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Photocatalytic Degradation of Indigo Carmine over $FeWO_4$-CuS Powder

Lalita Joshi, Jyotsana Panwar, Rakshit Ameta and Dipti Soni*

Department of Chemistry, J. R. N. Rajasthan Vidhyapeeth (Deemed to be University)
Udaipur-313001 (Raj.) **INDIA**
Email: lalitajoshi7007@gmail.com

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ABSTRACT

The photocatalytic degradation of Indigo carmine has been studied in presence of visible light over the $FeWO_4$-CuS powder as a photocatalyst. The photocatalytic activity of $FeWO_4$-CuS composite was observed for photodegradation of Indigo carmine dye under visible light exposure. The as-prepared composite was characterized by techniques such as EDX, FESEM and XRD. The effect of different parameters was evaluated on rate of degradation and optimum conditions were obtained as pH = 10.0, concentration of Indigo carmine = 1.40×10^{-4} M, amount of composite = 0.005 g and light intensity = 60.0 $mWcm^{-2}$. It was observed that this composite has the highest catalytic activity in basic medium. A tentative mechanism for the reaction has been proposed involving hydroxyl radical as an active oxidizing species.

Graphical Abstract:

$$FeWO_4 - CuS + Dye \longrightarrow \text{Photodegraded product}$$

Keywords: Indigo carmine, $FeWO_4$-CuS powder, Advanced oxidation process, Photocatalytic degradation.

INTRODUCTION

Poovaragan *et al.*, [1] synthesized iron tungstate–tungsten trioxide ($FeWO_4$–WO_3) composite nanoparticles via solid state method with different mole ratios (8:2, 6:4, 4:6 and 2:8). They studied photocatalytic degradation of methylene blue from aqueous solution using $FeWO_4$–WO_3 composite nanoparticles as photocatalyst under UV radiation.

Fatima *et al.*, [2] synthesized the as-functionalized cadmium tungstate, f-$CdWO_4$, nanoparticles via green and environmentally benign route using *Brassica rapa* leave extract. The average size of the prepared particles was 54 nm. The f-$CdWO_4$ was used for degradation of toxic bismarck brown R dye from aqueous solution under sun light irradiation. It was reported that the coloured water containing 10 mg L^{-1} concentration of dye could be treated with 1.5 g L^{-1} of f-$CdWO_4$ at optimum conditions. It was revealed that the f-$CdWO_4$ exhibited good photocatalytic degradation activity with 82.70% degradation of bismarck brown R.

A ternary photocatalyst was synthesized by Saher *et al*., [3] by thermal condensation of urea coupled with ferric tungstate ($FeWO_4$). Then it was doped with Ag resulting in visible light sensitive photocatalyst Ag/$FeWO_4$/g-C_3N_4. They used as-prepared Ag/FWO/GCN for degradation of rhodamine B (RhB) dye. It was revealed that composite (Ag/$FeWO_4$/g-C_3N_4) could achieve ~ 98% degradation of RhB dye under optimized conditions such as pH = 8, catalyst dose = 50 mg 100 m L^{-1}, oxidant dose = 9 mM, irradiation time = 120 min and [RhB] = 50 ppm.

The $FeWO_4$ was prepared by Stambouli *et al*., [4] via sol-gel method using sodium tungstate (VI) and iron(II) sulfate as precursors. They used it for photocatalytic degradation of malachite green. The optimal conditions were determined as pH = 3, and [$FeWO_4$] = 0.5 g L^{-1}.

Gao *et al*., [5] fabricated BiOBr/$FeWO_4$ composite photocatalysts via solvothermal method and used for degradation doxycycline in presence of visible light irradiation. It was reported that BiOBr/$FeWO_4$ composite exhibited higher photocatalytic degradation efficiency of doxycycline as compared to BiOBr and $FeWO_4$. The best photocatalytic degradation performance (90%) in 1 h was obtained with BiOBr/$FeWO_4$ (4:1). The $O_2^{\cdot-}$ and holes were responsible for higher photocatalytic activity due to reduced recombination of photogenerated carriers.

El-Hout *et al*., [6] synthesized rGO/CuS nanocomposites by reduction of graphene oxide (GO) and co-precipitation. It was observed that the photocatalytic performance of CuS was increased by loading reduced graphene oxide (rGO). They evaluated photocatalytic performance of the rGO/CuS nanocomposites for degradation of malachite green (MG) dye under sunlight. It was revealed that rGO/CuS-7 composite could achieve the highest efficiency of 97.6% on exposure to sunlight in 90 min. This photocatalyst can be recycled five times without any major loss in the activity.

Gunnagol and Rabinal [7] synthesized titanium dioxide / reduced graphene oxide / copper sulfide (TiO_2/rGO/CuS). They evaluated photocatalytic activity of degradation of rhodamine-B under ultraviolet as well as visible light exposures. It was reported that photocatalytic activity of TiO_2/rGO/CuS was higher than pure TiO_2 or TiO_2/rGO nanocomposites.

Mahanthappa *et al*., [8] synthesized CuS, CdS and CuS-CdS nanocomposite (photocatalysts) through hydrothermal route. The photocatalytic activity of the as-prepared materials was evaluated by the degradation of methylene blue (MB) dye in presence of hydrogen peroxide. It was reported that MB dye (10 ppm) was degraded by about 80, 59 and 99.97% for CuS, CdS and CuS-CdS nanocomposite, respectively in 10 min. The higher activity of that CuS-CdS nanocomposite was attributed to narrow band gap, large surface area, high adsorbing capacity of the dye and reduced recombination of the photo-generated electrons and holes. This as-prepared nanocomposite had good stability as evident for repeated usage.

Cui *et al*., [9] prepared copper-based heterojunction photocatalyst via hydrothermal method. Two copper-based nanostructures (nanodots $CuWO_4$ and nanorods CuS) were used to form a composite. The best performance for the photodegradation of rhodamine B was obtained when their ratio was kept 1:1. Ortiz *et al*., [10] investigated physicochemical degradation of indigo carmine (IC) in aqueous solution. It was reported that color removal with simultaneous TiO_2-UV/Sonolysis and TiO2-UV/O_3 reach could 77 and 96%, respectively.

Güy and Özacar [11] synthesized magnetic $ZnFe_2O_4$, $ZnFe_2O_4$/ZnO, tannin/$ZnFe_2O_4$ and tannin/$ZnFe_2O_4$/ZnO nanocomposites. The photocatalytic efficiencies of as-obtained zinc ferrite samples were evaluated for degradation of indigo carmine in aqueous solution under UV and visible-light. It was found that degradation ratio of indigo carmine was 82 and 99% over the tannin/$ZnFe_2O_4$/ZnO in presence of UV light and visible light in 90 min, respectively. It was also revealed that photocatalytic performance of tannin/$ZnFe_2O_4$/ZnO can reach to 89.79% after five cycles. There are some synergistic interactions between $ZnFe_2O_4$, tannin, which prolonged lifetime of photoexcited carriers resulting in greater absorption in both; UV as well as visible light. Tannin played a decisive role for enhancing the photocatalytic performance of $ZnFe_2O_4$ due to presence of phenolic groups. $ZnFe_2O_4$ makes the Tannin/$ZnFe_2O_4$/ZnO separable in a system easily on using a magnet.

Sakli *et al.*, [12] synthesized bismuth (III) oxide (α Bi_2O_3)/Carbon nanocomposites. They monitored degradation of the indigo carmine in aqueous solution in presence of Bi_2O_3/C nano composites. Sukhadeve *et al.*, [13] prepared TiO_2 nanoparticles doped with Ag via sol-gel method. They evaluated photocatalytic activity of as-prepared samples for degradation of indigo carmine under visible light irradiation. It was revealed that degradation efficiency was increased with increasing Ag concentration.

Prado *et al.*, [14] used Nb_2O_5 for the photodegradation of indigo carmine and compared with degradation by TiO_2 and ZnO. It was observed that almost 100% dye degradation was achieved in 20, 45 and 90 min for TiO_2, ZnO and Nb_2O_5, respectively. TiO_2, ZnO and Nb_2O_5 were recovered after use and applied again. The TiO_2 and ZnO show an abrupt loss in their catalytic activity, but Nb_2O_5 maintained 85% of its catalytic activity even after 10 reaction cycles. Agorku *et al.*, [15] synthesized C,N, S-doped ZrO_2 and a series of Eu doped C,N,S-ZrO_2 photocatalysts through coprecipitation method. They used thiourea as the source of C, N and S while $Eu(NO_3)\cdot 6H_2O$ was used as source of Eu. The particle size of as-prepared ZrO_2 was in the range of 8-30 nm. It was found that highest photocatalytic activity was observed with Eu,C,N,S-doped ZrO_2 (0.6 mol.% Eu).

MATERIALS AND METHODS

Preparation of ferric tungstate: Ferric tungstate was prepared as reported earlier by Joshi *et al.*, [16].

Preparation of composite: Ferric tungstate and copper sulphide were mixed in 1:1 ratio and grinded in mortar and pestle.

Photocatalytic process: The photocatalytic activity of the catalyst was evaluated by measuring the rate of degradation of indigo carmine dye (figure 1). A stock solution of indigo carmine of concentration 1.0 x 10^{-3} M was prepared in doubly distilled water. Working solution of 1.40 x 10^{-4} M solution of indigo carmine was prepared by diluting the stock solution and 0.005 g of $FeWO_4$-CuS powder was added to it. The pH of the reaction mixture was kept 10.0 and then this solution was exposed to a 200 W tungsten lamp. The absorbance of indigo carmine was determined with the help of spectrophotometer (Systonic Model 106) at λ_{max} = 620 nm. A decrease in absorbance of indigo carmine solution was observed with increasing exposure.

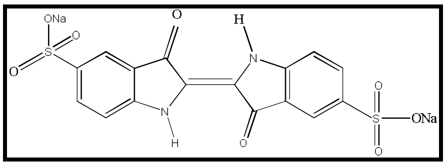

Figure 1. Structure of indigo carmine.

Characterization of Powder

Energy dispersive X-ray (EDX) Analysis: A Thermo Scientific instrument connected to an Energy-dispersive X-ray spectroscopy was used for the confirmation of the elemental composition. The results are presented in figure 2.

It was observed that peaks were there only for Fe, Cu, S, and W, which indicated that the composite contain these elements and there in no other impurities.

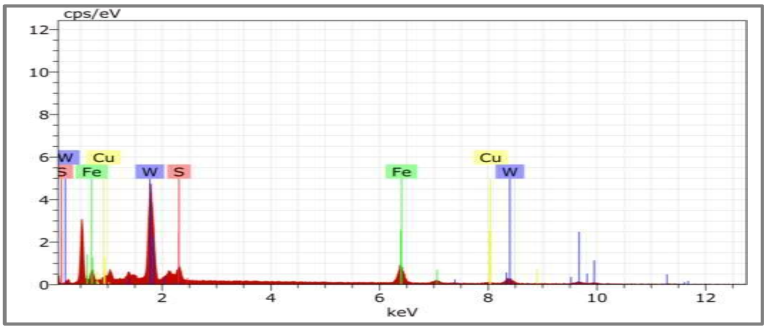

Figure 2. EDX of $FeWO_4$ – CuS composite

X- Ray diffraction (XRD) Analysis: Panalytical's X'Pert Pro. model was used with CuKα radiation (λ = 1.54060 Å) in the scanning ranges from 20° to 80° with a scan at 10^0 min^{-1}. The applied voltage and current were 45 kV and 40 mA, respectively. The powder XRD pattern of as-prepared $FeWO_4$ - CuS composite nanomaterials is given in figure 3.

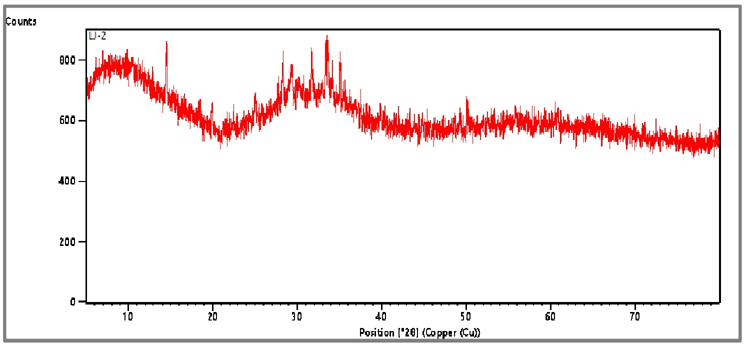

Figure 3. XRD of $FeWO_4$-CuS composite.

The crystallite size (D) was calculated using the Debye-Scherer's formula:

$$D = (k\lambda/\beta \cos \theta). \qquad \dots (1)$$

The average crystalline size of prepared composite was found to be 92.32 nm for $FeWO_4$-CuS composite, which is in order of nanoscale.

Field Emission Scanning Electron microscopy (FESEM) analysis: The field emission scanning electron microscopy analysis (FESEM) was performed using a JSM 6100 (Jerol) instrument. The structure is presented in figure 4.

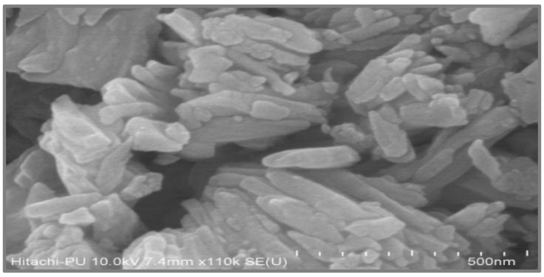

Figure 4. FESEM of $FeWO_4$-CuS composite.

The FESEM analysis of the photocatalyst showed the morphology of $FeWO_4$-CuS nanoparticles (figure 4), which shows the existence of almost rice like crystal structure.

RESULTS AND DISCUSSION

The rate constant was calculated by using the expression:

$$k = 2.303 \times \text{Slope} \qquad \ldots(2)$$

Typical Run: The results of a typical run are presented in table 1 and graphically in figure 5.

Table 1. A Typical Run

pH = 10.0 Amount of composite = 0.005 g,
[Indigo carmine] = 1.40 x 10^{-4} M Light intensity = 60.0 mWcm^{-2}.

Time (min)	Absorbance	1 + log A
0	0.89	0.94
15	0.79	0.89
30	0.70	0.84
45	0.64	0.80
60	0.57	0.75
75	0.48	0.68
90	0.41	0.65
105	0.37	0.60
120	0.35	0.54
135	0.32	0.50

Rate constant (k) = 8.95 x 10^{-5} s^{-1}

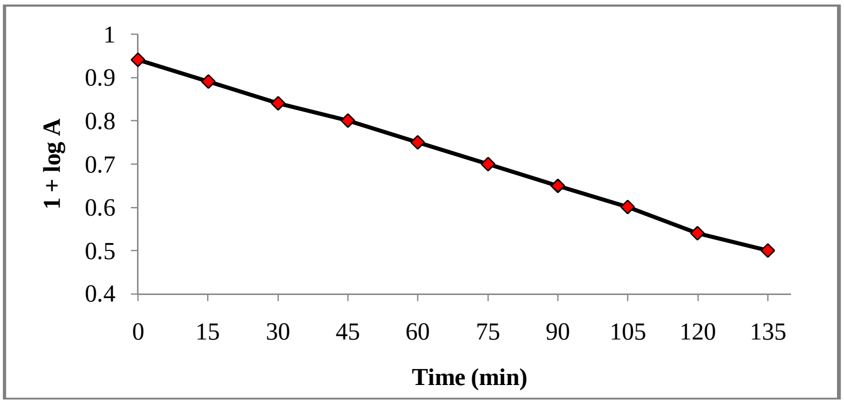

Figure 5. A typical run.

Effect of different parameters

Effect of pH: The effect of variation of pH was studied in the range 5.0-10.5 and the results are represented graphically in figure 6. It was observed that the rate increases with an increase in pH up to 10.0, but the rate of degradation decreases with a further increase in pH. The hole abstracts an electron from hydroxyl ion to generate hydroxyl radical. An increase in the rate of photocatalytic degradation of dye with the increase in pH may be due to the availability of more $^{\bullet}OH$ radicals. A decrease in the rate of photocatalytic degradation of the dye above pH = 10.0 may be due to the fact that indigo carmine is present in its anionic form, which will experience a force of repulsion withthe negatively charged surface of the semiconductor due to absorption of more OH^- ions on the surface of the photocatalyst.

Effect of dye concentration: The effect of dye concentration on the photocatalytic degradation of indigo carmine was observed in the range of 1.0 × 10^{-4} to 1.8 × 10^{-4} M and results are reported in figure 7. As the concentration of the dye was increased, it was observed that the dye degradation increases but after 1.4×10^{-4} M (optimum condition), the photocatalytic degradation showed a declining behaviour. Here, the dye will start acting as an internal filter and it will not allow the desired light intensity to reach the surface of the semiconductor present at the bottom of the reaction vessel.

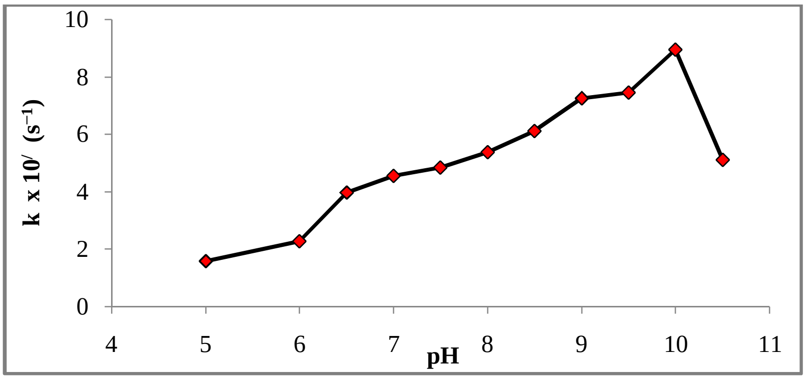

Figure 6. Effect of pH.

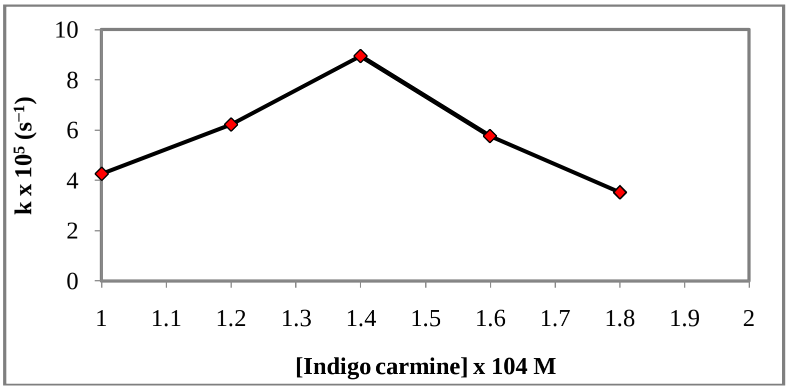

Figure 7. Effect of dye concentration.

Effect of amount of composite: The effect of variation of the amount of catalyst on the rate of dye degradation has been studied in the range from 0.002 to 0.060 g. The results of variation of rate constant with composite are represented in figure 8. It was observed that as the amount of composite was increased, the rate of photocatalytic activity increases. The rate of degradation was optimum at 0.005 g of the composite. Beyond 0.005 g, the rate constant decreases. Because after this value, an increase in the amount of photocatalyst will only increase the thickness of the photocatalyst layer and not the exposed surface area. This was confirmed by taking reaction vessels of different dimensions. This slight decline may be due to the fact that excessive amount of photocatalyst may create hindrance and blocks light penetration.

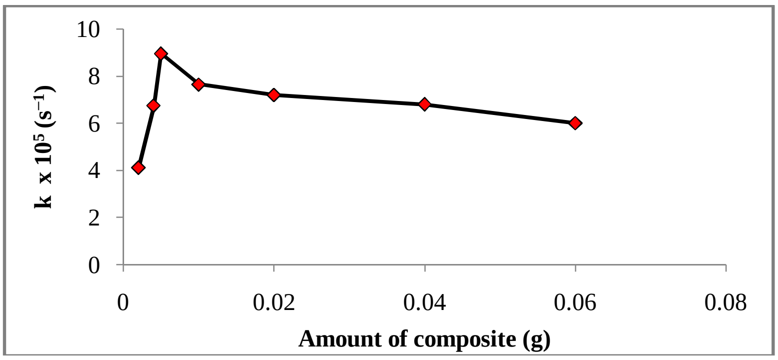

Figure 8. Effect of amount of composite.

Effect of light intensity: The distance between the light source and exposed surface area of photocatalyst was varied from 20.0 to 70.0 mW cm^{-2} to determine the effect of light intensity on the photocatalytic degradation. Rate constants with different light intensity are represented in figure 9. As it is known that number of photons per unit area per unit times increases on increasing light intensity, and therefore rate of reaction also increases up to 60.0 $mWcm^{-2}$. Then it decreases on further increasing the light intensity may be due to thermal reaction.

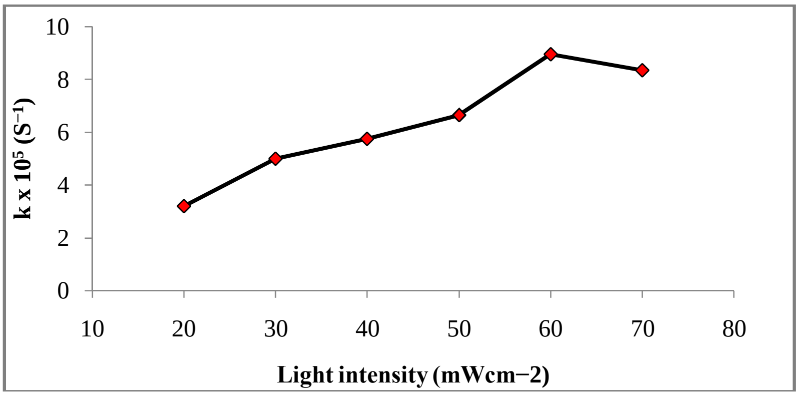

Figure 9. Effect of light intensity.

Mechanism: On the basis of the experimental observations, a tentative mechanism of photocatalytic degradation of indigo carmine in the presence of $FeWO_4$-CuS powder may be proposed as

$$^{1}IC_0 \xrightarrow{h\upsilon} {}^{1}IC_1 \quad \ldots(3)$$

$$^{1}IC_1 \xrightarrow{ISC} {}^{3}IC_1 \quad \ldots(4)$$

$$\text{Composite} \xrightarrow{h\upsilon} h^{+}\ (VB) + e^{-}\ (CB) \quad \ldots(5)$$

In basic medium

$$^{-}OH + h^{+} \rightarrow {}^{\bullet}OH \quad \ldots(6)$$

$$^{3}IC_1 \rightarrow \text{Leuco IC} \quad \ldots(7)$$

$$\text{Leuco IC} \rightarrow \text{Products} \quad \ldots(8)$$

Indigo carmine absorbs radiations of suitable wavelength and it is excited from its ground state to excited singlet state. Then this singlet singlet state undergoes to its triplet excited state through intersystem crossing (ISC). The composite also absorbs light to excite an electron from its valence band (VB) to its conduction band (CB); thus, leaving behind a hole. This hole abstracts an e^{-} from OH^{-} ion forming $^{\bullet}OH$ radical. This $^{\bullet}OH$ radical oxidatively degrade dye to from products via leuco-dye. The participation of hydroxyl radicals as active oxidizing species was confirmed by carrying out this reaction in the presence of $^{\bullet}OH$ radical scavenger, 2-propanol. This shows that $^{\bullet}OH$ radicals were involved in this reaction as an active oxidizing species.

APPLICATION

The composite $FeWO_4$–CuS can be used successfully for the degradation of various organic pollutants, industrial pollutants, pesticides, inorganic compounds, dyes etc.

CONCLUSION

The $FeWO_4$–CuS powder was prepared by mechanochemical methodand used for the photocatalytic degradation of indigo carmine dye. The particle size of prepared composite is 92.32 nm. The effect of different rate affecting parameters such as pH, dye concentration, amount of composite and light intensity was evaluated. It was observed that photocatalytic treatment increased the degradation of pollutants in contaminated water. In present work, powder $FeWO_4$–CuS successfully degraded indigo carmine. It may be further explored for removal of a variety of industrial effluents in future.

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