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Research Article

A Comparative Study on Photocatalytic Activity of ZnO, ZnS and ZnO-ZnS Composite

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Abstract

A comparative study was made on photocatalytic activity of ZnO, ZnS and their composite. A simple mechanochemical method was used for preparation of composite. The photocatalytic efficiency of ZnO-ZnS composite was compared with pure ZnO and ZnS. The effect of various parameters such as pH, dye concentration, semiconductor amount and light intensity was observed. The optimum conditions for this degradation were obtained as: Rose Bengal = 7.0×10^{-6}M, pH = 7.5, amount of composite = 0.08g and light intensity = 60.0 $mWcm^{-2}$. It was found that coupled chalcogenide ZnO-ZnS show better photocatalytic activity as compared with ZnO and ZnS alone for the degradation of rose Bengal in the presence of visible light.

Keywords: ZnO; ZnS; Composite; Photocatalytic Activity; Rose Bengal

Introduction

Developments in industrial and agriculture field have resulted in formation of large amount of waste water containing toxic pollutants. Organic dyes are one of the larger group of pollutants, which are released from textile industrial waste water. Some of the effects of dye containing waste water are aesthetic pollution of environment and also its carcinogenicity because of their degradation products. The importance of the waste water treatment, management and its disposal in environment gradually increases in the modern times and it becomes a major issue for public health and scientific interest.

Many techniques like electrochemical coagulation, reverse osmosis, nanofiltration, adsorption using activated materials, etc. are being used for the removal of pollutants from waste water. The sequential and concurrent use of these combined processes tends to create a greater efficient method in removing the pollutant aspects in liquid residues, restrictions in terms of execution, efficiency, and price are a factor; however, biological processes have been extensively used and show potential towards dairy and agricultural waste water treatment [1]. The chemical process deals with the photocatalysts like TiO_2, SnO_2, ZnO, ZnS, etc. mediated degradation of the industrials waste waters [2]. These processes have limitations, which can potentially affect degradation efficiency through controlled pH range, rapid organic-load variations, and also the effluent's physicochemical properties [3].

The possibility of solar photoelectrolysis was demonstrated for first time in 1969 by Fujishima., *et al* [4]. They used n- type TiO_2 electrode, which was exposed to near-UV light and was connected to a platinum black counter electrode through an electrical load.

Xie., *et al.* [5] synthesized mixed-phase TiO_2 nanoparticles by the oxidation of $TiCl_4$ in propane/air turbulent flame and used for photodegradation of benzene at ppb levels. Photodegradation was examined under the conditions: 70% relative humidity, 38 μg cm^{-2} catalyst loading, 24 $mWcm^{-2}$ UV irradiation of 254 nm and 5.7s residence time in the reactor. Photocatalytic degradation of Methylene blue under visible light has been reported by Ameta., *et al.* [6] using vanadium modified titanium dioxide supported on zeolite. The results indicated that the rate of photocatalytic degradation of Methylene blue was enhanced 5.7 and 8.6 times by using V doped TiO_2 for 1% and 2% loading, respectively.

Haritha., *et al.* [7] have synthesized tin oxide nanoparticles (SnO_2 NPs) using aqueous extract of *Catunaregam spinosa* (*C. spinosa*) root barks, which is a green chemical approach. SnO_2 NPs was found in spherical shape with average size of 47 ± 2 nm. They further used this bio-green synthesized SnO_2 NPs for the photocatalytic degradation of toxic Congo red dye, which resulted in higher percentage of degradation. Goharshadi., *et al.* [8] followed sonochemical method for the preparation of ZnS nanoparticles. They used zinc acetate and thioacetamide as starting materials followed by ultrasonic irradiation for 1h. The average particle size was found to be 2 nm. The photocatalytic behavior of semiconducting zinc sulfide quantum dots was studied using an azo dye called Reactive black 5 (RB5).

A simple hydrothermal method was used by Wang., *et al.* [9] for the preparation of well-dispersed ZnS microspheres on large-scale. They used $ZnSO_4 \cdot 7H_2O$ and $SC(NH_2)_2$ as reactant and polyvinyl pyrrolidone (Mr ≈ 10,000) as the surfactant. The growth process involves a special oriented accumulation of PVP stabilized ZnS nanoparticles into microspheres of 1.5 ~ 2.0 μm sizes. Methylene blue was used as a model organic compound to evaluate the photocatalytic activity of as-prepared ZnS microsphere.

ZnS nanoparticles were successfully fabricated by a simple low-temperature solid-state method by Chen., *et al* [10]. The phase composition, morphology, pore structure and optical property of the samples were also characterized. Methyl orange (MO) dye was used to evaluate photocatalytic activities of the as-synthesized samples under UV irradiation. ZnS sample prepared with sodium dodecyl sulfonate (SDS) showed the highest photocatalytic activity with nearly 95% of MO decomposition after irradiation for 60 minutes.

Chankhanittha and Nanan [11] prepared hexagon-like ZnO microstucture at low temperature via hydrothermal method without using any surfactant, capping agent or organic solvent. The formation of hexagon-like microstructure was observed with the grain size of about 480 x 720 nm and crystallite size of 45 - 51 nm. ZnO showed high photocatalytic efficiency of 95% in 80 minutes. Raheem., *et al.* [12] have carried out the photocatalytic degradation of Reactive green using zinc oxide as a photocatalyst. The optimum conditions for the photocatalytic degradation of Reactive green were 0.12 g100 mL^{-1} mass of photocatalyst, dye concentration 40 ppm and light intensity 8.22 $mWcm^{-2}$.

Shi., *et al.* [13] have successfully synthesized CdS-TiO_2 composites using hydrothermal technique at low temperature (180°C). It was found that CdS-TiO_2 composites consisted of anatase TiO_2 and cubic phase CdS. The photocatalytic efficiency of composites was investigated by photocatalytic degradation of Rhodamine B under visible light irradiation. The highest photocatalytic activity was observed for CdS and TiO_2 in the molar ratio of 0.25:1.

Kostova and Dutkova [14] have employed a simple solid-state mechanochemical method for the preparation of ZnS-TiO_2 composites. The photocatalytic properties of ZnS-TiO_2 composites were evaluated by decomposition of Methyl orange in aqueous solution. Results indicate lower recombination rate of photoexcited electrons and holes. Upadhyay., *et al.* [15] have investigated the use of copper hexacyanoferrate (II) in photocatalytic degradation of Azure B under visible light irradiation (λ_{max} = 640 nm). The reaction followed pseudo-first order kinetics.

Parveen and Vyas [16] have carried out the photocatalytic degradation of Rose Bengal dye over Ni-Doped TiO_2. The results showed that the higher degradation rate was found for 0.5% doped Ni-TiO_2(0.11g) at pH = 8 and dye concentration = 8.00×10^{-6}M under the visible light intensity of 60.0 $mWcm^{-2}$. The photocatalytic degradation of Rose Bengal was investigated over Bi_2S_3 photocatalyst by Sharma., *et al* [17]. The degradation rate was highly influenced by the variation in several parameters like pH, concentration of dye solution, photocatalyst load and light intensity.

Photocatalysis is an emerging technology, which is used for waste water treatment, self-cleaning of glasses, deodourization, synthesis of energy rich molecules, killing bacteria, etc. Various binary, ternary, and quaternary chalcogenides are used as photocatalyst quite commonly. Some work has also been reported on possible use of ZnO photocatalyst but little attention has been paid to use its composites with some semiconducting chalcogenides for photocatalytic degradation of organic contaminants in waste water. Therefore, a momentum is necessary in this field to explore the possibility of using some composites of ZnO for this purpose.

Experimental Study

Preparation of composite

A simple solid state mechanochemical method was used for the preparation of ZnO and ZnS composite. Composite (ZnO-ZnS) was prepared by mixing the equal amount of ZnO and ZnS (1:1 ratio) and then ground with the help of pestle and mortar and it was used for photocatalytic degradation of rose bengal.

Characterization of composite

X-rays diffraction pattern of the pure ZnO-ZnS composite is shown in figure 1. Average particle size of the crystalline composite powder was calculated by Debye-Scherrer's equation and it was found 87.03 nm, which is in the range of nanoscale.

Figure 1: XRD of ZnO-ZnS composite.

The surface morphology and elemental composition were analyzed by scanning electron microscope (SEM JEOL Japan make, 5610LV model) along with an energy dispersive X-ray (EDAX) spectrophotometer operated at 15 kV. The SEM image of ZnO-ZnS composite is figure 2. It shows that particles have rough surface with irregular size.

EDX technique was used to identify the elemental constituent of ZnO-ZnS composite. It was observed that three elements are present in nanomaterial i.e. Zn, O and S (Table 1).

Figure 2: SEM of ZnO-ZnS composite.

Elements	Weight (%)	Atomic (%)
Zn	67.63	46.41
O	16.39	34.40
S	15.97	19.18

Table 1: Elemental composition.

Photocatalytic degradation

0.1017g of Rose Bengal was dissolved in 100.0 mL of doubly distilled water to prepare 1.0 x 10^{-3}M concentration dye solution. Further, it was used as a stock solution. This stock solution was diluted further on need basis. The absorbance of Rose Bengal solution was monitored at λ_{max} = 550 nm with the help of a spectrophotometer (Systronic model 106). The dye solution was equally divided in four beakers:

- The first beaker containing rose Bengal dye solution was kept in dark.
- The second beaker containing rose Bengal dye solution was exposed to light.
- The third beaker containing rose Bengal dye solution and 0.10g ZnO-ZnS composite was kept in dark.
- The fourth beaker containing rose Bengal dye solution and 0.10g ZnO-ZnS composite was exposed to light.

After 3 - 4 hours, absorbance of solution was determined using a spectrophotometer.

There was no change in the absorption of solutions of first three beakers but the absorbance of fourth beaker solution had a decrease in its initial value. These results suggested that both; the presence of light as well as semiconductor composite is required to initiate this reaction. So, this reaction is photocatalytic in nature and not photochemical or chemical.

0.08g of ZnO-ZnS composite was added in 50 mL dye solution (7.0 x 10^{-6}M) at pH 7.5 to study the photocatalytic degradation of rose Bengal dye. Light intensity was measured using a solarimeter (Suryamapi CEL 201). A 200W tungsten lamp was used for irradiation (60.0 mW cm^{-2} light intensity). Water filter was used to cut off the thermal effect. pH of the dye solutions was measured using a digital pH meter. pH of the dye solutions were adjusted by addition of previously standardized 0.1N sulphuric acid and 0.1N sodium hydroxide solution. Absorbance (A) of the dye solution was measured using UV-Visible spectrometer (Systronic Model 106) at regular time intervals. Controlled experiments were also carried out to confirm that the degradation of rose Bengal by ZnO-ZnS was photocatalytic in nature. A linear line plot of 1 + log A and time shows that rose Bengal dye degradation follows pseudo-first order kinetics.

The following formula was used to calculate the rate constant:

$k = 2.303 \times slope$ ...(1)

Results and Discussion

[Rose Bengal] = 7.0 × 10^{-6} M		pH = 7.5
Amount of composite = 0.08g		Light intensity = 60.0 $mWcm^{-2}$
Time (min.)	Absorbance (A)	1 + log A (ZnO-ZnS)
0	0.527	0.7218
10	0.486	0.6866
20	0.464	0.6665
30	0.438	0.6415
40	0.393	0.5944
50	0.360	0.5563
60	0.337	0.5276
70	0.300	0.4771
80	0.282	0.4502
90	0.265	0.4232
100	0.242	0.3838

Table 2: A typical run.

Rate constant (k) with ZnO = 1.15 x 10^{-4} sec^{-1}.

Rate constant (k) with ZnS = 1.02 x 10^{-4} sec^{-1}.

Rate constant (k) with ZnO-ZnS = 1.53 x 10^{-4} sec^{-1}.

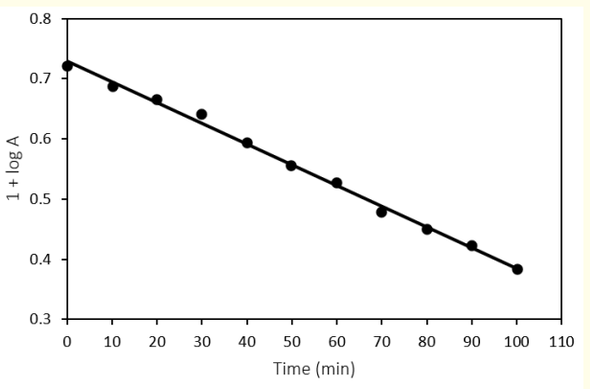

Figure 3: Typical run.

Effect of pH

The rate of degradation is highly influenced by the pH of dye solution. It was found that rate of degradation was increased by

increasing the pH of the solution up to a certain limit. The optimum pH was observed 7.5 for Rose Bengal degradation. The rate of photocatalytic degradation had a decrease on further increasing the pH above this optimum value. It was concluded Rose Bengal (an anionic dye) showed maximum degradation in lower basic pH range.

In basic medium, there is a greater possibility for the generation of hydroxyl radicals (•OH) by the interaction of OH– and hole (h+) of the composite semiconductor, which can act as an oxidant for the degradation of dye. The rate of photocatalytic degradation decreased after certain pH, because extra hydroxyl ions are available at higher pH and these will be adsorbed on the surface of the composite, which makes it negatively charged and the dye does not remain in its form and converted to its neutral form. Rose Bengal in neutral form will not have any force of attraction towards negatively charged surface of the composite due to adsorption of –OH ions, which caused decrease in the rate of degradation. Radicals scavenger test (using isopropanol) confirmed the involvement of •OH radical as an active oxidizing species, where the rate of degradation was completely reduced.

[Rose Bengal] = 7.0 x 10^{-6}M	Light intensity = 60.0 mWcm^{-2}
Amount of composite = 0.08g	
pH	Rate constant (k) × 10^4 (sec^{-1})
6.0	1.15
6.5	1.20
7.0	1.35
7.5	1.53
8.0	1.28
8.5	1.15
9.0	1.09
9.5	0.98
10.0	0.89

Table 3: Effect of pH.

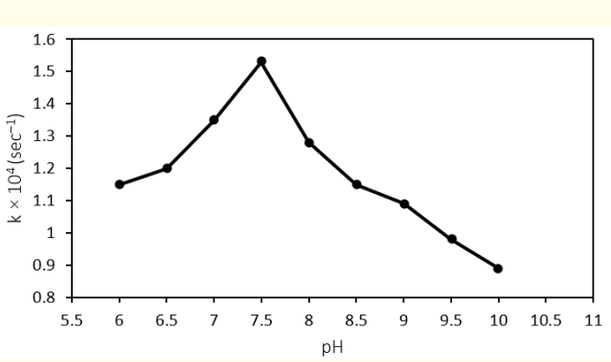

Figure 4: Effect of pH.

Effect of dye concentration

Different concentrations i.e. 0.4 - 1.4 x 10^{-5}M of rose Bengal dye were used to observe its effect on rate of photocatalytic degradation. It was observed that the rate of photocatalytic degradation increases with an increase in dye concentration. It may be explained by the fact that, as the concentration of dye was increased, extra dye molecules were available for excitation and energy transmission and as a result, the rate of photocatalytic degradation increased significantly. It was found that the rate of photocatalytic degradation decreased with an increase in the concentration of dye further. The rate constant was found optimum at 7.0 x 10^{-6}M for rose Bengal This may be attributed to the fact that after certain dye concentration, the dye may start acting as an internal filter itself and hence, it will not allow the required light intensity to reach the surface of the composite. As a consequence, decrease in rate of photocatalytic degradation was observed.

pH = 7.5	Light intensity = 60.0 mWcm^{-2}
Amount of composite = 0.08g	
[Rose Bengal] × 10^5 M	Rate constant (k) × 10^4 (sec^{-1})
0.4	1.31
0.5	1.39
0.6	1.45
0.7	1.53
0.8	1.31
0.9	1.15
1.0	0.81
1.2	0.64
1.4	0.51

Table 4: Effect of dye concentration.

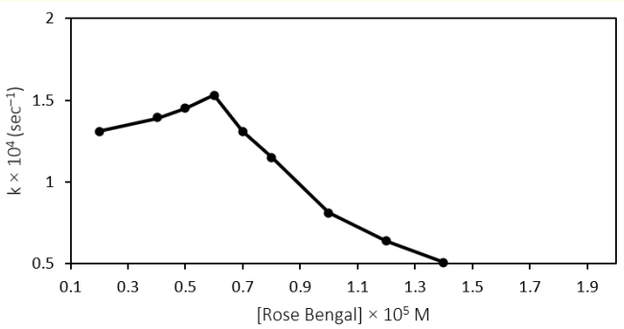

Figure 5: Effect of rose bengal concentration.

Effect of amount of semiconductor (ZnO-ZnS) composite

The effect of amount of semiconductor composite on the photocatalytic degradation of Rose Bengal was investigated by varying the amount of composite in the range of 0.02 to 0.14g. It was found that the rate of reaction had an increase on increasing the amount of composite up to a certain limit, i.e. 0.08g. Beyond this limit, the rate of reaction becomes almost constant. This may be attributed to the fact that as the amount of composite was increased, the exposed surface area of the composite increase; however, after a certain value (0.08g), an increase in the amount of composite will only increase the thickness of layer of the composite and not its ex-

posed surface area. This was confirmed by taking reaction vessels of several sizes. It was noticed that optimum amount was shifted to a higher value for vessels of larger volumes while a reverse trend was observed for vessels of smaller capacities.

[Rose Bengal] = 7.00 x 10^{-6} M	pH = 7.5
Light intensity = 60.0 mWcm^{-2}	
Amount of Composite (g)	Rate constant (k) × 10^4 (sec^{-1})
0.02	0.77
0.04	0.90
0.06	1.27
0.08	1.53
0.10	1.49
0.12	1.49
0.14	1.49

Table 5: Effect of photocatalyst.

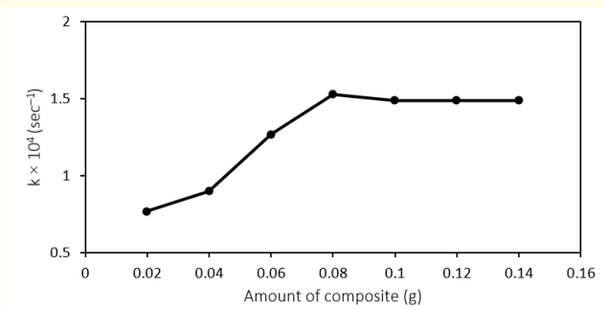

Figure 6: Effect of composite.

Effect of light intensity

The effect of light intensity on the rate of degradation of dye was examined by varying the intensity of light from 20 to 70.0 mWcm^{-2}. The rate of photocatalytic degradation was found to increase on increasing light intensity and maximum rates for Rose Bengal were found at 60 mWcm^{-2}. This can be explained on the basis that as the light intensity was increased, there was an increase in the number of photons striking per unit area per unit time, which leads to higher rate of degradation for both the dyes. Further increase in the light intensity may cause some other reactions so the rate of the reaction slightly decreased and therefore, higher intensities of light have been avoided.

[Rose Bengal] = 7.0 x 10^{-6}M Amount of composite = 0.08g	pH = 7.5
Light intensity (mW cm^{-2})	Rate constant (k) × 10^4 (sec^{-1})
20.0	0.51
30.0	0.81
40.0	0.89
50.0	1.07
60.0	1.53
70.0	1.31

Table 6: Effect of light intensity.

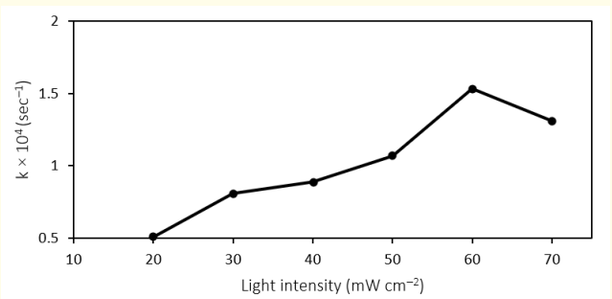

Figure 7: Effect of light intensity.

Mechanism

On the basis of all these observations, a tentative mechanism for degradation of rose Bengal (Dye) is proposed as follows:

$^1Dye_0 \xrightarrow{h\nu} {}^1Dye_1$ (Singlet excited state) .....(2)

$^1Dye_1 \xrightarrow{ISC} {}^3Dye_1$ (Triplet excited state) .....(3)

$SC \xrightarrow{h\nu} e^-$ (CB) + h^+ (VB) .....(4)

$h^+ + OH^- \rightarrow \cdot OH$ .....(5)

$\cdot OH + {}^3Dye_1 \rightarrow$ Leuco Dye .....(6)

Leuco Dye $\rightarrow$ Product .....(7)

Rose Bengal molecules absorb radiation of suitable wavelength and are excited to its first singlet excited state followed by intersystem crossing (ISC) to triplet state. On the other hand, the semiconducting composite also utilized the incident light energy to excite its electron from valence band to conducting band; thus, leaving behind a hole. This hole may abstract an electron from hydroxyl ions to generate •OH radicals. These •OH radicals will then oxidize the dye to its leuco form, which may ultimately degrade to products. The participation of hydroxyl radicals as an active oxidizing species was confirmed by radical scavenger test using isopropanol, where the rate of degradation was drastically reduced.

Conclusion

A comparative study has been carried out between photocatalytic activity of pure ZnO and ZnS and their composite. Rose Bengal dye was used as a model system to compare their photocatalytic performance. The rate constants for photocatalytic degradation of rose Bengal using ZnO, ZnS and ZnO-ZnS were 1.15 x 10^{-4} sec^{-1}, 1.02 x 10^{-4} sec^{-1} and 1.53 x 10^{-4} sec^{-1}, respectively. These results clearly shows that the composite ZnO-ZnS showed better activity as compared to individual ZnO and ZnS. The observation of present work will explore the use of composites in enhancing photocatalytic performance of a photocatalyst.

Bibliography

1. Sin JC., *et al*. "Degrading Endocrine disrupting chemicals from wastewater by photocatalysis: A review". *International Journal of Photoenergy* (2012): 185159.

2. Nakata K and Fujishima A. "TiO_2 photocatalysis: Design and applications". *Journal of Photochemistry and Photobiology C: Photochemistry Review* 13.3 (2012): 169-189.

3. Vilar VJ., *et al*. "Solar photocatalysis of a recalcitrant coloured effluent from a wastewater treatment plant". *Photochemical and Photobiological Sciences* 8.5 (2009): 691-698.

4. Fujishima A., *et al*. "Photosensitized electrolytic oxidation on semiconducting n-type TiO_2 electrode". The *Journal of the Society of Chemical Industry, Japan* 72 (1969): 108-113.

5. Xie H., *et al*. "Photodegradation of benzene by TiO_2 nanoparticles prepared by flame CVD process". *Particuology* 9.1 (2011): 75-79.

6. Ameta A., *et al*. "Photocatalytic degradation of methylene blue by nanosized vanadium doped TiO_2 loaded on zeolite". *International Journal of Chemical Sciences* 13.3 (2015): 1485-1494.

7. Haritha E., *et al*. "Green chemical approach towards the synthesis of SnO2 NPs in argument with photocatalytic degradation of diazo dye and its kinetic studies". *Journal of Photochemistry and Photobiology B: Biology* 162 (2016): 441-447.

8. Goharshadi E., *et al*. "Photocatalytic degradation of reactive black 5 azo dye by zinc sulfide quantum dots prepared by a sonochemical method". *Materials Science in Semiconductor Processing* 16.4 (2013): 1109-1116.

9. Wang X., *et al*. "Large-scale synthesis well-dispersed ZnS microspheres and their photoluminescence, photocatalysis properties". *Material Characterization* 59.12 (2008): 1765-1770.

10. Chen F., *et al*. "Facile synthesis of ZnS nanoparticles and their excellent photocatalytic performance". *Ceramics International* 41.5A (2015): 6645-6652.

11. Chankhanittha T and Nanan S. "Hydrothermal synthesis, characterization and enhanced photocatalytic performance of ZnO toward degradation of organic azo dye". *Material Letters* 226 (2018): 79-82.

12. Raheem RA., *et al*. "Photocatalytic degradation of reactive green dye by using zinc oxide". *Journal of Chemical and Pharmaceutical Sciences* 9.3 (2016): 1134-1138.

13. Shi JW., *et al*. "Low-temperature synthesis of CdS/TiO_2 composite photocatalysts: Influence of synthetic procedure on photocatalytic activity under visible light". *Journal of Molecular Catalysis A: Chemical* 356 (2012): 53-60.

14. Kostova N and Dutkova E. "Mechanochemical synthesis and properties of ZnS/TiO^2 composites". *Bulgarian Chemical Communications* 48 (2016): 161–166.

15. Upadhyay R., *et al*. "Photocatalytic degradation of azure B using Copper Hexacyanoferrate (II) as semiconductor". *International Journal of Chemical Sciences* 11.1 (2013): 331-340.

16. Parveen K and Vyas K. "Photocatalytic degradation of Rose Bengal by Ni-doped titanium dioxide". *Acta Chimica and Pharmaceutica Indica* 6.4 (2016): 135-143.

17. Sharma S., *et al*. "Use of semi-conducting bismuth sulfide as a photocatalyst for degradation of rose Bengal". *Macedonian Journal of Chemistry and Chemical Engineering* 30.2 (2011): 229-234.