

Photocatalytic Degradation of Acid Alizarin – Violet N Dye in Visible Light over Nano TiO₂ and Ag-doped Nano TiO₂ Catalysts

B. Vijayalaxmi, Ch. Vijayatha, Mamathasri and A. Hari Padmasri*

(Department of Chemistry, University College of Science, Osmania University, Tarnaka,
Hyderabad 500007, Telangana State, India).

*For Correspondence: ahpadmasri@gmail.com; ahpadmasri@osmania.ac.in

Abstract:

Ag doped nano TiO₂ was found to be an efficient photocatalyst in degrading acid alizarin violet N (AAVN) under visible light. The Ag doped nano TiO₂ catalyst was synthesized by sol-gel method. XRD analysis as well as SEM micrographs showed these catalysts to be in nano size with a spherical morphology. The higher photocatalytic activity of Ag-TiO₂ is explained due to the red shift in absorption as compared to nano TiO₂ in turn owing to reduction in the band gap observed from UV-DRS analysis. AAVN dye was degraded to an extent of more than 98% on Ag doped TiO₂ as compared to 90% by nano TiO₂. The recycle studies on Ag-doped catalyst showing a stable degradation rates even after 5 runs indicate it to be a highly potential photo catalyst that may be employed in the successive degradation of AAVN dye in presence of visible light.

Keywords: Acid Alizarin Violet N,

Date of Submission: 08-01-2022

Date of Acceptance: 23-01-2022

I. Introduction

Global dye market shows a constant growth in terms of its revenue owing to their application in textiles, leather, paper, printing and inks industry. This rising demand also results in constant global threat with the extent of pollution these dyes pose to the environment especially to the water bodies [1]. The effluents in the streams from the end use of the various dyeing industries cause various health hazards to humans and also contaminate the flora and fauna. Different chemical and biological methods are employed in the removal of the dyes by the treatment of effluent streams from the industries. Photocatalytic degradation is one of such proven phenomenon in addressing this issue [2]. TiO₂ is one of the most viable photocatalyst owing to its high activity [3]. However its use is hindered in the visible/solar light regime due to its bandgap being more suitable for UV radiation. Doping of TiO₂ and other semiconductors with non-metal or metal ions have paved path in expanding their absorption wavelengths [4]. Visible light driven photocatalysis is of greater interest today owing to the advantage of complete mineralization of contaminants in effluents to enviro-friendly products by the use of economically viable materials and also to the inexhaustible use of solar light that is available in vast. Some of the photocatalysts suffer loss in activity due to the recombination of holes and electrons formed during the activation of catalysts. However, doped TiO₂ and perovskite based catalysts can overcome this drawback owing to the reduction in the band gap, formation of stable and composite structures favoring the separation of holes and the electrons formed [5,6]. Simple titania based photocatalysts are most viable and favorable for the degradation of dyes.

Hence, the present work is aimed at utilization of simple nano TiO₂ and Ag doped nano TiO₂ based catalysts for the degradation of acid alizarin violet N (AAVN) dye which studied to a less extent over these catalysts reported here. AAVN dye is an azo dye with absorption maximum at 501 nm. Its applications range from use as inks, dye lasers, in manufacture of vinyl polymers, textiles determination of iron, calcium, aluminum, tantalum, monitoring hardness in industrial water, measuring chlorine dioxide in drinking water, hypoglycemic agents and nuclear fluorochrome.

The photocatalytic activities of these catalysts have been found to be high enough to degrade AAVN dye in visible light. Their activity was found to be on par/much higher in visible/solar light upon comparison with UV light.

II. Experimental methods

2.1. Synthesis of nano TiO₂ and Ag-doped TiO₂ photocatalysts

5wt% Ag-doped nano TiO₂ catalyst was prepared by an acid modified sol-gel method [7]. In a typical method, silver nitrate precursor in desired amount taken in aqueous acetic acid solution and titanium isopropoxide in anhydrous ethanol were added drop wise with constant stirring to obtain a sol that was aged for 3 days at room temperature. The as-prepared gel was then dried and finally calcined at 500° C for 5 h in static air. The nano TiO₂ nanoparticles were prepared using the same method for comparative studies.

2.2. Characterization Techniques

Powder X-ray diffraction (XRD) analysis of the prepared catalysts was done using a Rigaku miniplex powder X-ray diffractometer operated at 40kV and 15mA with Cu-K α (1.5406 Å) radiation source. The surface properties of fresh samples were measured by N₂ adsorption at -196 °C (Micromeritic ASAP 2010 surface area analyzer). The specific surface areas were calculated by applying the BET method. Surface morphology analysis was carried out by field emission scanning electron microscopy (FE-SEM) using a Carl Zeiss model Ultra 55 electron microscope. Energy dispersive of X-ray (EDX) analysis was used to determine the composition and distribution of the constituting elements in the samples with Oxford Instruments X-MaxN SDD (50mm²) system interfaced at 5kV and INCA analysis software. UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded using JASCO V650 UV-Vis spectrophotometer in region of 200–800 nm.

2.3. Photocatalytic activity studies

The photocatalytic activity studies were carried out on a reactor supplied by Lelesil Innovative System, India equipped with a 250 W visible lamp. In a typical run, 0.50 – 0.150 g catalyst was dispersed in aqueous AAVN solution of concentration ranging from 50-200 ppm in variable amounts was irradiated by visible light with stirring. The catalyst was filtered and the absorption spectra of the obtained supernatant were measured on a UV-visible spectrometer to monitor the degradation of AAVN. The photocatalytic degradation efficiency was $\% \eta = \frac{C_0 - C}{C_0} \times 100 = \frac{A_0 - A}{A_0} \times 100$ where C₀ is the concentration before the reaction and C is the concentration obtained using centrifugation every 30 min during the reaction. A₀ is the absorbance before the reaction, and A is the absorbance obtained using centrifugation every 30 min during the reaction.

III. Results & Discussion

BET-surface areas of the nano titania and Ag doped nano titania (Ag/TiO₂) were found to be 57 and 60 m²g⁻¹ respectively which shows not much change in the surface area of TiO₂ with Ag doping.

3.1. X-Ray Diffraction (XRD)

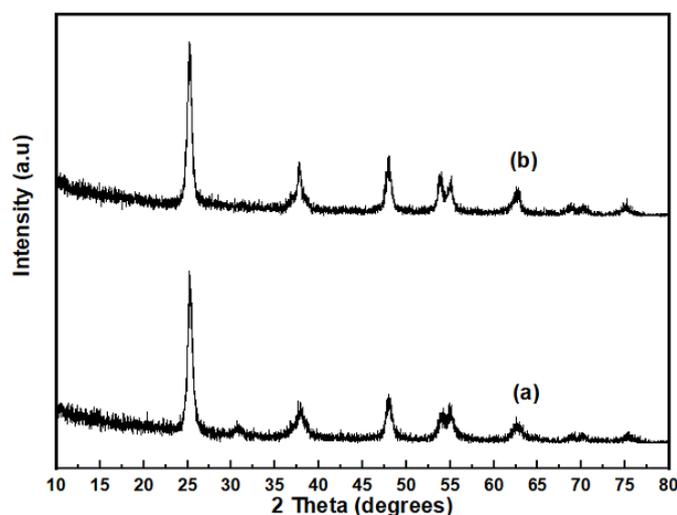


Figure 1: Powder X-ray diffraction patterns of the samples calcined in air at 500 °C/5 h (a) TiO₂ (b) Ag/TiO₂.

TiO₂ exhibited dominant diffraction peaks (Fig.1) at $2\theta = 25.07, 37.59, 47.98, 53.72$ and 54.86° corresponding to the (101), (004), (200), (105) and (211) planes respectively of anatase phase (JCPDS: 21-1272) with good crystallinity in the nano range calculated by Debye-Scherrer formula. Ag doping did not alter the structure of TiO₂ as observed from Figure 1. The determined values of average crystallite size of nano TiO₂ and Ag doped TiO₂ were found to be 8.24 and 8.85 nm respectively.

3.2. **UV-DRS analysis:**

Figure 2 represents the UV-DR spectra of both nano TiO₂ and Ag-TiO₂ that showed an absorbance in between 300-480 nm and band gap energy values are found to be 2.59 and 3.09 eV for Ag doped TiO₂ and nanoTiO₂ photocatalysts. These along with their corresponding absorption wavelength edge are presented in the Table 1.

Catalyst	Absorption Wavelength (nm)edge	Band gap Energy (ev)
TiO ₂	401	3.0922
Ag/TiO ₂	478	2.59

Table 1: Band gap energies of the catalyst

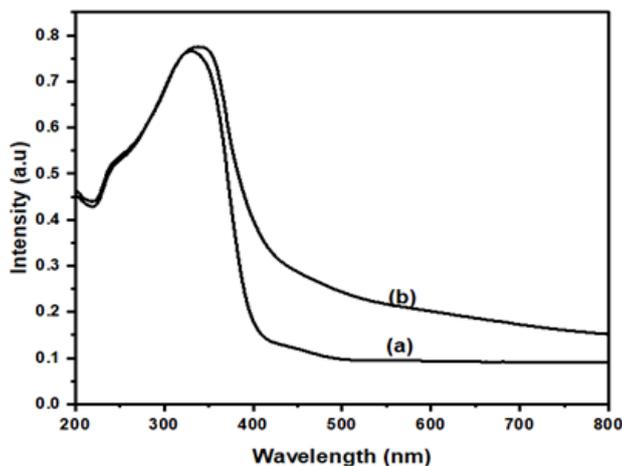


Figure 2: UV-DRS of (a) nano TiO₂ (b) Ag/TiO₂

3.3. **SEM-EDX**

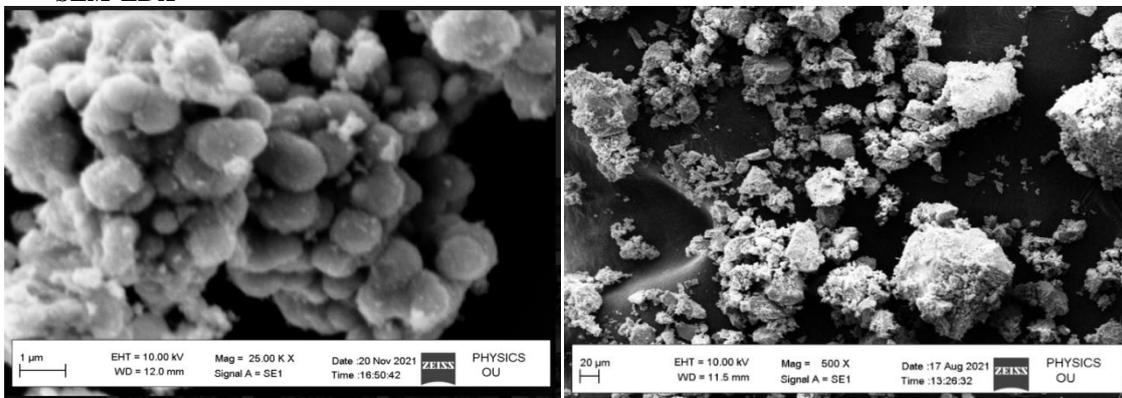


Figure 3: SEM micrographs of (a) TiO₂ and (b) Ag/TiO₂

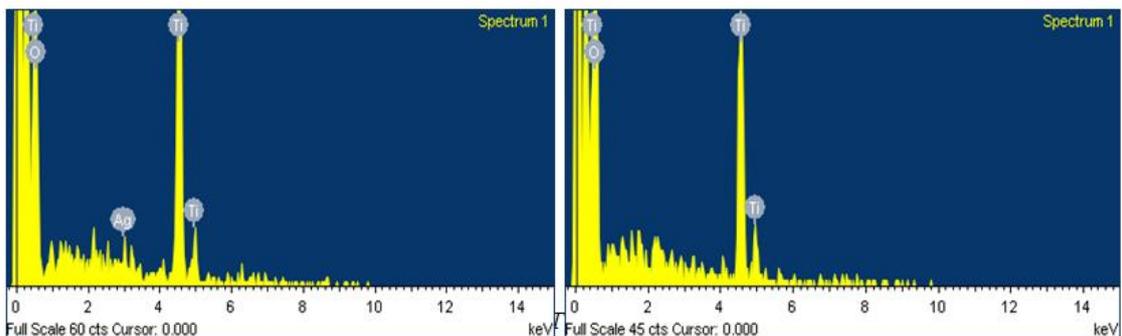


Figure 4: EDX spectra of (a) nano TiO₂ and (b) Ag/TiO₂

SEM analysis of Ag doped nano TiO₂ showed well defined spherical shape with nano sized particles with minimal agglomeration compared to nano TiO₂. EDX analysis showed the doped components in desired amounts.

3.4. Photocatalytic degradation of AAVN

The photocatalytic activity of the catalysts studied in visible light clearly demonstrated a very high efficiency of the catalyst in degrading acid alizarin violet N (AAVN) dye to an extent of more than 98% on Ag doped TiO₂ as compared to nano TiO₂ upto 90% shown in Figures 5a and 5 b. A 75mg of Ag doped TiO₂ catalyst was found to degrade 100 ppm of AAVN dye upto 98% (Figure 6a). However, the doped catalyst maintained a nearly 80-90% degradation activity with higher concentrations of dye up to 150 ppm also whereas nano TiO₂ degraded the AAVN dye only to 70% at higher concentrations.

The kinetics of dye degradation follows first order fitting into a Langmuir-Hinshelwood model (Fig.6b) as reported by many others [8]. The rate constant observed is 0.6 and 0.67 min⁻¹ with the nano TiO₂ and Ag doped nano TiO₂ catalysts indicating high intrinsic activity of the catalysts studied. These results correlate with their degradation efficiencies indicated in the previous figures shown here. The reusability test was conducted with most efficient catalyst (5wt% Ag-TiO₂) for AAVN degradation in order to check the stability of catalyst for practical application as represented in the Figure 7 below. The recyclability of the catalyst was monitored for four cycles. The photocatalytic activity over these catalysts decreased slightly from 98% to 92%. However, the aforementioned results suggest good stability of the photo catalyst which remains unchanged even after five successive runs. Total organic carbon removal rate is 97.5% over this catalyst estimated using TOC analyzer.

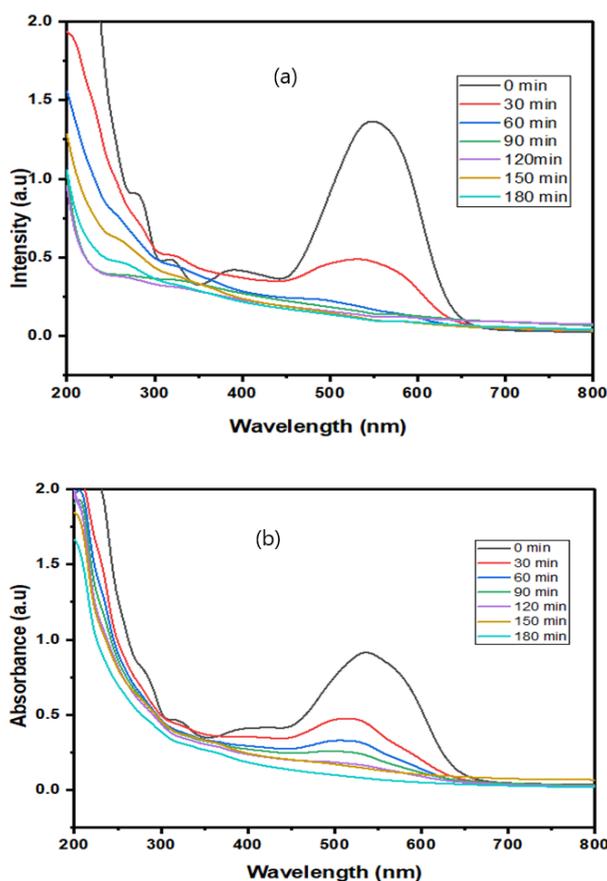


Figure 5: Photo degradation of 50 ppm AAVN in visible light (a) nano TiO₂ and b) Ag/TiO₂ using ~ 50 mg catalysts.

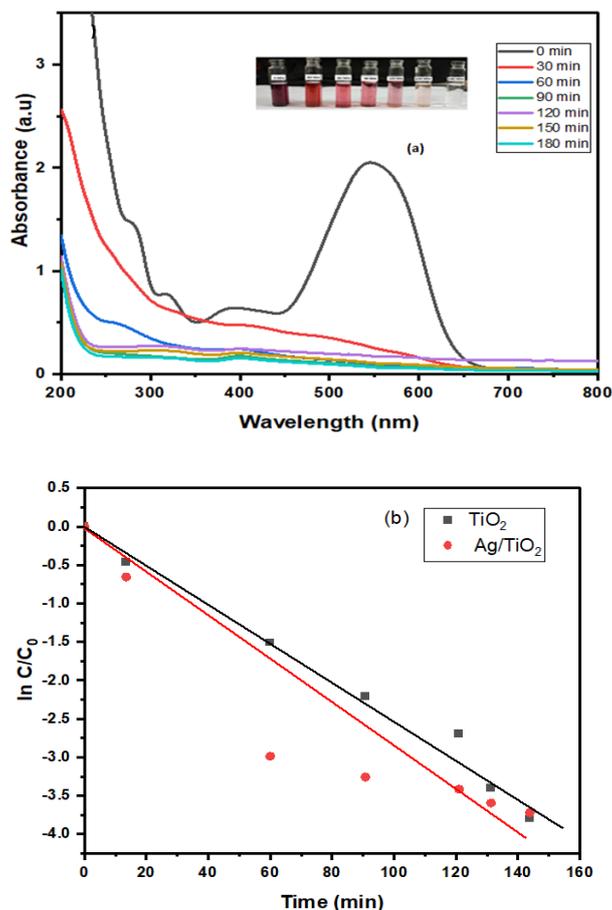


Figure 6: (a) Degradation of AAVN (100 ppm) in visible light over Ag/TiO₂ and (b) Photocatalytic degradation rate of 50 ppm AAVN over nano TiO₂ and Ag/TiO₂ catalysts.

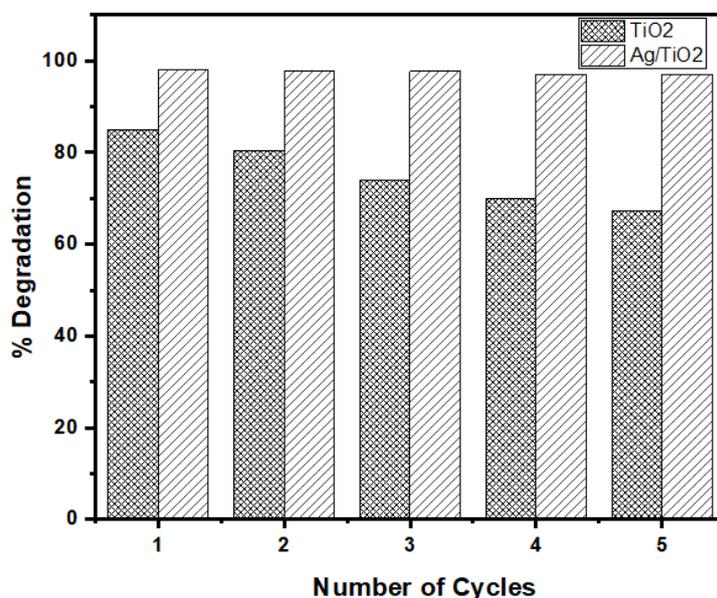
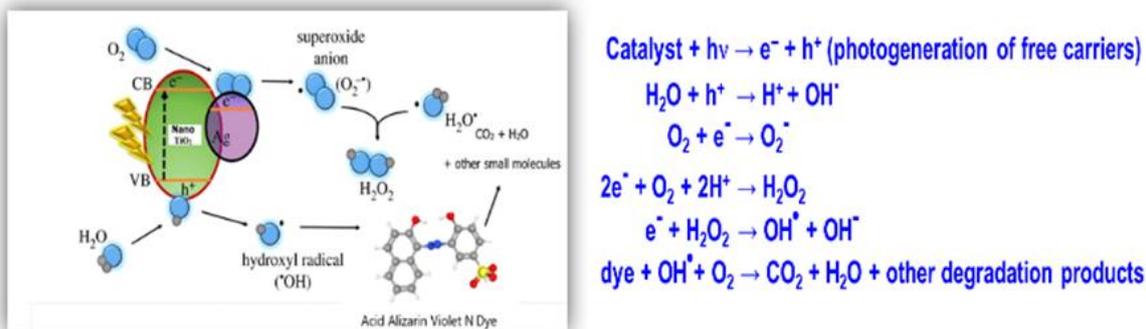


Figure 7: Catalyst recyclability in the photo degradation of 100 ppm AAVN in visible light over Ag/TiO₂.

The scheme below indicates the reaction mechanism of the photodegradation of AAVN dye. The first step in the photocatalytic process involves the generation of electron-hole pair on irradiation which are trapped on the surface of the catalysts separated by the lowest energy valence band and highest energy conduction band regions. The next step is the generation of peroxide and hydroxyl radical on interaction of the holes and electrons with water. The important step is then the interaction of the radicals generated with the dye molecule

leading to its degradation forming back water molecule, carbon dioxide and other simpler products of degradation. The reduction in the total organic content with time clearly supports the degradation of the dyes due to photocatalytic activity. Metal ion doping on TiO₂ is known to form a dopant energy level within the band gap resulting in a red shift in the absorption spectra of the doped TiO₂. The same has been observed from the UV-DRS spectra of the nano TiO₂ and Ag doped nano TiO₂ in the present study.

Scheme of Reaction Mechanism [9]



IV. Conclusions

Nano TiO₂ and Ag-doped nano TiO₂ synthesized by sol-gel method have shown high efficiency for the photocatalytic degradation of AAVN dye. The doped catalyst is more efficient in degrading higher concentrations of the dye also supported by the red shift observed in the absorption spectra of the doped catalyst in comparison to the nano TiO₂. The XRD pattern and SEM images indicate that the catalysts studied were in nano crystalline form and with spherical morphology respectively. The Ag-doped catalyst had further shown a stable activity even after 5 runs confirming Ag-doped TiO₂ catalyst to be an efficient degradation catalyst that can work in visible region for AAVN dye.

Acknowledgements

The authors thank OU-DST-PURSE II for the financial support and Prof M Vithal, Department of Chemistry, Osmania University for permitting to use his laboratory equipment.

References

- [1]. Kant, R. Textile dyeing industry an environmental hazard, *Natural Science*, 4 (2012).
- [2]. Basem Mohammed Al-Sakkaf, Sadia Nasreen, Naeem Ejaz, Degradation Pattern of Textile Effluent by using Bio and Sono Chemical Reactor, *Journal of Chemistry*, 3 (2020); 1-13.
- [3]. Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K. and Taga, Y, Visible Light Photocatalysis in Nitrogen-Doped Titanium Oxides, *Science*, 293 (2001); 269–271.
- [4]. Huo Y, MiO M, Zhang Y, Zhu J and Li H, Aerosol-spraying preparation of a mesoporous hollow spherical BiFeO₃ visible photo catalyst with enhanced activity and durability, *Chemical Communications*, (2011); 2089-2091.
- [5]. Hao Zhang, Xiaojun Ly, Yueming Li, Ying Wang and Jinghong Li, P25-Graphene Composite as a High Performance Photocatalyst, *ACS Nano* 4 (1), (2010); 380–386.
- [6]. K. M. Prabu, P. M. Anbarasan, Preparation and Characterization of Silver, Magnesium & Bismuth Doped Titanium Dioxide Nanoparticles for Solar Cell Applications, *International Journal of Science and Research*, 3(9) (2014).
- [7]. Ioannis K. Konstantinou and Triantafyllos A. Albanis, TiO₂- assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations; A review, *Applied Catalysis B: Environmental*, 49 (2004); 1–14.
- [8]. A. Mills, R.H. Davies and D. Worsley, Water purification by semiconductor photocatalysis, *Chem. Soc. Rev.*, (1993); 417-425.

B. Vijayalaxmi, et. al. "Photocatalytic Degradation of Acid Alizarin – Violet N Dye in Visible Light over Nano TiO₂ and Ag-doped Nano TiO₂ Catalysts." *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 15(01), (2022): pp 01-06.