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PHOTOCATALYTIC DEGRADATION OF CONGO RED USING BISMUTH VANADATE-NICKEL SULPHIDE COMPOSITE

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ABSTRACT
A composite of $BiVO_4$-NiS was synthesized and used as a photocatalyst for the photocatalytic degradation of Congo red dye. $BiVO_4$ and NiS were mixed in a 1:1 ratio. The composite was characterized on the basis of XRD, EDX, and FESEM data. The progress of photocatalytic degradation was monitored with a spectrophotometer. The effects of different parameters such as pH, dye concentration, amount of composite and light intensity on the degradation rate were investigated. The composite exhibited the highest catalytic activity in a neutral medium. It was found that higher activity, more stable nature, and recyclability of $BiVO_4$-NiS composite were beneficial for the photodegradation of Congo red dye.
Keywords: Photocatalytic Degradation, Congo Red, XRD, EDX, FESEM, $BiVO_4$-NiS Composite.
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INTRODUCTION

Textile, dyeing, and printing industries are responsible for pollution problems worldwide. About 17-20% of industrial water pollution is caused by the accidental discharge of contaminated wastewater into surrounding water sources. It is a large environmental challenge and now there is a demand for environmentally-friendly techniques to remove toxic dyes from industrial and municipal wastewaters. Advanced oxidation processes (AOPs) provide alternate ways for the treatment of polluted water by green chemical pathways. Photocatalysis is one such AOP, which can degrade some toxic dyes into smaller harmless products. Various photocatalysts as such or in some modified forms are utilized for this purpose. Li *et al.*[1] constructed a highly efficient p-n heterostructure photocatalyst, NiS/$BiVO_4$ (NiS/BVO), and applied it for photodegradation of anionic dye while Zhang *et al.*[2] synthesized ternary $BiVO_4$/NiS/Au nanocomposite, which exhibited significant results in organic pollutant degradation as compared to pure $BiVO_4$ or binary composites ($BiVO_4$/NiS or $BiVO_4$/Au). Zheng *et al.*[3] prepared $BiVO_4$-modified hexagonal h-MoO_3 ($BiVO_4$/MoO_3) composites for the photocatalytic degradation of tetracycline hydrochloride (TCH) whereas Prabhavathy and Arivuoli[4] synthesized $BiVO_4$ photocatalyst co-doped with silver and lanthanum and used for the photocatalytic degradation of xylenol orange and rhodamine B. Hemmatpour *et al.*[5] reported the synthesis of coupled CdS/$BiVO_4$ catalyst via mechanical mixing of CdS and $BiVO_4$ NPs. Zhao *et al.*[6] prepared ternary magnetic photocatalyst $BiVO_4$/Fe_3O_4/reduced graphene oxide ($BiVO_4$/Fe_3O_4/rGO) and used for degradation of rhodamine B. Bashir *et al.*[7] synthesized reduced graphene oxide-based gadolinium-doped bismuth vanadate (rGO/Gd/$BiVO_4$) composite and used for photodegradation of methylene blue dye under visible light irradiation. Xu *et al.*[8] prepared Z-scheme photocatalyst $BiVO_4$/protonated g-C_3N_4/AgI and used it for the degradation of rhodamine B. Omrani and Nezamzadeh - Ejhieh[9] synthesized ternary Cu_2O-$BiVO_4$-WO_3 nano-composite and evaluated catalytic activity in the photodegradation of sulfasalazine (SSZ).

Ali *et al.*[10] prepared a cobalt ferrite catalyst and used it for the degradation of Congo red from an aqueous solution. Taghavi *et al.*[11] synthesized $ZnMn_2O_4$ spinel nanoparticles and it was observed that $ZnMn_2O_4$ NPs displayed high photocatalytic activity for the degradation of Congo red dye. Ma *et al.*[12] prepared a SnO_2 photocatalyst and used it for the photocatalytic degradation of Congo red dye. Panwar *et al.*[13] studied the photocatalytic degradation of amaranth dye using a bismuth vanadate-nickel sulfide composite.

EXPERIMENTAL

Synthesis of Bismuth Vanadate

Bismuth vanadate powder was synthesized by using chemical precipitation method. 0.1 M ammonium metavanadate solution was mixed with 0.1 M bismuth nitrate pentahydrate. It was stirred continuously until a yellow solution was obtained. This solution was titrated with ammonium hydrogen carbonate to induce the precipitation. The precipitate formed was filtered and then washed several times with doubly distilled water. Then, it was dried in a hot air oven at 60℃ overnight. It was ground and then followed by calcination in airflow at 450℃ for 4 h to obtain a yellow crystalline powder of bismuth vanadate.

Composite Preparation

$BiVO_4$ and NiS were mixed in 1:1 proportion and ground in a motor with a pestle.

Congo Red Dye

Congo red is an azo dye. It is a sodium salt of 3,3′-([1,1′-biphenyl]-4,4′-diyl)bis(4-aminonaphthalene-1-sulfonic acid) (Fig.-1). Congo red is soluble in water and its solubility is more in organic solvents. It gives a red colloidal solution.

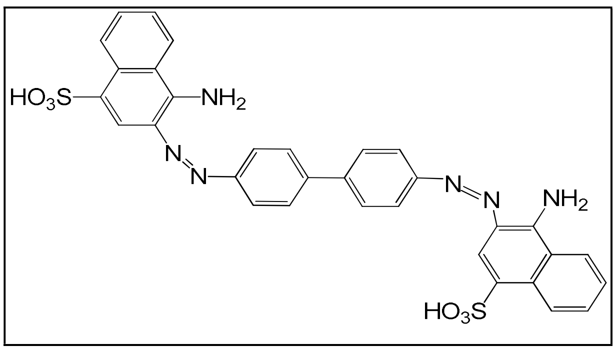

Fig.-1: Structure of Congo Red

Characterization of Composite

Energy Dispersive X-ray (EDX) Analysis

The sample is irradiated with an electron beam and X-ray emissions are measured from the sample to determine its elemental makeup. EDX was obtained on the interaction between the X-ray excitation source and the sample. The results are shown in Fig.-2 and reported in Table-1, respectively.

Table-1: EDX of $BiVO_4$-NiS Composite

Element	Norm. C (wt. %)	Atom. C (at. %)
Bismuth	78.96	47.62
Vanadium	20.73	51.29
Sulfur	0.24	0.93
Nickel	0.08	0.16
Total	100.00	100.00

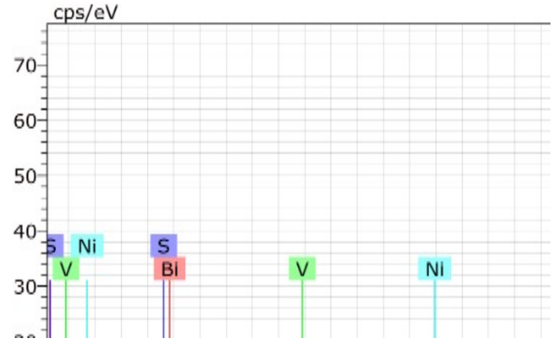

Fig.-2: EDX of $BiVO_4$-NiS Composite

X-Ray Diffraction (XRD)

X-ray diffraction is a technique to assess crystalline structure. The X-ray diffractometer system XPERT-PRO was used with CuK radiation (x = 1.54060 Å) in the 2 scanning range from 20 to 80 with a scan rate of 10 min^{-1} to measure the crystal size of the composite. 45 kV and 40 mA were the applied voltage and current, respectively. Figure-3 displays the $BiVO_4$-NiS powder XRD pattern.

The Debye-Scherer's formula was used (D) for crystal size:

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

Where D = Particle size, K = Scherer's constant (K = 0.94), λ = X-ray wavelength (1.54060) Å, β = Diffraction peak's full width at half maximum (FWHM), and θ is Bragg's angle. The crystalline size for the $BiVO_4$-NiS composite was calculated to be 25.32 nm, which is in the nanoscale range.

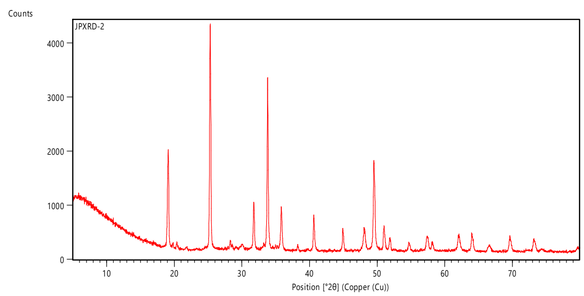

Fig.-3: XRD of $BiVO_4$-NiS Composite

Field Emission Scanning Electron Microscopy (FESEM)

The FESEM examination of $BiVO_4$-NiS composite revealed the morphology of the nanoparticles (Fig.-4), which revealed the presence of crystal structures that resembled almost real flowers (nanoflowers).

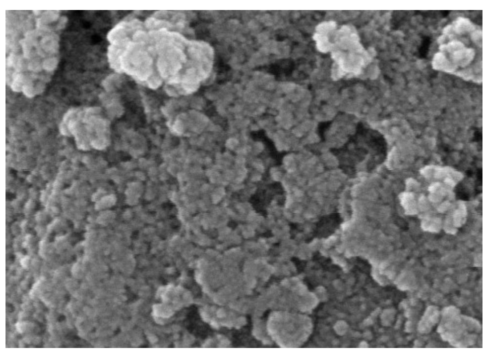

Fig.-4: FESEM of $BiVO_4$-NiS Composite

RESULTS AND DISCUSSION

The following formula was used to determine the rate constant -

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

Photocatalytic process: The rate at which Congo red dye was degraded indicated the photocatalytic activity of the composite. The 0.0696 g of dye was dissolved in 100 mL of doubly distilled water to prepare a stock solution of the dye (1.0 x 10^{-3} M). A digital pH meter (Systronics Model 335) was used to measure pH, and it was kept constant at 7.0. A 200 W tungsten lamp with an intensity of 70.0 mW cm^{-2} was used to illuminate the reaction mixture having 0.10 g of composite. The λ_{max} = 490 nm was used to determine absorbance (A). The intensity of light was used by adjusting the distance between the vessel and the light source. A spectrophotometer (Systronics Model 106) was used to observe the absorbance of the solution at different time intervals. It was noticed that the absorbance of the solution was decreased with increasing exposure time (Fig.-5), indicating the decrease in Congo red dye's concentration.

[Congo red] = 1.90×10^{-4} M pH = 7.0

$BiVO_4$- NiS composite = 0.10 g Light Intensity = 70.0 $mWcm^{-2}$

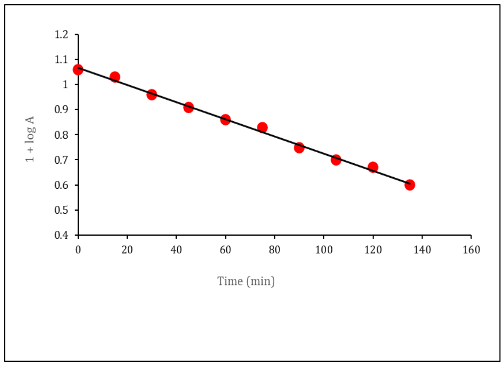

Fig.-5: A Typical Run

Rate constant (k) = 1.30×10^{-4} (s^{-1})

Effect of pH

The impact of pH on photocatalytic degradation was examined in the pH range of 5.5 to 9.0. The finding is presented in Fig.-6.

[Congo red] = 1.90×10^{-4} M

Light Intensity = 70.0 $mWcm^{-2}$

$BiVO_4$-NiS Composite = 0.10 g

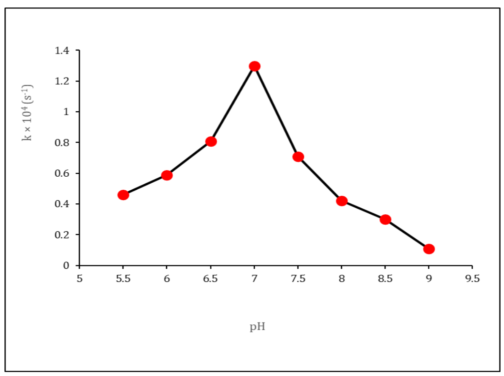

Fig.-6: Effect of pH

It is evident from the observations that the maximum rate of photodegradation of Congo red was obtained at pH 7.0. The anionic dye molecules start converting into neutral form, when pH was decreased below 7.0, so the rate constant decreases accordingly because of repulsion between cationic dye and the positively charged surface of the composite due to the adsorption of H^+ ions. On the other hand, when pH was increased above 7.0, Congo red (anionic form) experienced a force of repulsion with the negatively charged surface of the semiconductor due to the adsorption of more OH^- ions on the surface of the composite, and as a result again rate constant decreased at higher pH.

Effect of dye concentration

The effect of dye concentration on the degradation rate was also investigated using various concentrations of Congo red dye solution. The results are given in Fig.-7.

pH = 7.0 Light Intensity = 70.0 $mWcm^{-2}$

$BiVO_4$-NiS Composite = 0.10 g

The results revealed that as the concentration of the Congo red dye was increased above 1.20×10^{-4} M, reaction rate increased and the optimum rate of photodegradation was obtained at 1.90×10^{-4} M. It may be due to the reason that as the dye concentration was increased, there are more dye molecules present for excitation and subsequent breakdown. As a result, the rate was increased. When dye concentration was further increased above 1.90×10^{-4} M, the rate of photocatalytic degradation was reduced. This could be explained on the basis that now dye acts as a light filter, preventing the desired light intensity from reaching the photocatalyst surface, resulting in a decrease in photocatalytic degradation rate.

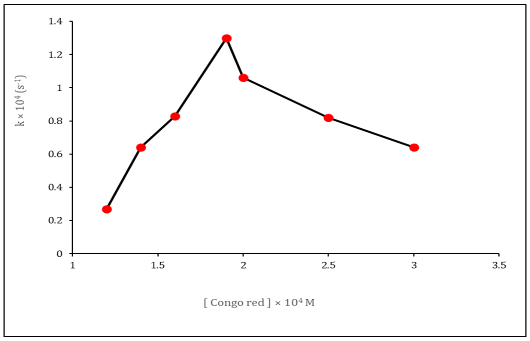

Fig.-7: Effect of Dye Concentration

Effect of Amount of Composite

The amount of photocatalyst also affects the degradation of Congo red and hence, it was varied from 0.02 to 0.16 g to observe its impact. Figure-8 presents the findings.

[Congo red] = 1.90×10^{-4} M pH = 7.0
Light Intensity = 70.0 $mWcm^{-2}$

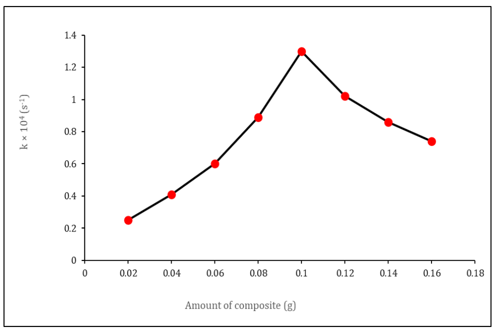

Fig.-8: Effect of Amount of Composite

It was observed that as the amount of composite was increased from 0.02 to 0.10 g, the rate was also increased but on further increasing the amount of composite, the rate was decreased. This could be explained due to the fact that on increasing the amount of photocatalyst, the exposed surface area of the composite also increases, which increases the rate; however, once this limiting value of 0.10 g was reached, an increase in the amount of composite further will only increase the thickness of the composite layer, not the exposed surface area. This will make recombination of e^- and h^+, easier as layers are quite close. Thus, the rate of degradation decreases.

Effect of Light Intensity

The effect of light intensity on Congo red degradation was also studied. Figure-9 represents the experimental findings.

[Congo red] = 1.90×10^{-4} M pH = 7.0
$BiVO_4$-NiS Composite = 0.10 g

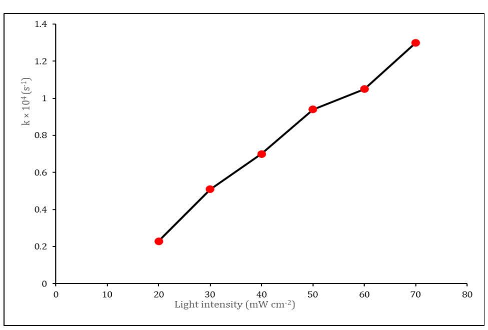

Fig.-9: Effect of Light Intensity

The relationship between light intensity and reaction rate was found to be almost linear. The data revealed that the degrading action was accelerated as the light intensity was increased since an increase in light intensity increases the number of photons striking per unit area of composite per unit time.

Tentative Mechanism

Based on experimental findings, the following mechanism may be suggested as a possible process for the photocatalytic degradation of Congo red:

$$^1CR_0 \xrightarrow{hv} {^1CR_1} \quad (3)$$
$$^1CR_1 \xrightarrow{ISC} {^3CR_1} \quad (4)$$
$$BiVO_4/NiS \rightarrow BiVO_4/NiS^* \quad [h^+(VB)+e^-(CB)] \quad (5)$$
$$O_2 + e^- \rightarrow O_2^{\bullet -} \quad (6)$$
$$^3CR_1 + O_2^{\bullet -} \rightarrow \text{Products} \quad (7)$$

When the dye solution with $BiVO_4$-NiS composite was exposed to light, the dye molecules were excited to the first excited singlet state. The excited molecules were subsequently moved to the triplet state via intersystem crossing (ISC). On the other hand, the $BiVO_4$-NiS composite absorbs photons, resulting in the formation of electron-hole pairs. Dissolved oxygen will use electrons from the conduction band to generate $O_2^{\bullet -}$ anion radicals. The colored dye molecules will be degraded into colorless byproducts by these radicals. It was observed that $^{\bullet}OH$ radicals did not participate as active oxidizing species because the rate was unaffected by the addition of 2-propanol, which is the specific scavenger of the hydroxyl radical.

CONCLUSION

The effluent of textile and dyeing industries is a big challenge for the environment, if not treated before discharge in nearby water resources. Complete degradation of dye molecules is more important rather than its adsorption or bleaching. In the present investigation, the composite of $BiVO_4$-NiS has been successfully used in the degradation of Congo red dye.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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