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Photocatalytic Degradation of Gentian Violet Using Doped Zinc Oxide Nanoparticles

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Abstract:
This research was carried out to investigate the photocatalytic degradation of Gentian Violet dye using doped zinc oxide nanoparticles as catalyst. The photocatalysis was carried out under UV-irradiation and in dark which serves as control. The morphological structures of nanomaterials were investiged by X-ray diffraction (XRD) and scanning electronic microscope (SEM). The absorption spectra wavelength and absorption edge wavelength of the as-synthesized photocatalyst was determined by UV- Visible spectrophotometer. The effect of catalyst dosage on the degradation process was assessed by varying the catalyst from 0.1-0.4g/100ml. Results reveal catalysts doses of ZnO nanoparticles 0.3g/100ml dose with the percentage degradation (ZC 71.5%, ANZ 94.5%, AZ 76.5%, NZ 91.2%) as the most suitable catalyst dosage for degrading GV under UV irradiation at 120 mins time. The result also shows that the highest percentage of photocatalytic degradation was achieved using silver-nitrogen co-doped zinc oxide photocatalyst (ANZ) both under solar and Uv irradiation. Under solar irradiation NZ tend to give better degradation than (AZ). Photocatalytic degradation in the dark is negligible. Degradation of gentian violet dye in the absence of light was performed to demonstrate that the presence of light and catalyst was essential for the photo degradation to occur.

Keywords: Dyes, Gentian Violet, Zinc Oxide Nanoparticles, Photocatalytic Degradation, Textile Wastewater Treatment, Gentian Violet.

INTRODUCTION

Dyes are widely used in various industries, including textile, paper, leather, and cosmetics. The discharge of dye-containing wastewater into water bodies can result in decreased aesthetic value of water, decreased light penetration, and toxic effects on aquatic organisms. Some dyes and their degradation by-products are known to be carcinogenic, mutagenic, and toxic to aquatic organisms (Sudarshan *et al.*, 2022). Wastewater pollution and inadequate wastewater treatment pose significant environmental challenges globally. The discharge of untreated or inadequately treated wastewater, as well as the presence of dyes in wastewater, can have detrimental effects on ecosystems, human health, and water resources. The presence of a trace amount of colored organic compounds in the aquatic system can result in coloration of the water. The consequence of colored water is detrimental to aquatic environment since the color obstructs the sunlight access to aquatic organisms and plants, diminishing the photosynthetic process thereby affecting the entire aquatic ecosystem (Senthilvelan *et al.*, 2013). Therefore, the removal of color and sanitization has become an ecological concern and is vital for environmental sustainability. Industrial development and its association with discharge of organic matter into the aquatic systems demand technological development to solve the environmental problems related to organic effluents (Zhou, 2013). Many practices have been widely applied in the treatment of organic effluent such as biological treatment, reverse osmosis, ozonation, filtration and adsorption on solid phases, incineration, and coagulation (García-Montaño, 2008). However, each of the methodologies has their limitations. Incineration can result in deadly toxic volatiles products (Vinita and Dorathi, 2010); biological treatment needs prolonged treatment time and results in ghastly smell; ozonation can be effective way for the treatment of organic effluent but the stability of ozone is the biggest concern which is highly influenced by the existence of salts, pH, and temperature (Vinita and Dorathi, 2010). The traditional physical methods (adsorption, filtration, reverse osmosis and coagulation) are quite expensive and do not eliminate the organic molecules utterly but just transform them from one phase to another (Zelmanov and Semiat, 2008).

In recent era, advanced oxidation processes (AOPs) have been found as an effective and alternative way for the treatment of organic effluent in aqueous system (Boczkaj and Fernandes, 2017). Recent researches have demonstrated that AOPs based on photocatalysts are valuable and employs complete mineralization of organic molecules into nontoxic CO_2 and H_2O at the atmospheric conditions (Vinu and Akki, 2010). Furthermore, AOPs result in the generation of hydroxyl radicals (•OH) as main oxidizing agents which can remove even nonbiodegradable organic compounds from wastewater stream (Xia *et al*., 2020). Photocatalytic degradation of organic effluent emerged as one of the best methodologies for the treatment of toxic organic effluents which uses the semiconductor as catalyst such ZnO, TiO_2, ZnS, WO_3, CdS, Fe_2O_3, and $SrTiO_3$ (Sathishkumar, 2013). Among them ZnO and TiO_2 have been widely applied as photocatalyst due to their high activity, nontoxicity, chemical stability, lower costs, optical and electrical properties, and environment friendly characteristics (Xia *et al*., 2020). It is against this backdrop that it becomes imperative to investigate the photocatalytic degradation of Gentian violet using doped zinc oxide nanoparticles.

MATERIALS AND METHODS

The synthesis of Zinc Oxide, Silver Doped Zinc Oxide, Nitrogen Doped Zinc Oxide and Silver Nitrogen Co-Doped Zinc Oxide Nanoparticles was carried out in Federal University of Technology Owerri, FUTO, Nigeria. The UV visible diffuse absorbance spectra characterization was also carried out at Federal University of Technology Owerri, FUTO. SEM analysis was carried out at Ahmadu Bello University, Samaru Campus, Zaria, Nigeria and the XRD analysis was carried out at national steel raw materials exploration agency, Kaduna, Nigeria.

Materials and Apparatus

The materials and apparatus used where X-ray diffraction with machine model: Shimadzu XRD, model 6000, Scanning Electron Microscope (SEM): Phenom prox, model no MVE 016477830 manufactured by PhenomWold Eindhoven Nethalands, LASANY UV-VIS spectrophotometer LAB 722, PH meter, Artificial UV irradiation system, crucibles, beakers, analytical weighing balance, desiccators, volumetric flask, measuring cylinder, muffle furnace, oven ceramic mortar, spatula, quartz curvette, syringe. Whatman filter paper, centrifuge, magnetic stirrer, shaker and glass rod.

Chemicals Used

The chemicals used in the experiment was, Burgoyne zinc oxide, kernel urea, deionized water, sodium hydroxide (NaOH). Hydrochloric Acid (HCL), silver nitrate, Gentian Violet dye.

Methods

Synthesis of Photocatalysts:

Preparation of Zinc Oxide Nanoparticles (Zc):

Pure 60g of Burgoyne pure Zinc oxide reagent was measured using analytical weighing balance; the weighed zinc oxide was placed in a ceramic crucible, then placed in a muffle furnace and calcined for four (4) hours at 600°C. It was then cooled to room temperature, ground in a mortar and labeled as calcine zinc oxide (Zc).

Preparation of Nitrogen-Doped Zinc Oxide (Nz):

40g of uncalcined Zinc Oxide was measured using analytical weighing balance and 80g of urea was also measured. The weighed Zinc Oxide and Urea was placed in a ceramic crucible and agitated vigorously with a glass rod, the mixture was placed in a muffle furnace and calcined for four (4) hours at 600°c. It was cooled to room temperature, grinded in a mortar and labeled NZ.

Plate 1: calcined nitrogen doped Zinc.

Preparation of Silver-Nitrogen Co-Doped Zinc Oxide Nanoparticles (ANZ):

4.5g of silver nitrate was measured using analytical weighing balance and mixed with 250ml of distilled water in a volumetric flask. 20g of Nitrogen doped Zinc Oxide was measure and put in a crucible, 20ml of silver nitrate was also measured using measuring cylinder and put into crucible containing 20g of Nitrogen-Doped Zinc Oxide. The mixture was then agitated with glass rod and placed in an oven for 30 min at 120°c. It was then placed in a furnace for four (4) hours at 600°c, cooled to room temperature and grinded to fined particles and labeled ANZ.

Preparation of Silver Doped Zinc Oxide Nanoparticles (AZ):

20g of uncalcined Zinc Oxide was measured using analytical weighing balance and placed in a crucible. 20ml of silver nitrate was measured using measuring cylinder and mixed with 20g of uncalcined Zinc Oxide. The mixture was then agitated with a glass rod and placed in an oven for drying for 30min at 120°c. It was then calcined in a furnace for four (4) hours at 600°c. It was then cooled to room temperature and grinded to fined particles and labeled AZ.

Plate 2: calcined silver doped zinc

Characterization of Photocatalysts:

To observe the absorption edge of the as-synthesized photocatalysts, UV-Vis absorption spectra was measured using LASANY UV spectrophotometer LAB 722 at Federal University of Technology, Owerri. 0.1 g of the photocatalyst was dissolved in 10 ml of deionized water. The UV Visible spectrometer was turned on and made the baseline using the deionized water. Then the absorbance of the photocatalyst solution was measured using a quartz tube. For determining the crystallite size of the as-synthesized photocatalysts, X-ray diffraction (XRD) analysis was carried out at national steel raw materials exploration agency, Kaduna. The machine model is Shimadzu XRD, model 6000, using a Cu target Kα (λ = 1.5406 Ao) with measurements made at room temperature and Scanning Electron Microscope (SEM). For determining average particle size of as-synthesized photocatalyst, analysis was carried out at Ahmadu Bello University, Zaria with machine model: Phenom prox, model no MVE 016477830 manufactured by PhenomWold Eindhoven Netherlands.

Photocatalytic Degradation Studies:

For each Photocatalyst:

0.1-0.4g of photocatalyst was ultrasonically dispersed in Gentian Violet aqueous solution and agitated in the dark for 30min to ensure the adsorption/desorption equilibrium of GV aqueous solution with the catalyst. The mixture was then loaded in an open beaker exposed to UV light from a low-pressure lamp (Philips 15 W) positioned parallel to reactor. UV–Vis absorption spectra of samples were measured at regular intervals of 30 min to monitor the reaction of GV aqueous solution decolorization, and the absorption range of 350–800 nm was recorded as a function of irradiation time. The 10 mL suspension withdrawn at 30 min interval was centrifuged for 15 min and filtered using Whatman No. 1 filter paper to remove the catalyst particles, if any, before recording the absorbance at _max = 590 nm using UV/Vis spectrophotometer. Percentage degradation of GV was calculated using the relation (Kang *et al.*, 2010):

$$\% \text{ degradation} = [(A_o - A_t)/A_o] \times 100$$

Where Ao is absorbance of dye at initial stage, A_t is absorbance of dye at time "t". The Photocatalytic Degradation study was carried out using the procedure described by Tesfay. Experiment Variable included.

RESULT AND DISCUSSION

UV Spectral Characterization

The optical absorption spectra of photocatalysts i.e. (Zc, AZ, NZ and ANZ) are depicted in Figures (1-5). UV-Visible absorption spectra for Zc, AZ, NZ and ANZ are: 373, 423, 473, and 523 nm, respectively. UV-Vis absorption spectra of NZ and ANZ photocatalysts are well extended to visible region spectrum compared to Zc and AZ. This may be due to the modification of electronic levels of zinc oxide by nitrogen-doping.

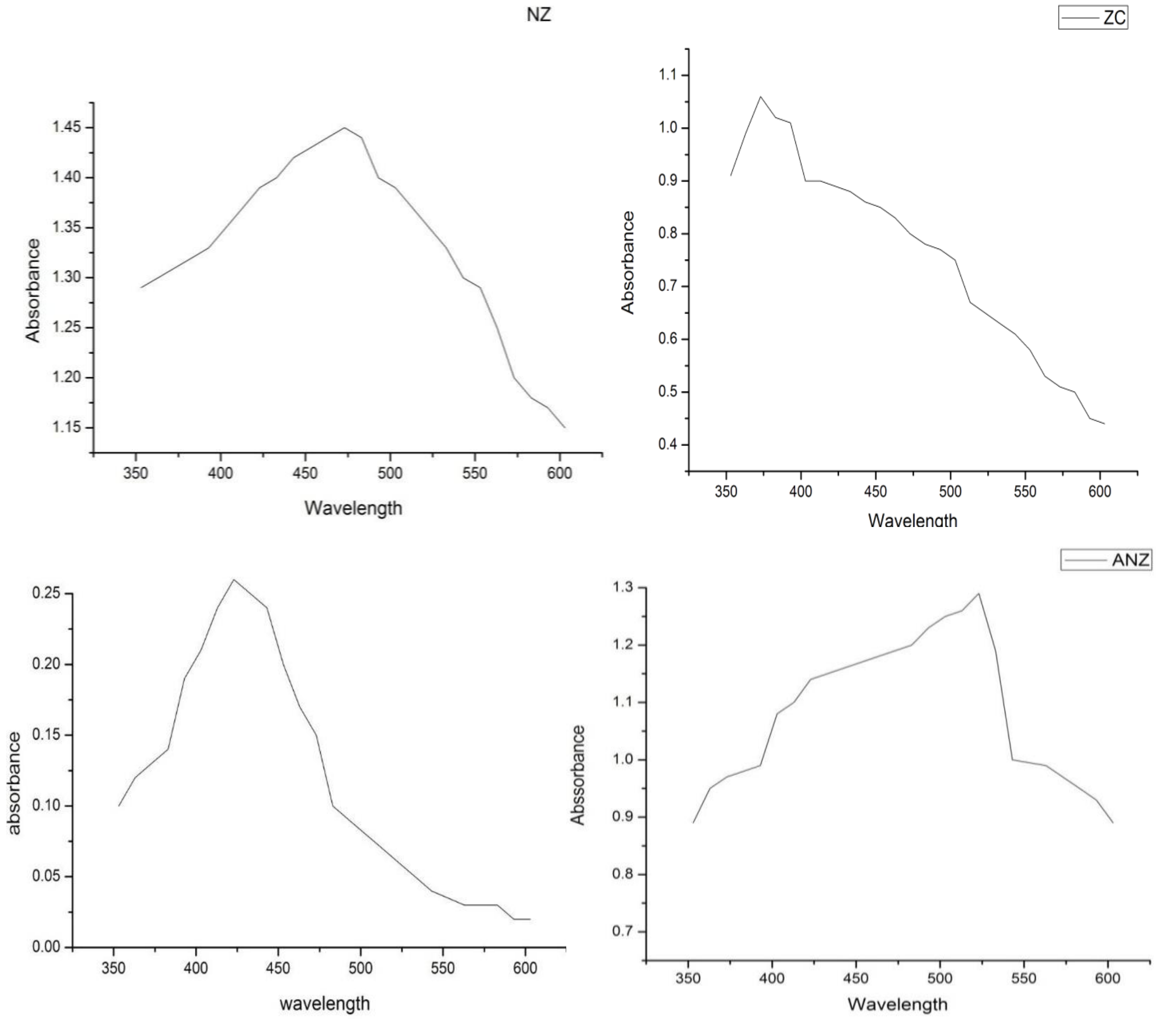

Figure 1 4.1: UV-Visible absorption spectra of Nitrogen doped zinc oxide, zinc Oxide, silver doped zinc oxide and nitrogen doped- silver co-doped zinc oxide.

Band gap energy of the as-synthesized photocatalysts was obtained using the relation (El-Kemary *et al.*, 2010). Eg (eV) = [1240/λ] Where Eg is band gap energy in electron volts, λ is wavelength (nm) corresponding to absorption spectra. The band gap energies (Eg) of photocatalysts Zc, AZ, NZ, and ANZ were found as 3.32, 2.93, 2.62, 2.37 eV, respectively. Nitrogen-doping in zinc oxide resulted significant decrease of band gap energy of NZ and ANZ Incorporation of silver in Zc caused comparatively smaller change relative to nitrogen incorporation. It may be because of doped silver adheres near the surface of zinc oxide and does not modify the band gap energy of zinc oxide (Ren *et al*., 2010). Silver only traps the electrons and prevented from recombination of electrons in the conduction band and holes in the valence band (Aal *et al.*, 2009).

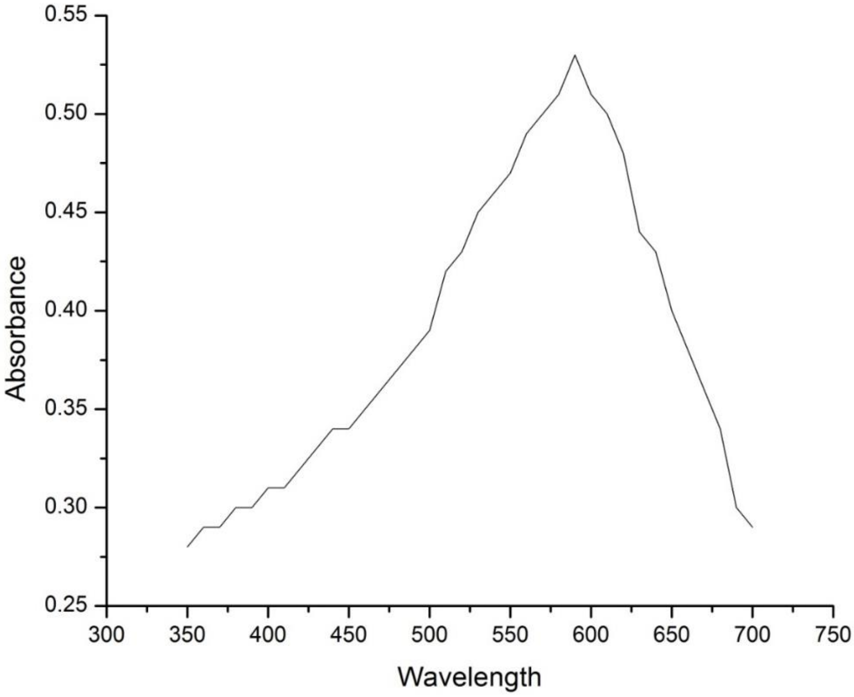

Figure 2: Plot of Graphs of Absorption Edge of Gential Violet Dye on UV-VIS Spectrophotometer

X-Ray Diffraction

The XRD characterization was performed to show the crystalline structure of the ZnO photocatalysts. The peaks at 2θ values of 24.09°, 24.39°, 27.64°, 27.76°, 64. 31°, 37°, 35.44°, 49.27°, 49.46°, 52.26°, 59°.38°, observed in the XRD spectra of ANZ are indicative of the typical hexagonal wurtzite structure of ZnO. (According to (JCPDS NO.20-0781). An XRD spectrum of silver-doped zinc oxide (AZ) is the exact reproduction of the spectra of calcined zinc oxide (Zc). It suggests that doped silver atoms may be located just at the zinc oxide crystal surface rather than at lattice sites in zinc oxide. Therefore, it may not alter its crystal structure. XRD spectra of nitrogen-doped zinc oxide (NZ) showed slight strong and broad diffraction peaks. In case of silver nitrogen co-doped zinc oxide (ANZ); its XRD spectra (Figure 3) again have narrow and sharp diffraction peaks. The difference in the XRD spectra of nitrogen-doped zinc oxide and silver-nitrogen co-doped zinc oxide may be attributed to the difference in their calcination's periods and the doping nature. The former (NZ) sample was calcined only for 4 hours whereas the later (ANZ) sample was calcined for much longer periods (8 hours). A prolonged thermal treatment in case of ANZ may induce crystallinity. The crystallite size of as-synthesized photocatalysts are: Zc (20) AZ (10.71) ANZ (10.16 nm) NZ (11.44 nm). Lower size of ANZ than Zc and AZ may be due to longer time of calcinations in case of ANZ. The size of ZnO nano is calculated.

By using Scherrer's formula,

$$D = 0.9\,ג\,/B\cos\theta$$

Where,
K= constant (0.9)

ג= Radiation of wavelength
β= FWHM (Full Width Half Wave Maxima)
θ= Bragg angle in degree
D= Particle Size.

Scanning Electron Microscope

SEM Micrograph Analysis:

Plates 3-6 show the micrograph images of the prepared Photocatalyst. The surface morphology of ZnO, photocatalyst has been studied using High Resolution Scanning Electron Micro graphs. The SEM investigations revealed that the synthesized particles were of nanometer size in all of the samples.

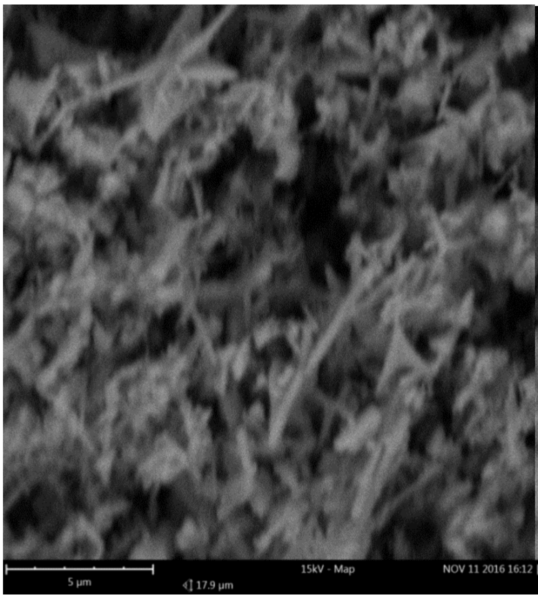

Plate 3: SEM Silver doped Zinc oxide

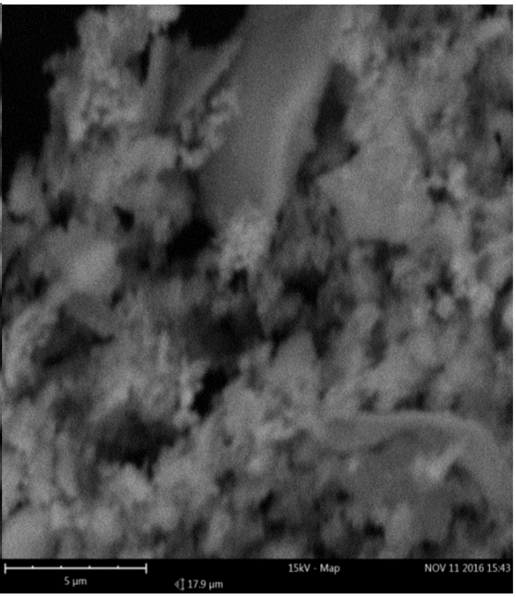

Plate 4: SEM Nitrogen doped Zinc oxide

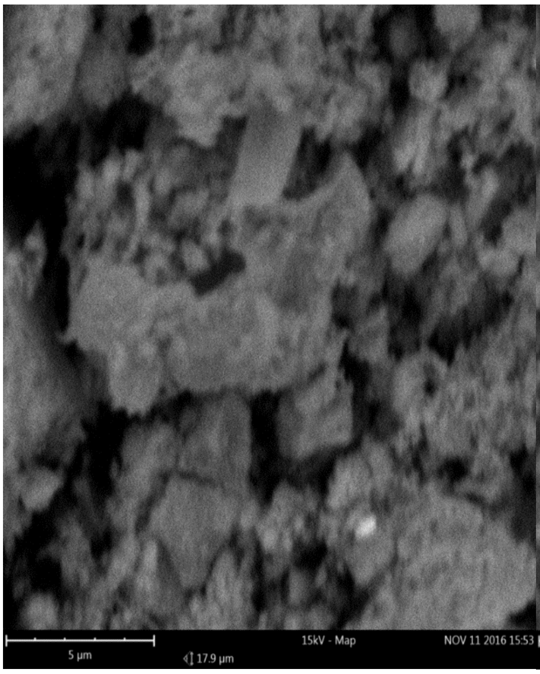

Plate 5: SEM Silver Nitrogen doped Zinc oxide

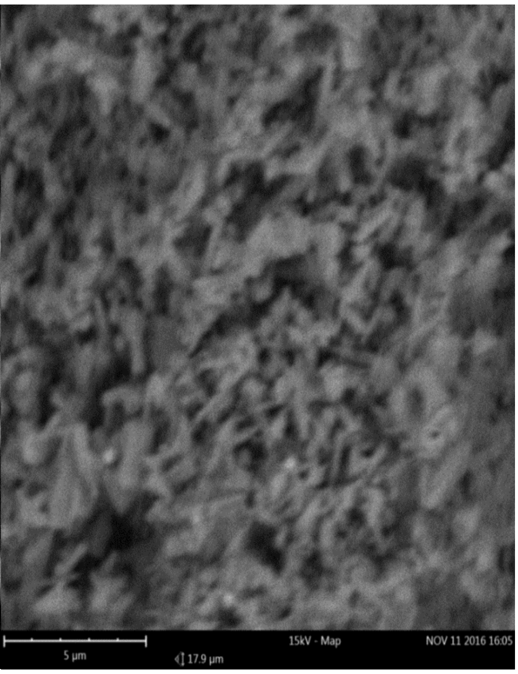

Plate 6: SEM Zinc Oxide

ZnO image indicates that the highly dispersed nano materials have been obtained with an average diameter of 50 nm. The nitrogen doped ZnO exhibits hexagonal shaped nanoparticles and are highly aggregated such agglomeration makes it difficult to evaluate the grain size from SEM images and average diameter was calculated as 40 nm. In the case of AZ and ANZ, shows that the hexagonal shaped nano materials grew in high density. The average diameter of the grown nanomaterials was about 45 and 50nm

Photocatalytic Degradation Study

The percentage adsorption of Gentian Violet without irradiation using the adsorbents: Zc, AZ, NZ, and ANZ at 120 minutes were 7.1%, 7.2%, 10.5%, and 13.2%, The percentage of photo-degradation of GV under solar and UV irradiations using these photocatalysts, Zc, AZ, NZ, and ANZ at 120 minutes were 69.2%, 71.1%, 89.4%, and 91.6, then for UV, 71.5%, 76.5%, 91.2%, and 94.5%.

The photocatalytic activity of Zc is lowest among studied photocatalysts under both UV and solar irradiations. This may be due to its small specific surface area or amorphous nature. Photocatalytic activity of AZ is higher than Zc both under solar as well as UV irradiations. It may be because doping of a noble metal, such as silver, in a semiconductor which can entrap the photo-generated electron thereby diminishing the recombination of electron-hole pairs, and thus resulting in higher photocatalytic activity of AZ. It is worthwhile to compare the photocatalytic activity of NZ and Zc under both solar as well as UV irradiations. Nitrogen doped (NZ) zinc oxide shows more photocatalytic activity than Zc. This may be due to narrowing of band gap energy on doping nitrogen to zinc oxide. It is also possible to compare the photocatalytic activity of AZ and NZ under both solar as well as UV irradiations. It is observed that under solar irradiations the percentage degradation of Gentian Violet is higher for NZ than AZ. Under UV irradiations the percentage degradation of GV solution is higher for AZ than NZ. Nonmetals such as nitrogen incorporated in the crystal of zinc oxide, may modify the electronic levels of zinc oxide resulting in its band gap narrowing, thus, rendering it more responsive to sunlight (Zheng & Wu, 2009; Li & Haneda, 2004). In case of AZ under UV irradiations, since silver can trap the photo-generated electron the recombination of electron hole pair is inhibited and thus enhancing its photocatalytic activity (Zhang & Mu, 2007). However, in case of NZ, under UV irradiations although there is equal probability of formation of electron-hole pairs since there is no other species which can trap the photogenerated electrons and hence there is lower photoactivity of NZ than AZ.

The effect of ZnO photocatalyst dosage was studied. Four different amount of photocatalyst was tried, which are 0.1, 0.2, 0.3 and 0.4 g. According to the result, increase of photocatalyst amount from 0.1 g to 0.3 g will lead to an increase in percentage removal. The increase of percentage degradation by increasing photocatalyst loading is because the presence of more ready availability surface area, causing the number of active site increase and therefore enhance the photodegradation rate (Chen *et al.*, 2007).

Nevertheless, it was observed that the percentage removal of Gentian Violet decreased when 0.4 g of photocatalyst was applied in the experiment. This may be due to excessive of photocatalyst leads to agglomeration and sedimentation of ZnO nanoparticles. In other words, 0.4 g of photocatalyst may be considered too much in this experiment set up. However, above the optimum concentration, the excess catalyst can inhibit illumination of the sample due to catalyst agglomeration, which effectively reduces the available surface area. Consequently, the degradation rate will decrease. The other possible cause of the reduced photocatalytic degradation rate is absorption of scattered light by the excess of catalyst, which then could increase the optical density in the active site of the catalyst. (Kapinus, 2010)

For Comparison Studies, Table 1-3 illustrated the effect of dosage on the photocatalytic degradation of gentian violet under UV, Solar and No irradiation.

Table 1: Comparison Table of Photocatalyst Dosage from 0.1-0.4 at 120min under UV irradiation

Photocatalyst Dosage	**ZC (%)**	**NZ (%)**	**AZ (%)**	**ANZ (%)**
0.1	38.1	58.3	62.1	67.2
0.2	56.2	63.2	77.3	90.2
0.3	71.5	76.1	91.2	94.5
0.4	66.4	72.4	87.2	90.1

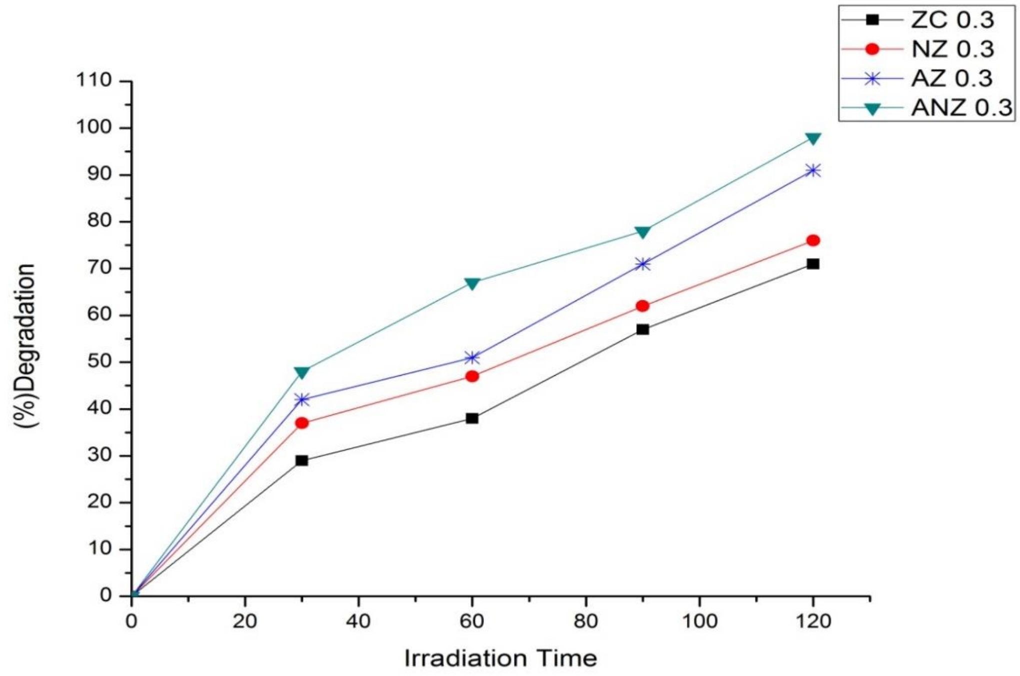

Fig. 3: Plots of Percentage Degradation of Gentian Violet as Function Of time Under UV Irradiation

Table 2: Comparison Table of Photo catalyst Dosage from 0.1-0.4 at 120min under Solar irradiation

Photocatalyst	**ZC (%)**	**AZ (%)**	**NZ (%)**	**ANZ (%)**
0.1	39.2	53.2	55.1	60.1
0.2	52.3	55.1	73.2	79.3
0.3	69.2	71.1	89.4	91.6
0.4	59.1	78.3	81.1	87.3

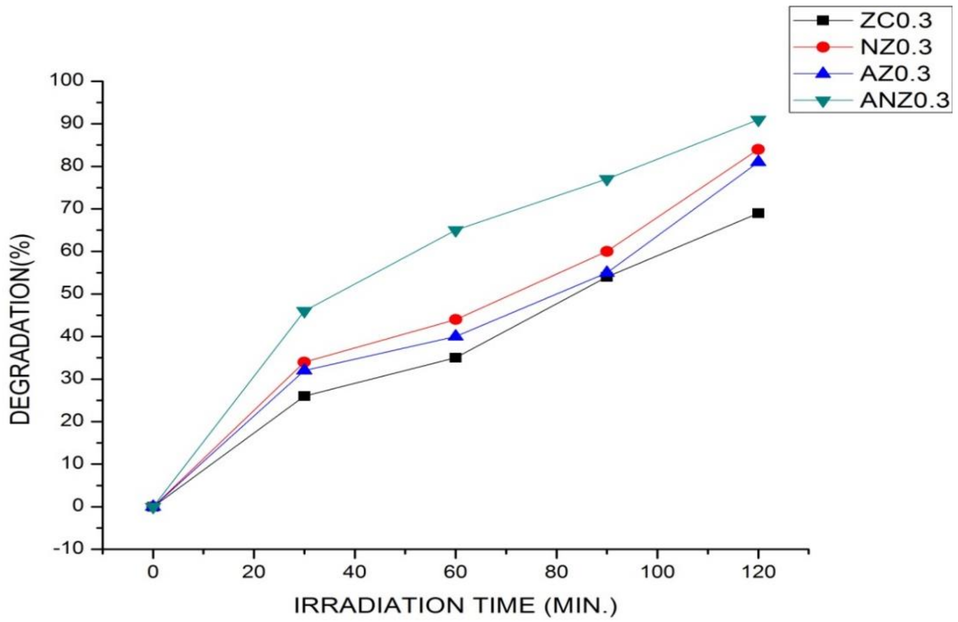

Fig. 4: Plots of Percentage Degradation of Gentian Violet as Function Of time Under Solar Irradiation

Table 3: Comparison Table of Photo catalyst Dosage from 0.1-0.4 at 120min under No Irradiation.

Photocatalyst Dosage	**ZC (%)**	**NZ (%)**	**AZ (%)**	**ANZ (%)**
0.1	5.1	6.3	9.2	12.0
0.2	6.3	7.1	9.3	12.1
0.3	7.1	7.2	10.5	13.2
0.4	6.5	6.2	9.4	12.1

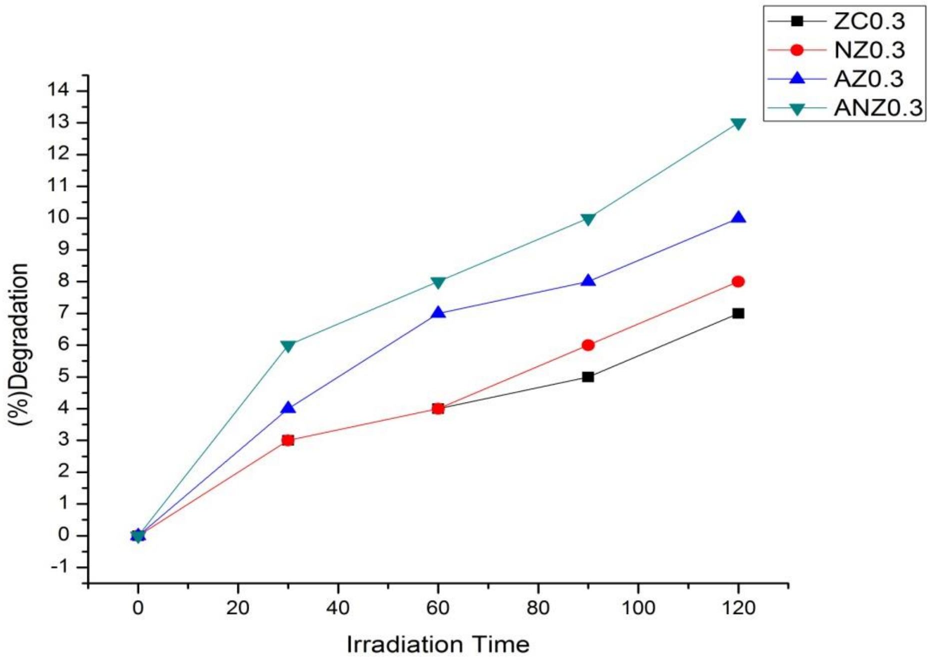

Fig. 5: Percentage Degradation of Gentian Violet as Function Of time Under No Irradiation.

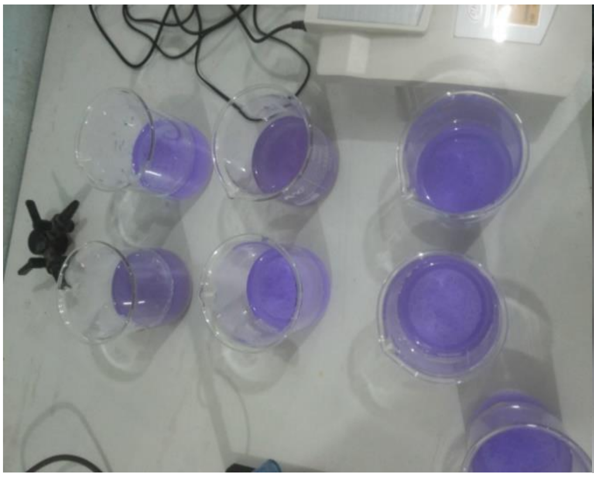

Plate 7: Gentian violet before irradiation

Plate 8: Gentian violet after irradiation

CONCLUSION

From the studies, it can be concluded that ZnO-assisted photocatalytic dye degradation proved to be significantly improved process over catalytic Reactions carried out in the dark, UV and Solar irradiation. On the basis of the results obtained from this preliminary study, the experimental methodology for subsequent studies has been established. The preparation of nanoparticles for Photocatalytic dye degradation was carried out using the "*one step liquid impregnatrion method.* For determining the crystallite size of the as-synthesized photocatalysts, X-ray diffraction (XRD) was used while SEM was used for determining average particle size of as-synthesized photocatalyst.

Result, shows that ANZ exhibited the highest degradation efficient than ZC, AZ and NZ both under UV and solar irradiation, while under solar irradiation NZ exhibited the highest degradation efficient than ZC and AZ. This implies that doping silver and nitrogen into zinc oxide modifies the electronic properties of zinc oxide, narrows its band-gap energy, extending its optical absorption to the visible light region. It enables N-doped ZnO to harvest more photons of solar radiations; thus, improving the photocatalytic activity of the semiconductor. Silver doped zinc oxide showed an enhanced photocatalytic activity for the degradation of Gentian Violet by facilitating electron-hole pair separation. Ag-N co-doping in zinc oxide had synergetic effect in enhancing its photo-catalytic activity. The optimum photocatalyst loading was determined at 3.0g.

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