



Composite of Titanium Dioxide and Nickel Vanadate Application and Its Effect on Photocatalytic Degradation of Azure A Dye

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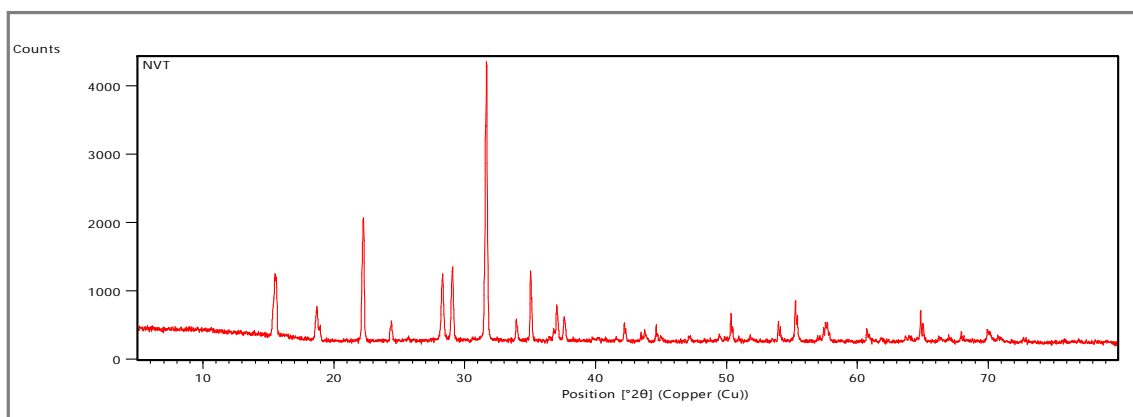
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ABSTRACT

Different dyes have been extracted from their aqueous solutions using a variety of photo catalysts. A combination of titanium oxide and nickel vanadate was utilized as a photo catalyst for dye degradation. The effects of many factors, including pH of the dye solution, dye concentration, quantity of semiconductor, and light intensity, were investigated. There has been some discussion on a potential mechanism for the photocatalytic breakdown of dye in which the hydroxyl radical has been seen to be an active oxidizing species.

Graphical Abstract:



XRD of Nickle vanadate and Titanium Dioxide.

Keywords: Photo catalysis, Degradation, Nickel vanadate, Azure A Dye.

INTRODUCTION

Water contamination is a serious problem in the contemporary world, with several causes. The main source of water contamination is dyes, which are used in the textile, paper, culinary, and other sectors. The environment has been severely degraded and polluted as a result of human activities, including

industrialization and agricultural practises, which in turn has a negative impact on water bodies, which are essential for life. Several metal oxide semiconductors, including TiO₂, ZnO, WO₃, and SnO₂, have been investigated and used as photo catalysts. TiO₂ is regarded as the most efficacious photosensitizer due to its wide availability, low cost, and chemical stability. Recent studies, however, have demonstrated that ZnO may be utilised as a more effective photocatalyst than TiO₂ [1, 2].

Attia [3] reported the photocatalytic oxidation of iodide ion in an aqueous solution of zinc oxide and its sensitization with riboflavin, whereas Habibi and Askari [4] degraded anazo textile dye using a Mn-doped ZnO nanocomposite thin film deposited on glass using a simple spin-coating process.

Using Bi₂O₃ and Bi₂S₃, Sharma *et al.* [5]. Photocatalytically destroyed azure B dye. The impact of several factors, including pH, dye concentration, semiconductor quantity, and light intensity and so forth, were noted and spoken about. The absorbance was measured to identify the photochemical oxidation process. Experimental research was used to find the ideal reaction conditions. Pseudo-first order kinetics controls dye photochemical oxidation. The breakdown products and a potential mechanism for dye photochemical oxidation were outlined.

The photocatalytic degradation of Crystal Violet, a triphenyl methane dye (also known as Basic Violet 3), in aqueous solutions was recommended to be examined using Ag⁺ doped TiO₂ under 27 UV and simulated solar light by Sahoo *et al.*, [6]. Untreated TiO₂ and TiO₂ doped with Ag⁺ were both used to compare the degradation of dyes. Ag⁺ doped TiO₂ was discovered to be marginally more effective. Alkaim *et al.*, [7] research focused on titanium dioxide (TiO₂) particles doped with 0.5% Pt, Rh, and Ru metals (Hombikat UV 100). They are created using the photo deposition technique. Researchers have looked examined CV dye photocatalytic degradation and adsorption on undoped TiO₂, Pt/TiO₂, Pd/TiO₂, Rh/TiO₂, and Ru/TiO₂. The sorption and photocatalytic breakdown of CV dye are significantly enhanced by the addition of Pd or Pt 32.

Durmus *et al.*, [8] created a graphene oxide/zinc oxide (GO/ZnO) nanocomposite by decorating thermally expanded and chemically oxidised graphite oxide nanosheets with zincoxide (ZnO) nanoparticles synthesized via a two-step sol-gel deposition method and using it as an effective photocatalyst for basic fuchsin (BF) dye degradation. By accessorizing thermally expanded and chemically oxidized graphite oxide nanosheets with zinc oxide (ZnO) nanoparticles produced via a two-step sol-gel deposition method,

SnO₂ quantum dots/TiO₂ nanosphere composite frameworks, according to Bhatt *et al.* [9], are good candidates for use as photocatalysts due to their great capacity to absorb visible light, high tunability, high specific surface areas, and semi-conductive characteristics. Here, a bottom-up strategy has been used to create a SnO₂ quantum dots/TiO₂ nanosphere hybrid that is driven by visible light.

E.B. Azevedo *et al.*, [10] It could be interesting to look at how organic solvents affect the photodegradation of a dye that is soluble in organic solvents but insoluble in water. Therefore, our work has looked at how solvents and mixed-solvent systems affect the photodegradation of Sudan III. Metal ions are also present in dye made from contaminated water. Inorganic salts, such as NaCl, have been shown in several studies to slow down the photodegradation of pollutants, such as phenol.

Bi₂O₃ and Bi₂S₃ were employed by Sharma *et al.*, [11] to photocatalyze the degradation of the blue B dye. We saw and spoke about the effects of many factors, including pH, dye concentration, semiconductor quantity, and light intensity. Spectrophotometric monitoring was used to track the development of the photochemical oxidation. Experimental research was used to find the ideal reaction conditions. Dye oxidation by photochemistry follows pseudo-first order kinetics. A possible process for the photochemical oxidation of dyes was given, and the final breakdown products were described.

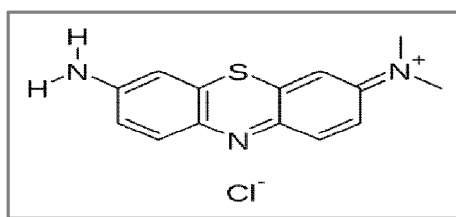


Figure 1. Structure of Azure A Dye.

MATERIALS AND METHODS

Synthesis of Nickle Vanadate: The amount of nickel sulphate (NiSO_4) that was dissolved was 4.68 g in 400 mL of distilled water. And solution A is the official name for it. Ammonium metavanadate (NH_4VO_3) weighing 21.02 g was dissolved in 400 mL of distilled water to create Solution B.

Solutions A and B were vigorously magnetically stirred for 4 hours to combine them. In order to remove the water from the material, the resultant slurry was then transferred to a new beaker and heated for 20 minutes at 180°C . The precipitate was repeatedly washed with distilled water after being progressively brought to room temperature and it was then dried for 5–6 hours to produce greenish yellow nickel vanadate powder.

Titanium dioxide: Titanium dioxide is used from Suvidhinath Laboratories.

Solution Preparation: All of the solutions were made with double-distilled water. Nickle Vanadate was added in titanium dioxide in the ratio of 1:1.

Characterization of composite: EDX Analysis: Energy-dispersive X-ray spectroscopy (EDS) detects X-rays emitted from the sample during bombardment by electron beam to characterize the elemental composition. The results are reported in table 1 and presented in figure 2.

Table. The elemental composition

Element [wt.%]	Series [wt.%]	C norm [wt.%]	. C Atom [wt.%]
Vanadium	K-series	60.47	52.21
Titanium	K-series	30.80	28.30
Oxygen	K-series	6.43	17.67
Aluminium	K-series	0.10	0.16
Nickel	K-series	2.20	1.65

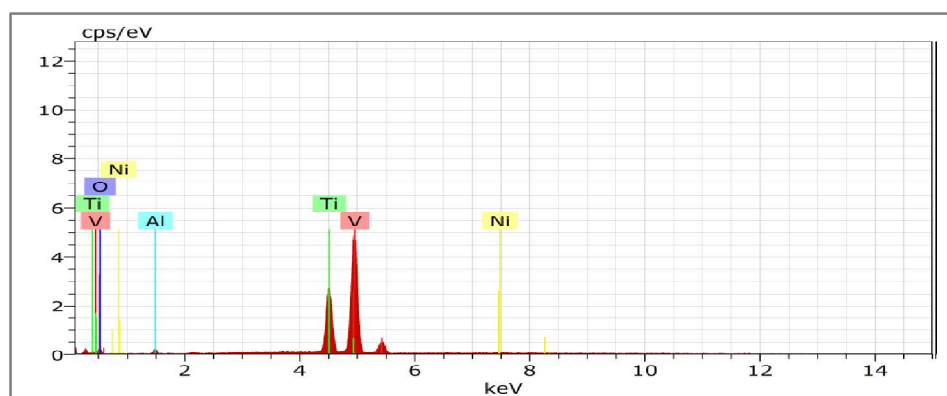


Figure 2. EDS of Nickle vanadate and Titanium Dioxide.

XRD Analysis: X-rays can be thought of as electromagnetic radiation waves, whereas crystals are regular arrangements of atoms. Crystal atoms primarily interact with their electrons to scatter incoming X-rays. The electron is the scattered in this event, which is referred to as elastic scattering. A regular array of spherical waves results from a regular array of scatterers. These waves interfere destructively in the vast majority of directions, but according to Bragg's rule, they add constructively in the following few directions: $2d\sin\theta = n\lambda$ non-destructive method known as X-ray diffraction analysis (XRD) may offer accurate data on a material's crystallographic structure, chemical makeup, and physical characteristics. It shows Minimum step size 2Theta:0.001; Minimum step size Omega: 0.001, Start Position [$^{\circ}2\theta$] 5.0084, End Position [$^{\circ}2\theta$] 79.9784. Divergence Slit Size [$^{\circ}$] 0.4354, K-Alpha1 [\AA] 1.54060, the powder XRD pattern of as prepared nickel vanadate and titanium dioxide is given in figure 3.

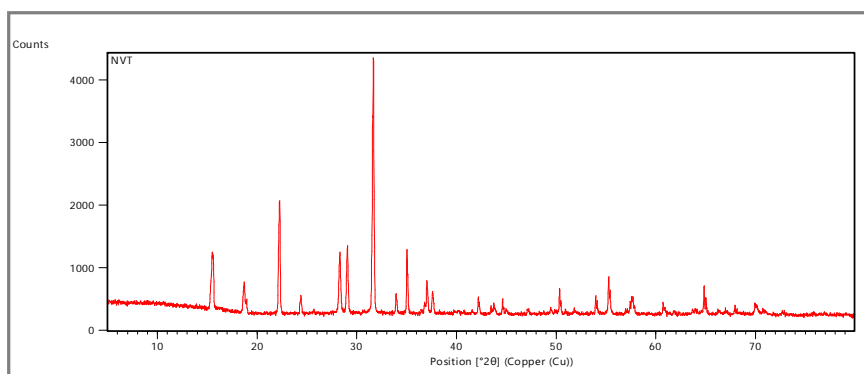


Figure 3. XRD of Nickel vanadate and Titanium Dioxide.

Photocatalytic Process: 0.0291 g of Azure A were dissolved in 100.0 mL of doubly distilled water to create 1.0×10^{-3} M of dye solution. It is administered as a stock solution. This stock solution was further diluted. The absorbance of an Azure A solution was measured using a spectrophotometer at $\lambda_{\text{max}} = 630$ nm. The dye solution was divided equally among the four beakers. After being stored in these beakers for three to four hours, the absorbance of the solution was measured using a spectrophotometer. It was found that the fourth beaker's solution had a lower starting absorbance value than the beakers' prior three solutions. This finding demonstrates that for this reaction to occur, both light and a compound of the semiconductors nickel vanadate and titanium dioxide are required. As a result, this is actually a photocatalytic reaction.

Table 1. presents a typical run

pH = 7.0, [Azure A] = 2.8×10^{-5} M, Nickel Vanadate and TiO₂ composite = 0.10 gm, Light intensity = 50.0 mWcm⁻²

Time (min)	Absorbance A	1+log OD
0.0	0.634	0.8020
10.0	0.612	0.7867
20.0	0.602	0.7795
30.0	0.589	0.7701
40.0	0.571	0.7566
50.0	0.552	0.7419
60.0	0.539	0.7315
70.0	0.512	0.7092
80.0	0.490	0.6901
90.0	0.465	0.6674
100.0	0.442	0.6454

Rate Constant = 5.47×10^{-5} Sec⁻¹

The absorbance of the Azure A solution was shown to decrease with increased exposure durations. A plot of $1 + \log A$ against time was found to be linear, demonstrating that pseudo first order kinetics controls the photocatalytic degradation of Azure A. The rate constant was calculated using an equation

$$k = 2.303 \times \text{slope} \quad \dots(1)$$

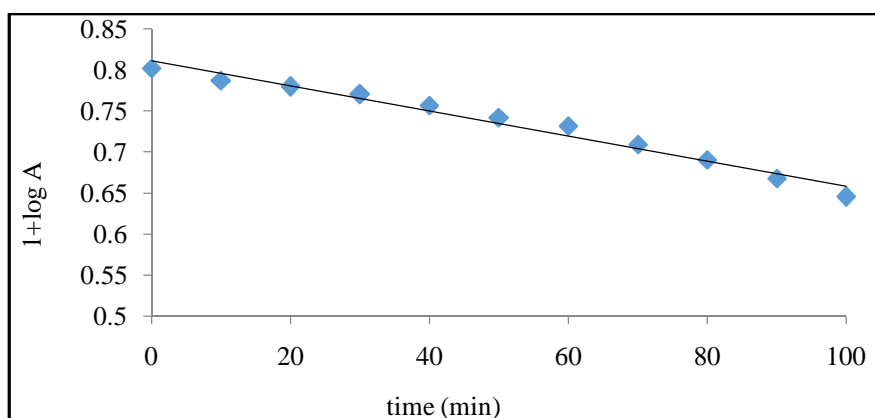


Figure 4. Typical run for photocatalytic degradation of azure A dye.

RESULTS AND DISCUSSION

Effect of pH: Azure A degradation is anticipated to be influenced by the solution's pH. The impact of pH on the pace of Azure A's breakdown was looked at in the pH range of 5.0-10.5. They are visually shown in the Figure.

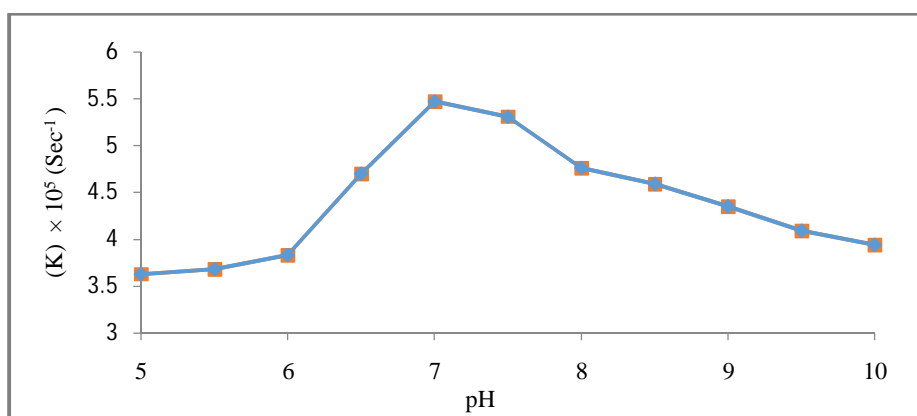


Figure 5. Effect of pH on photocatalytic degradation of Azure A Dye.

Effect of Concentration of Dye Solution: Using different concentrations of Azure A, the effect of dye concentration was studied. Figure visually shows them. It was found that the rate of dye degradation by photo catalysis increased when the concentration of Azure A was raised to 2.8×10^{-5} M. It could be because the rate of dye breakdown accelerated as the dye concentration increased since there were more dye molecules available for excitation and energy transmission. Since the dye barrier was now acting as an internal barrier and preventing the necessary light intensity from reaching the semiconductor present on the reaction vessel's bottom, the rate decreased when the dye concentration was increased over 2.8×10^{-5} .

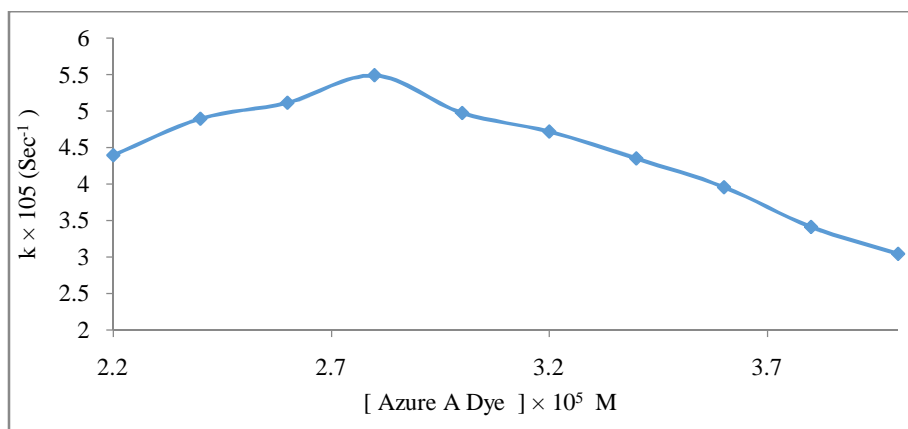


Figure 6. Effect of dye concentration on photocatalytic degradation of Azure A Dye.

Effect of Amount of Photo catalyst: Since it is expected that the amount of semiconductor would also have an effect on the degradation of dye, several photo catalyst concentrations were used. Outcomes and presents the findings visually. It was discovered that the rate of reaction rises as the amount of semiconductor nickel vanadate and titanium dioxide composite increases. The rate of deterioration peaked at 0.10 g of the photo catalyst. Above 0.10g, the rate constant was almost constant. This can be the case because when semiconductor was used, the exposed semiconductor surface area increased. However, the semiconductor layer just gets thicker and the surface area is not exposed when the amount of semiconductor is more than this limiting value (0.10g). This was confirmed using reaction containers of various sizes. The saturation point rises upward for bigger vessels whereas smaller vessels show the opposite tendency.

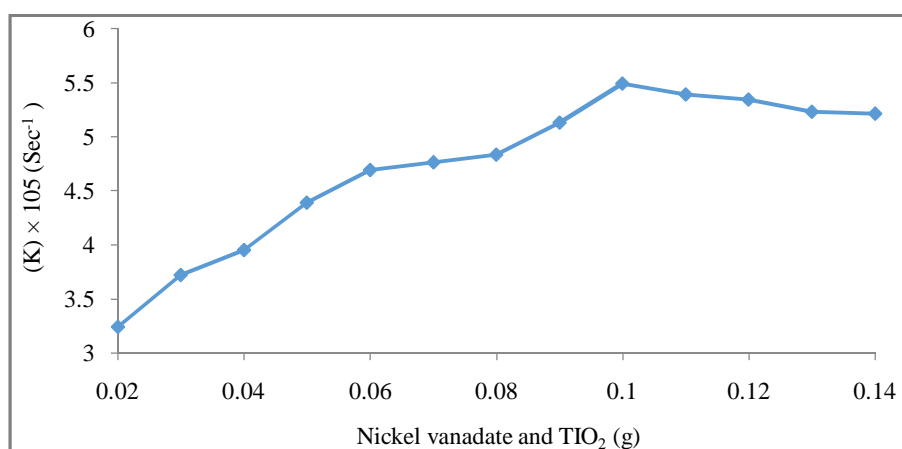


Figure 7. Effect of amount of composite on photocatalytic degradation of Azure A Dye.

Effect of Intensity of Light: To investigate the effect of light intensity on the photocatalytic degradation of Azure A, the distance between the light source and the exposed photocatalyst surface area was altered. The data are summarised and the results are illustrated visually in figure 8. The findings indicate that breakdown accelerated as light intensity rose because more photons are hitting a given area of semiconductor powder in a given amount of time with each rise in light intensity. However, a little reduction in the degradation rate was seen when the intensity was increased above 50.0 mWcm⁻². This might be a result of certain negative consequences.

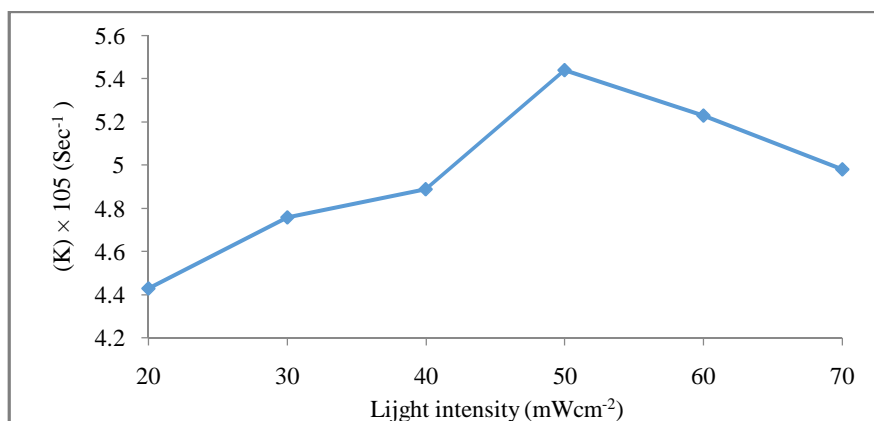
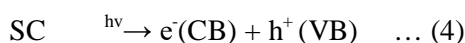
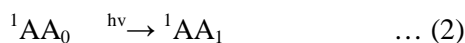


Figure 8. Effect of light intensity on photocatalytic degradation Azure A Dye

Mechanism: Based on these findings, the following probable mechanism for photocatalytic degradation of Azure A dye is proposed:



[AA] Azure A Dye When a dye (AA) absorbs light with the proper wavelength, the dye creates its initial excited singlet state. The dye then enters the triplet state as a result of intersystem crossover (ISC). In contrast, the semiconducting nickel vanadate and titanium dioxide composite also excites an electron from the valence band to the conduction band using radiant energy. When this electron is abstracted by an oxygen molecule (dissolved oxygen), superoxide anion radical (O_2^-) is created. This anion radical will change the Azure A dye into its leuco form, and it may eventually decompose into by-products. As an oxidation by-product, the OH radical does not actively contribute to this degradation. Furthermore, the rate of deterioration was unaffected by the addition of a hydroxyl radical absorber, demonstrating that reduction rather than oxidation is the mechanism behind this degradation (2-propanol).

APPLICATION

This research is particularly effective for removing contaminants from industrial effluent, such as pigment industries, health industry, and papermaking, among others.

CONCLUSION

Azure A dye was degraded using a photo catalyst composite made of nickel vanadate and titanium dioxide. The experimental findings demonstrated that pH, dye solution concentration, semiconductor quantity, and light intensity all had an impact on the photocatalytic degradation efficiency of AzureA dye. The degradation of different contaminants may be examined in relation to the application of the photo catalyst.

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