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PHOTOCATALYTIC DEGRADATION OF NAPHTHOL GREEN B OVER FEWO$_4$-CUS PARTICULATE SYSTEM

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ABSTRACT

The photocatalytic degradation of naphthol green B (NGB) has been studied under visible light in the presence of $FeWO_4$ – CuS composite as a photocatalyst. Ferric tungstate was prepared by hydrothermal method. The photocatalytic activity of $FeWO_4$ - CuS composite was evaluated for photodegradation of naphthol green B dye under visible light. As-prepared composite was characterized by techniques such as XRD, EDX and FESEM. The effect of various parameters was investigated on rate of degradation and optimum conditions were obtained as pH = 9.0, concentration of NGB = 1.9×10^{-4} M, amount of $FeWO_4$ – CuS = 0.10 g and light intensity = 70.0 $mWcm^{-2}$. It was observed that 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 $\xrightarrow{h\upsilon}$ Photodegraded products

KEY WORDS: Photocatalytic degradation, Naphthol green B, $FeWO_4$–CuS composite, Advanced oxidation process.

INTRODUCTION

Organic pollutants in industrial and agricultural sewage are a serious threat to the environment and human health. Achieving continuous photocatalytic degradation of organic pollutants under light and dark conditions would have exciting implications for practical sewage treatment.

Water is the most important component of life support machine. The sources of water pollution are sewage, cultivation discharge, commercial effluents and industrial waste from chemical factories. They produce a major problem of water pollution. Because of water pollution, thousands of children die every day from different water borne diseases such as diarrhea, cholera, typhoid etc. Four common methods of waste water treatment are biological, chemical, physical and sludge treatment.

Iron oxide, tungsten oxide and iron-tungstate oxide nanoparticles (NPs) were synthesized via simple precipitation, acid precipitation, and hydrothermal method, respectively (Narendhran *et al.*, 2020). They used as-synthesized NPs as a photocatalyst for the degradation of methyl orange (MO) in presence of visible irradiation. It was found that $FeWO_4$ NPs were more effective in the degrading MO. It was confirmed that degraded by-products were non-hazardous in nature. The $FeWO_4$/polypyrrole nanocomposite ($FeWO_4$/PPy NC) were prepared by oxidative polymerization of pyrrole (monomer) with $FeWO_4$ NPs (Hussain *et al.*, 2022). Then these were used for the adsorption and photocatalytic degradation of rose Bengal and alizarin red S.

Optimum conditions were determined as irradiation time = 100-120 min, dye concentration =

40mg l^{-1}, photocatalyst = 0.5 g l^{-1} and pH = 6.0. It was reported that as-prepared NCs have good regeneration capacity up to four repetitive cycles, better photodegradation efficiency, and high saturation capacity. Iron tungstate–tungsten trioxide ($FeWO_4$–WO_3) composite nanoparticles using solid state method and different mole ratios (8:2, 6:4, 4:6 and 2:8) was synthesized (Poovaragan *et al.,* 2019). They carried out photocatalytic degradation of methylene blue in aqueous solution in presence of $FeWO_4$–WO_3 composite nanoparticles under ultraviolet radiation.

Nitrogen doped RGO-$FeWO_4$/Fe_3O_4 (NRGO-$FeWO_4$/Fe_3O_4) ternary nanocomposite was synthesized using microwave irradiation (Sadiq *et al.,* 2017). They used ammonium tungstate, iron acetate and graphene oxide as precursors of W, Fe and RGO. They used as-prepared nanocomposite in photodegradation of methylene blue (MB) and reduction of 4-nitrophenol. It was observed that MB was mineralized within 100 min. under visible light irradiation retaining excellent stability and efficiency even after ten cycles. It was interesting to note that the composite also reduced 4-nitrophenol within 45 seconds and catalyst exhibited good catalytic activity even after twenty cycles. The $FeWO_4$/ZnO photocatalyst was prepared via simple co-precipitation method (Buvaneswari *et al.,* 2015). XRD results showed that the average particle size of $FeWO_4$/ZnO was found to be 22.59 nm. As-prepared photocatalyst was composed of rods and plates with little agglomeration. This composite was used as photocatalyst to degrade methylene blue in water under visible light. It was revealed that $FeWO_4$/ZnO photocatalyst can effectively degrade about 96% of MB in 3 h under visible light.

A nanocomposite of reduced graphene oxide/ iron tungstate (rGO/$FeWO_4$) was synthesized via one-step solvothermal strategy (Rani *et al.,* 2016). The morphology of $FeWO_4$ was flower shaped, which was densely covered by rGO sheets. They evaluated catalytic activity of as-prepared nanostructures in degradation of methyl orange in the presence of $NaBH_4$. Copper sulphide nanoparticles (CuS NPs) was synthesized via solvothermal method (Ayodhya *et al.,* 2016). They used xanthan gum as a capping agent. The particle size of the products was calculated to be in the range of 8–20 nm. They used these NPs for degradation of some organic dyes (rhodamine B, methylene blue, Congo red and eosin Y) under solar, visible and UV lights.

The effect of adsorption was observed on methylene blue degradation using pectin–CuS nanocomposite (PCSNC) (Gupta *et al.,* 2012). They observed adsorption and photocatalytic activity of PCSNC and compared with copper sulphide nanoparticle (CSNP). It was revealed that simultaneous adsorption and photodegradation process was a most efficient process for fast degradation of adsorbed methylene blue molecules. The complete COD removal could be achieved in 10 h using PCSNC/A + P. The crosslinked gelatin/ CuS/PVA nanocomposite was prepared using gamma irradiation as initiator (Al-Kahtani, 2017). They used this nanocomposite for degradation of rhodamine B (RhB) (model contaminant) under solar light irradiation. It was revealed that this catalyst can be repeatedly used for five times retaining its efficiency with rate of the degradation process > 80%. The rGO/CuS nanocomposites were synthesized via co-precipitation technique (El-Hout *et al.,* 2020). It was observed that photocatalytic performance of CuS was increased by loading reduced graphene oxide (rGO). They evaluated photocatalytic performance of rGO/CuS nanocomposites for removal of malachite green (MG) under direct sunlight. It was revealed that the (rGO/CuS-7) composite exhibited the highest efficiency (97.6%) for degrading MG in sunlight for 90 min and this photocatalyst could also be recycled for five times without any significant loss in its activity. Titanium dioxide/ reduced graphene oxide/copper sulfide (TiO_2/rGO/CuS) composite was synthesized (Gunnagol and Rabinal, 2019). They observed its photocatalytic activity in degradation of rhodamine-B under ultraviolet as well as visible light exposures. It was reported that photocatalytic activity was enhanced is case of TiO_2/ rGO/CuS as compared to pure TiO_2 or TiO_2/rGO nanocomposites. This increase was attributed to wide range of optical absorption of CuS and also to efficient charge transport and charge separation.

A novel g-C_3N_4/CuS p-n heterostructured photocatalyst was fabricated and it was observed that CuS nanoparticles were closely anchored on g-C_3N_4 surface with good dispersion (Cai *et al.,* 2017). It was also observed that g-C_3N_4/CuS heterojunctions exhibited better photocatalytic performance in degradation of rhodamine B and methylene blue as compared to pure g-C_3N_4 and CuS. It was revealed that degradation of these dyes with g-C_3N_4/CuS_{-2} photocatalyst were 8.914 and 13.543 times higher in comparison to pure g-C_3N_4,

and 3.023 and 6.373 times higher than that of pure CuS, in case of rhodamine B and methylene blue, respectively. The CuS/g-C_3N_4 composite catalysts (CuS nanoparticles anchored on g-C_3N_4 sheets) were fabricated via solvothermal approach (Ma *et al.*, 2019). It was reported that the as-fabricated CuS/g-C_3N_4 catalysts exhibited higher photocatalytic degradation in using CuS/g-C_3N_4 under visible light. Ag-AC (activated carbon) composite was synthesized and used for photocatalytic removal of napthol green B in presence of solar irradiation (Devi and Ahmaruzzaman, 2017). These AgNPs and activated carbon were synthesized using *Coccinia grandis* peel extract, and waste biomass material (saw dust), respectively. It was observed that Ag-AC composite exhibited better catalytic activity as compared to pure AgNPs. It was reported that only 40% of dye was adsorbed within 1 h but 97% of dye was degraded during photodegrdation within 1 h.

A nanocomposite CdS-$ZnWO_4$ was synthesized via hydrothermal method (Jayamani and Shanthi, 2020). They observed degradation of naphthol green B (NGB) in aqueous solution using CdS-$ZnWO_4$ as photocatalyst under UV-A light. It was found that as-prepared CdS-$ZnWO_4$ was more efficient in degrading NGB at pH 9 as compared to other photocatalysts. The CdS-$ZnMoO_4$ (36.6 wt%) coupled nanophotocatalyst was synthesized via hydrothermal method (Swaminathan and Shanthi, 2021). It was reported that CdS-$ZnMoO_4$ catalyst exhibited higher photocatalytic activity of naphthol green B in presence of UV-A light (365 nm). Higher activity of CdS-$ZnMoO_4$ was attributed to higher surface area (18.5 m^2g^{-1}), which was only 10.8 m^2g^{-1} in case of $ZnMoO_4$. Polypyrrole/Attapulgite-supported nanoscale zero-valent iron (PPy/APT-nZVI) composites were fabricated via chemical oxidative polymerization and liquid-phase reduction method (Chen *et al.*, 2019). It was reported that PPy/APT-nZVI (1:0.5) could achieve 99.59% degradation of NGB after 25 min.

MATERIALS AND METHOD

Synthesis of ferric tungstate

Solution A was prepared by dissolving 70 g of ferrous ammonium sulphate in minimum amount of doubly distilled water. The 20 g urea was added with a few drops of dil. H_2SO_4 in this solution and the volume was made up to 1000 mL with doubly distilled water. Solution B was prepared by dissolving 18 g of sodium tungstate in minimum amount of doubly distilled water. The 20 mL of hydrogen peroxide was added in this solution and the volume was made up to1000 mL with doubly distilled water. Solutions A and B were then mixed and stirrered on a magnetic stirrer for 1 h at 60^0 C. The product obtained was washed with hot water 6-8 times until the sulphate impurities were completely removed. The product was filtered and dried in an oven at 100 ^{0}C for 8-11 h. Ferric tungstate was obtained in the form of brownish black crystalline form.

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 naphthol green B dye (Fig. 1). A stock solution of dye (1.0 x 10^{-3} M) was prepared by dissolving 0.087 g of dye in 100 ml doubly distilled water. pH of the dye solution was measured by a digital pH meter (Systronics model 335), and the desired pH of the solution was adjusted by the addition of standard 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. The reaction mixture containing 0.10 g composite was exposed to a 200 W tungsten lamp, and about 3 ml aliquot was taken out every 20 min. Absorbance (A) was measured at λmax = 680 nm. A water filter was used to cut off thermal radiations. The intensity of light was varied by changing the distance between the light source and reaction mixture, and it was measured by Suryamapi (CEL model SM, 201). The absorbance of the solution at various time intervals was measured with the help of spectrophotometer (Systronics Model, 106). It was observed that the absorbance of the solution decreases with increasing time of exposure, which indicates that the concentration of naphthol green B dye decreases with increasing time.

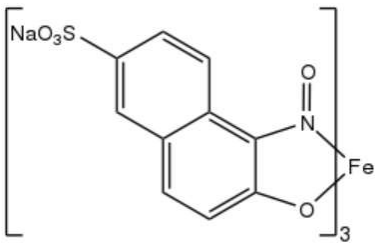

Fig. 1. Structure of naphthol green B

Characterization of Composite

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 Fig. 2.

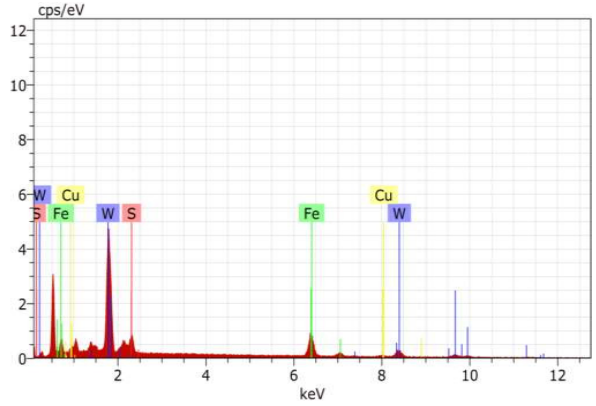

Fig. 2. EDX of $FeWO_4$ – CuS composite

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

X – Ray diffraction (XRD) Analysis

Panalytical's X'Pert Pro. model using CuKá radiation ($\lambda = 1.54060\ A^0$) in the scanning range from 20^0 to 80^0 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 Fig. 3.

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

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

Where:

D = Crystalline size, where D is the size of the particle, K = Scherer's constant (K = 0.94),

λ is the X-ray wavelength (1.54060Å), and

β is full width at half maximum (FWHM) of the diffraction peak.

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 Fig. 4.

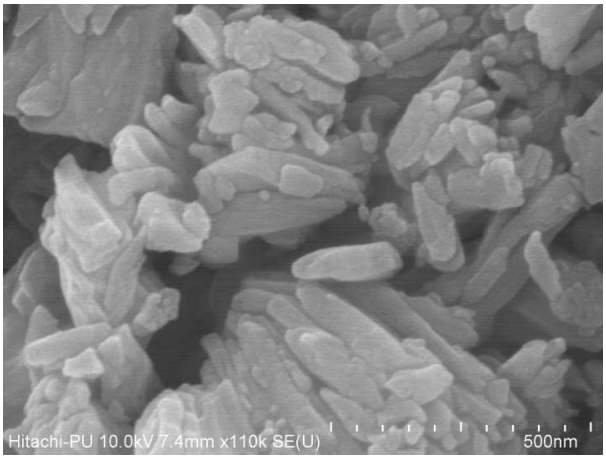

Fig. 4. FESEM of $FeWO_4$-CuS composite

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

RESULTS AND DISCUSSION

The rate constant was calculated by using the expression:

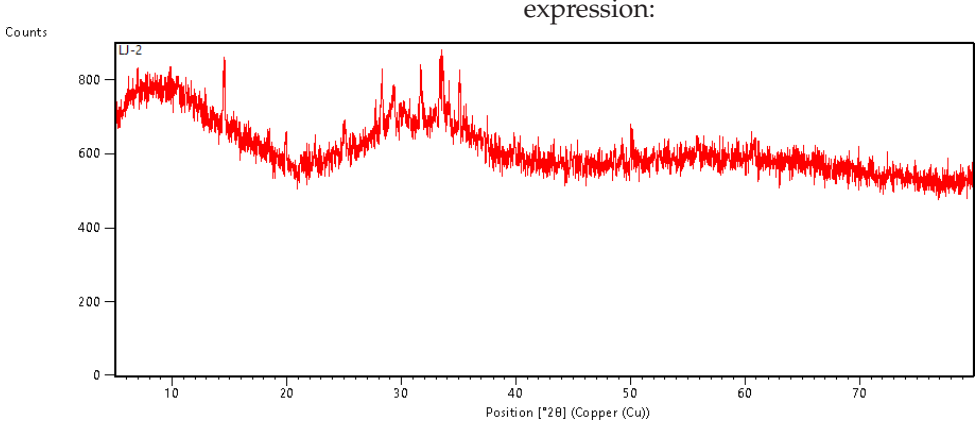

Fig. 3. XRD of $FeWO_4$-CuS composite

$$k = 2.303 \times \text{Slope} \quad .. (2)$$

Typical Run

The results of a typical run are presented in Table 1 and graphically in Fig. 5

Table 1. A typical run

pH = 9.0 Amount of composite = 0.10 g,
[Naphthol Green B] = 1.90×10^{-4} M Light intensity = 70 $mWcm^{-2}$.

Time (min)	Absorption	1 + log A
0	1.13	1.05
20	1.06	1.02
40	0.96	0.98
60	0.73	0.86
80	0.55	0.74
100	0.38	0.57
120	0.26	0.41
140	0.18	0.25
160	0.13	0.11
180	0.10	0.00

Rate constant (k) = 2.68×10^{-4} s^{-1}

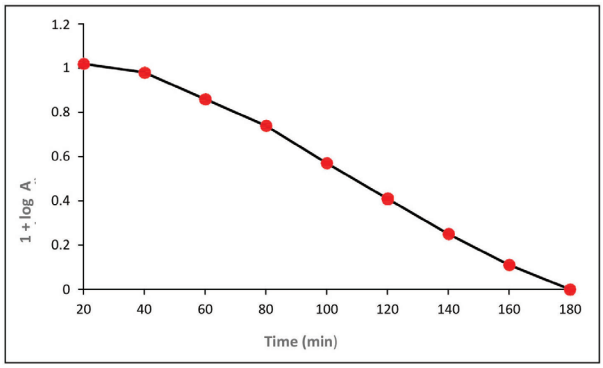

Fig. 5. A typical run

Effect of pH

The effect of variation of pH was studied in the range 4.0-9.5 and the results are represented in Fig. 6.

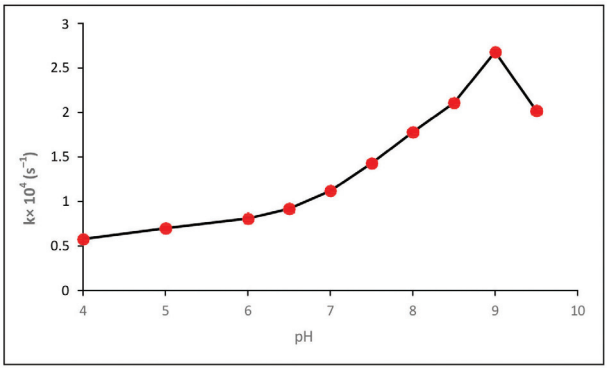

Fig. 6. Effect of pH

It was observed that the rate increases with an increase in pH up to 9.0, 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 •OH radicals. A decrease in the rate of photocatalytic degradation of the dye above pH = 9.0 may be due to the fact that naphthol green B is present in its anionic form, which will experience a force of repulsion with the 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 naphthol green B was observed in the range of 0.8×10^{-4} to 2.0×10^{-4} M and results are reported in Fig. 7.

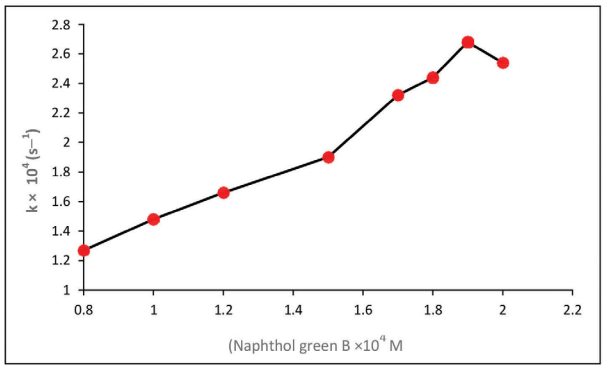

Fig. 7. Effect of dye concentration

As the concentration of the dye was increased, it was observed that the dye degradation increases but after 1.9×10^{-4} M (optimum condition), 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.

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 0.02 to 0.12 g. The results of variation of rate constant with composite are represented in Fig. 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

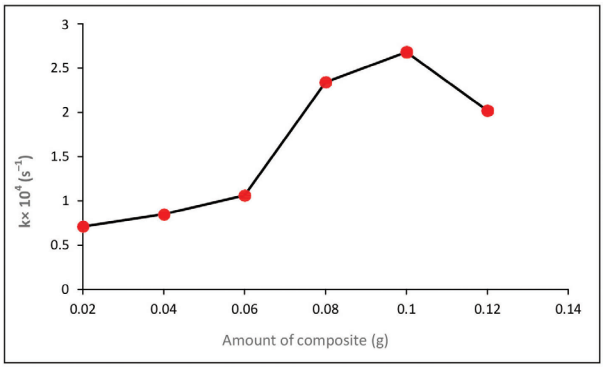

Fig. 8. Effect of Amount of composite

0.10 g of the composite. Beyond 0.10 g, the rate constant decreases slightly 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.

Effect of light intensity

The effect of light intensity on the photocatalytic degradation was observed by changing the distance between the light source and exposed surface area of photocatalyst in the range of 20.0 to 70.0 mW cm^{-2}. The results are reported in Fig. 9.

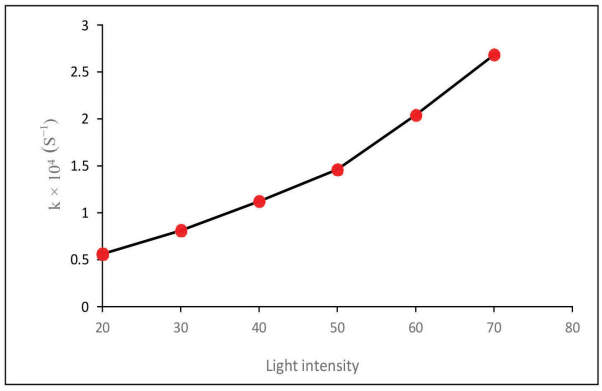

Fig. 9. Effect of light intensity

It was observed that photocatalytic degradation of naphthol green B was more on increasing the intensity of light as the number of photons striking per unit area of photocatalyst surface per unit time will also increase. The maximum rate was observed at 70.0 mW cm^{-2} for degradation of naphthol green B.

MECHANISM

On the basis of the experimental observations, a tentative mechanism has been proposed for the degradation of naphthol green B in the presence of $FeWO_4$ - CuS composite. Naphthol green B absorbs radiations of suitable wavelength and transformed to singlet excited state and then 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). The h^+ in valence band will abstract an electron from OH^- ions to produced $^{\bullet}OH$ radicals. These radicals can degrade dye to its leuco form and ultimately to products.

$$^1NGB_0 \xrightarrow{h\upsilon} {}^1NGB_1 \quad .. (3)$$

$$^1NGB_1 \xrightarrow{ISC} {}^3NGB_1 \quad .. (4)$$

$$SC \xrightarrow{h\upsilon} SC\ h^+ (VB) + e^- (CB) \quad .. (5)$$

In basic medium

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

$$^3NGB_1 + {}^{\bullet}OH \rightarrow \text{Leuco NGB} \quad .. (7)$$

$$\text{Leuco NGB} \rightarrow \text{Products} \quad .. (8)$$

It was found that the reaction rate of degradation was reduced 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.

CONCLUSION

$FeWO_4$–CuS composite was prepared by mechanochemical method and used for the photocatalytic degradation of naphthol green B dye. The particle size of as-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 composite $FeWO_4$–CuS successfully degraded naphthol green B. It may be further explored for removal of a variety of industrial effluents in future.

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