	1.78
8.0	1.16
8.5	0.99
9.0	0.72

Effect of rose Bengal concentration

The concentration of rose Bengal was varied form 1.0×10^{-6} M to 8.0×10^{-6} M. The rate of degradation was found to increase with increasing concentration of rose Bengal up to 5.0×10^{-6} M. With further increase in dye concentration, rate of reaction decreases. It is due to the fact that at higher concentration of dye, it will start acting as an internal filter and will not permit the desired light intensity to reach the surface of semiconductor. As a consequence, the rate of degradation decreases.

Table 2: Effect of rose Bengal concentration

pH = 7.0 $ZnFe_2O_4$ = 0.10 g

Light intensity = 60.0 mW cm^{-2}

[Rose Bengal] × 10^5 M	k x 10^4 (sec^{-1})
1.0	0.53
2.0	0.66
3.0	0.78
4.0	0.86
5.0	2.45
6.0	0.53
7.0	0.43
8.0	0.31

Amount of semiconductor

The amount of semiconductor was varied from 0.02 g to 0.14 g. The exposed surface area increases on increasing the amount of semiconductor and therefore, the rate of degradation also increases. Optimum condition was obtained at 0.10 g. On further increasing semiconductor amount, only thickness of semiconductor layer increases and not the exposed surface area as it will form multilayers and electron (e^-) hole (h^+) recombination may take place as the semiconductor particles will be in close contact in multilayers. As a result, decrease in the rate of reaction was observed.

Table 3: Effect of semicoductor

[Rose Bengal] = 5.0 × 10^{-6} M pH = 7.0

Light intensity = 60.0 mW cm^{-2}

Amount of semiconductor (g)	k x 10^4 (sec^{-1})
0.02	0.6
0.04	0.62
0.06	0.77

Cont…

Amount of semiconductor (g)	k x 10^4 (sec^{-1})
0.08	1.30
0.10	2.45
0.12	0.84
0.14	0.70

Effect of light intensity

The light intensity was varied from 20.0 to 70.0 $mWcm^{-2}$ to know the effect of light intensity on the rate of degradation. As it is known that number of photons per unit area per unit times increases on increasing light intensity, rate of reaction also increases up to 60.0 $mWcm^{-2}$ and then it decreases on further increasing the light intensity It may be due to some side thermal reactions.

Table 4: Effect of light intenstiy

[Rose Bengal] = 5.0×10^{-6} M pH = 7.0

$ZnFe_2O_4$ = 0.10 g

Light intensity ($mWcm^{-2}$)	k x 10^4 (sec^{-1})
20.0	0.70
30.0	0.85
40.0	1.02
50.0	1.27
60.0	2.45
70.0	1.03

A typical run

The typical run for the photocatalytic degradation of rose Bengal in the presence of $ZnFe_2O_4$ photocatalyst has been presented in Table 5. The plot of 1 + log A v/s time was linear and hence, it may be concluded that the reaction followed pseudo-first order kinetics. The rate of this reaction was determined by the expression k = 2.303 x slope, which was found to be 2.45 x 10^{-4} sec^{-1}.

Table 5: A typical run

Time (min)	Absorbance	1 + log A
0.0	0.661	0.8202
10.0	0.569	0.7551
20.0	0.495	0.6946
30.0	0.426	0.6294
40.0	0.369	0.5670
50.0	0.320	0.5051
60.0	0.275	0.4393
70.0	0.337	0.3747
80.0	0.205	0.3118
90.0	0.178	0.2504
100.0	0.152	0.1818

Mechanism

On the basis of the experimental observations, a tentative mechanism of photocatalytic degradation of rose Bengal may be proposed as –

$$^{1}RB_{0} \xrightarrow{h\nu} {}^{1}RB_{1} \qquad \ldots(1)$$

$$^{1}RB_{1} \xrightarrow{ISC} {}^{3}RB_{1} \qquad \ldots(2)$$

$$SC \xrightarrow{h\nu} e^{-}\,(CB) + h^{+}\,(VB) \text{ or } SC^{+} \qquad \ldots(3)$$

$$h^{+} + OH^{-} \longrightarrow {}^{\bullet}OH \qquad \ldots(4)$$

$$^{3}RB_{1} + {}^{\bullet}OH \longrightarrow \text{Leuco RB} \qquad \ldots(5)$$

$$\text{Leuco RB} \longrightarrow \text{Product} \qquad \ldots(6)$$

Dye rose Bengal (RB) absorbs radiation of suitable wave length and it is excited from its ground state to excited singlet state. Then this singlet singlet state undergoes intersystem crossing (ISC) to its triplet state. On the other hand, the semiconductor absorbs light of suitable wave length and excite its e^{-} from valence band to conduction band; thus, leaving behind a hole. This hole abstracts an one e^- from OH^- ion forming $^{\bullet}OH$ radical. This $^{\bullet}OH$ radical helps in oxidative degradation of dye to form products via leuco-dye. The participation of hydroxyl radicals as active oxidizing species was confirmed by carrying out this reaction in the presence of hydroxyl radical scavenger, isopropanol, when the rate of degradation decreases drastically.

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