

# Photocatalytic degradation of Congo red using doped zinc oxide nanoparticles

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## Abstract

The photocatalytic degradation of Congo Red (CR) was studied using zinc oxide (ZnO) nanoparticles as catalyst (ZC, NZ, AZ and ANZ) under UV light, solar and dark. ZnO nanoparticles were synthesized by one-step liquid impregnation and each nanoparticles was calcined at 60 °C for 4 hours. The UV-vis spectra study assured that the band gap decreased as N and Ag doped to ZnO and hence the absorption band shifts toward the longer wavelength region (red shift). The morphological structures of as-synthesized nanomaterials were investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM). The parameters studied were catalyst dosage and the pH of the reaction mixture. The degradation of the dye was found to be effective in the range; catalyst dose of 0.10, 0.20, 0.30 and 0.4 g ZnO catalyst/100 mL of dye solution, initial concentration 10 mg/L, and pH 8.11. Experimentation on different catalyst dosage of ZnO nanoparticles showed that 0.2 g ZnO catalyst/100 mL with the percentage degradation (ZC 70%, ANZ 99.7%, AZ 92.5%, NZ 85.8%) is the most suitable catalyst dosage for degrading CR under UV irradiation at 120 min of irradiation time. Photocatalytic processes were found to work better in basic condition and the best pH value was 8.0. The results showed that a percentage Congo Red degradation of 99.7% could be obtained when treating an effluent with 10 mg/L of Congo Red for 120 mins at 0.2 g ZnO catalyst/100 mL of effluent and pH 8 under UV irradiation using nitrogen doped silver co-doped zinc oxide, ANZ) both under solar and UV than (NZ) and silver- nitrogen doped zinc oxide (A), this was attributed to the lower rate of recombination of the photo-generated electrons and holes as well as its lower gap energy..

## Keywords

*Dyes, Textile Wastewater Treatment, Zinc Oxide Nanoparticles, Photocatalytic Degradation, Congo Red.*

## Introduction

Dyes play an important role in various industries. The main sources of dyes are from industrial processes such as textile, leather, cosmetic, paper, food processing, distillation, fabric, plastic, ink, electroplating, agriculture research and pharmaceuticals that involved the use of dyes (Lam *et al.*, 2012; Suresh *et al.*, 2014; Zangeneh *et al.*, 2015). Dyes are usually hard to be decomposed in

water due to their composite molecular structures which ensures their stability against light and resist biodegradation (Sivakumar *et al.*, 2011). Water pollution has been a serious threat to the environment. The major sources of pollutants are from manufacturing, processing industries, particularly chemical and textile industries in which organic dyes are widely used. Contaminated wastewater may be treated with conven-

tionnal physicochemical methods like reverse osmosis, ion exchange, chemical precipitation or lime coagulation, and oxidation; the application of these techniques has been restricted due to high energy consumptions or expensive synthetic resins and chemicals. In addition, most organic dye compounds ordinarily contain benzene and naphthalene rings; they cannot be decomposed easily by conventional, biological and chemical methods (Amogne, 2013). There are many physical methods available for textile wastewater treatment. One of the classes of such methods is the membrane processes and they are being increasingly used in the dye removal process for the recovery of valuable compounds from the wastewater and the recycling of the water (Riera-Torres *et al.*, 2010). However, the processes have flaws. One of the major problems is the decline of flux with time due to membrane fouling (Riera-Torres *et al.*, 2010; Verma *et al.*, 2012, LamLek, 2016). The biological treatment technique is regarded as one of the most common and widespread methods used in dye effluent treatment. The limitation associated with biological treatment in treating organics is that the azo compound is xenobiotic which makes it resistance against biodegradation. It has already been reported that dyes were resistant to biodegradation in conventional activated sludge treatment units. Furthermore, the process took a long time and the operating temperature range was narrow (Verma *et al.*, 2012). Chemical methods of treating organic compounds involve the use of either pre-treatment, post-treatment, or even as a main treatment process. However, this method has flaws such as low efficiency with respect to soluble dyes as well as the generation of large amount of sludge due to the flocculation of reagents and dye molecules (Riera-Torres *et al.*, 2010; Verma *et al.*, 2012). Effluents from textile industries are major contributors to water pollution. Dyes have become the focus of environmental issue because they are usually hard to degrade in water due to their composite molecular structures which makes them stable against light and resist biodegradation. The contamination of coloured wastewater even at low concentrations can give toxic effects to human and animals, as well as reducing the light penetration in contaminated water. Congo red dye is a highly water-soluble diazo dye. It exists as brownish-red crystal. It is an anionic acid dye used as a laboratory aid in testing for free hydrochloric acid in gastric contents, in the diagnosis of amyloidosis, as an indicator of pH, and also as a histological stain for amyloid. It has a strong affinity to cellulose fibers and thus is employed in textile

industries. It is a derivative of benzidine and naphthoic acid and metabolizes to carcinogenic products (Attallah *et al.*, 2013). It is investigated as a mutagen and reproductive effectors. It is a skin, eye, and gastrointestinal irritant. It may affect blood factors such as clotting, and induce somnolence and respiratory problems. Congo red (CR) dye is difficult to biodegrade due to its complex aromatic structures, which provide them physicochemical, thermal and optical stability. Therefore, the effective removal of dyes from aqueous systems becomes environmentally important. To date, a number of chemical, physical, and biological methods have been developed for removing dyes from wastewater. However, these methods are inefficient and expensive. There is the need to develop new techniques for wastewater treatment that are inexpensive and ensures complete elimination of pollutants. On the other hand, the photocatalytic degradation method can potentially mineralize the dye completely. Furthermore, it has lower requirements compared to the other processes as the photocatalysis can be activated under sunlight and no extreme conditions are required. With the limitations of the other methods, photocatalysis being inexpensive could be a good alternative to eliminating dye pollutants. Among the semiconductors, ZnO was considered as one of the most popular catalysts because of its high activity, good photo, environmentally friendly, non-toxic, and water insolubility. Even though the ZnO is widely used as a catalyst, it has limitations such as wide band energy (3.32 eV) which makes it to absorb light only from UV, unstable, faster photo recombination nature (Sahoo *et al.*, 2020). These limitations led to the modification of ZnO by doping it with a metal (silver) and a non-metal (nitrogen) in this study.

## **Materials and methods**

### **Materials preparation**

UV visible spectrophotometer, oven, muffle furnace, ceramic crucible, agate mortar, pH meter, centrifuge, volumetric flasks, cylinder, desiccators, magnetic stirrer, UV light.

### **Chemicals used**

Zinc oxide, urea, silver nitrate, sodium hydroxide, Congo red dye which was obtained in solid state, were all purchased from chemistry lab Owerri Imo state. All materials were used as sourced without further purification.

### **Method of synthesizing photocatalyst**

Photocatalyst were synthesized following existing Zinc

procedure by Mirkhani *et al.*, (2009).

#### Preparation of zinc oxide nanoparticles

Pure oxide (60 g) was placed in ceramic crucible and was calcined in a muffle furnace for 4 hours at 600 °C, cooled to room temperature, ground in agate mortar and labeled as calcined zinc oxide (ZC).

#### Preparation of nitrogen-doped zinc oxide

Urea (80 g) was added to a ceramic crucible containing 40 g of uncalcined zinc oxide the mixture was agitated using a glass rod until a uniform mixture is achieved. It was then placed to calcined for 4 hours at 600 °C in the furnace, cooled at room temperature, grinded in agate mortar and labeled as NZ.

#### Preparation of Silver-Doped Zinc Oxide

Silver nitrate (20 mL) was added to 20 g of uncalcined zinc oxide. The mixture was agitated and dried in the oven for 30 min at 120 °C. The mixture was cooled to room temperature, calcined at 600 °C for 4 hours and then ground in an agate mortar. The powder obtained was labeled as AZ.



Plate 1. Preparation Silver-Doped Zinc Oxide

#### Preparation of Silver-Nitrogen Co-Doped Zinc Oxide

Silver nitrate (20 mL) was transferred into ceramic crucible containing 20 g of NZ, and was agitated with glass rod. The crucible was placed in an oven for drying at 120 °C for 30 min. The dried mixture was calcined at 600 °C for 4 hours, cooled to room temperature and was ground in an agate mortar. The obtained product was labeled as silver-nitrogen co-doped zinc oxide (ANZ).

#### Characterization of Photocatalyst

**UV-visible Absorbance Spectra.** To determine the



Plate 2. Preparation of silver-nitrogen co-doped zinc oxide

absorption edge of the synthesized photocatalysts (NZ, AZ, ANZ, and ZC), the UV-Visible absorption spectra were obtained using LASANY UV/Visible spectrophotometer (Labtech-722). The photocatalyst (0.01 g) was dissolved in 10 mL of deionized water. The UV-Visible spectrometer was turned on and the deionized water was used as blank. Then the absorbance of the photocatalyst solution was measured in a quartz cuvette.

#### X-Ray Diffraction

For determining the particle size and type of oxides of the as-synthesized samples, X-ray diffraction (XRD) experiments were carried out using an Shimadzu XRD (model 6000) with a Cu target  $K\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ). The measurements were made at room temperature.

#### Scanning Electron Microscope (SEM)

SEM image of the ZnO particles were synthesized by impregnation method at 600 °C.

#### Photocatalytic Degradation Experiment

Photodegradation was carried out using the procedures described by Xu *et al.*, (2011). Photocatalytic activities of the as-synthesized photocatalysts were studied for degradation of Congo red dye (CR). The experiments were carried out under dark, solar light and ultraviolet illumination using as-synthesized photocatalysts. 0.1-0.4 g weighed amount of the as synthesized photocatalyst powder was placed in a reactor containing 100 mL of aqueous solution of CR dye (10 mg/L). The resulting mixture was agitated for specific time interval using shaker to obtain adsorption/desorption equilibrium before irradiating the dye in the reactor. The UV lamp (Fozhao light)

that predominantly emits at 294 nm with the definite power 15 W, 220 V and 60 Hz frequency was employed as UV source. The distance between the top of the reactor and light source was 10 cm. 10 mL of the suspension was withdrawn at 30 minutes interval. The suspension was centrifuged at 3000 rpm for 5 minutes and filtered with Whatman 0.45 μm Millipore filter paper to remove the catalyst particles before measuring the absorbance using UV spectra. The absorbance of CR dye solution was determined at wavelength of 490 nm and the percentage degradation of CR was calculated using the relation in equation [1]:

$$\% \text{ degradation} = [(A_0 - A_t) / A_0] \times 100 \quad [1]$$

where  $A_0$  is absorbance of the dye at initial stage and  $A_t$  is absorbance of the dye at time “t”. All experiments were performed in triplicate and the average values obtained.

**Result and discussion**

Zinc oxide (ZnO), Ag doped ZnO and N-doped ZnO were synthesized using a liquid impregnation method. Photocatalyst characterization was done using X-ray diffraction (XRD), scanning electron microscopy (SEM) and after that, studies on the performance of ZnO photocatalysts for congo red dye degradation was carried out under UV light, under sunlight and the in dark.

**Characterization of Nanoparticles**

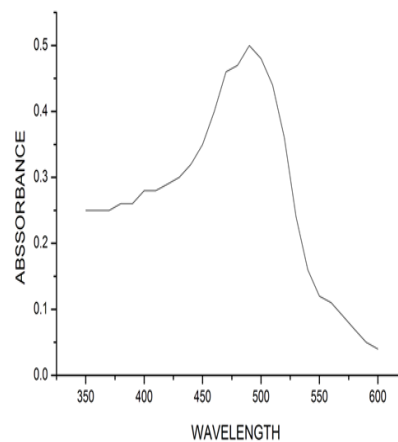
**UV-Vis diffuse absorption maxima.** UV absorption measurements were carried out to determine the absorption spectra of the prepared catalyst This

show the absorption spectra of ZC, AZ, NZ and ANZ and their corresponding absorption parameters (landmarks). 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. Band gap energy,  $E_b$ , of the as-synthesized photocatalysts was obtained using equation [2]:

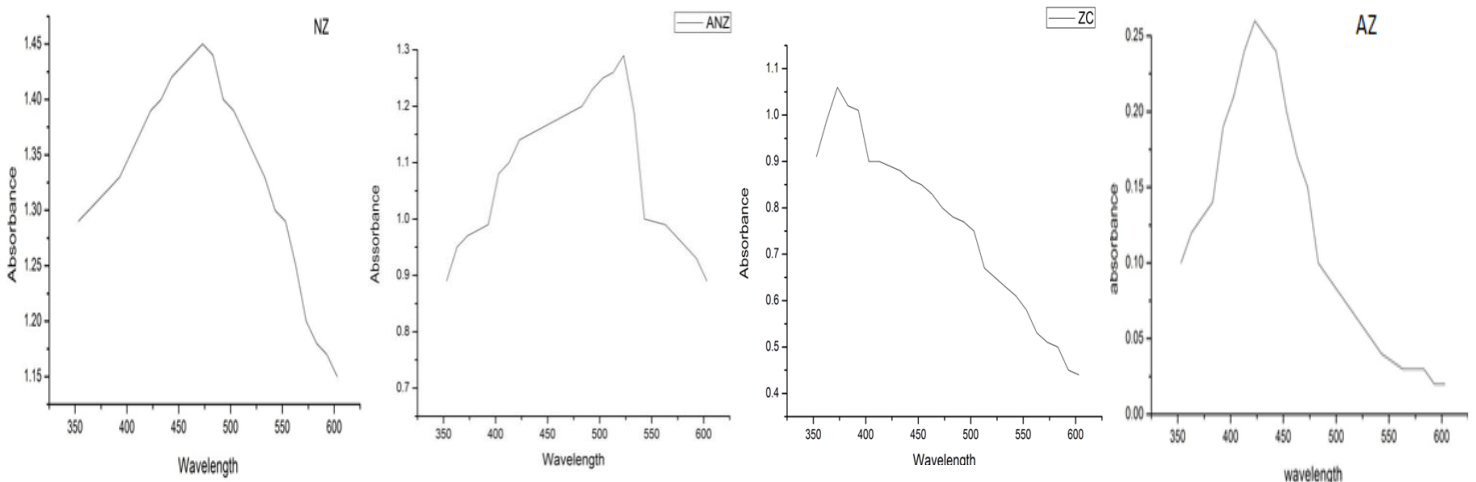
$$E_b = 1240 / \lambda \quad [2]$$

where,  $E_b$  is band gap energy (eV) and  $\lambda$  is wavelength (nm) corresponding to absorption maxima. The  $E_b$  of photocatalysts ZC, AZ, NZ and ANZ were found as 3.32, 2.93, 2.62 and 2.37, respectively..

The absorption spectra of AZ, NZ and ANZ photocatalyst were extended to the visible region than the calcined zinc. This is due to silver and nitrogen doping of ZnO photocatalyst in other to modify the electron levels of ZnO.



**Figure 1.** UV-Visible absorption spectra of Congo red dye solution



**Figure 2.** UV-Visible absorption spectra of Nitrogen doped zinc oxide (NZ), nitrogen doped-silver co-doped zinc oxide (ANZ), zinc oxide (ZC) and silver doped zinc oxide (AZ).



**Table 1.** UV-Vis absorption spectra of ZC, AZ, NZ, ANZ

Samples	Absorbance	Maximum Wavelength (nm)	Band gap (eV)
ZC	1.06	373	3.32
AZ	1.26	423	2.93
NZ	1.45	473	2.62
ANZ	1.04	523	2.37

The landmark values increased in the order  $ZC < AZ < NZ < ANZ$  with the values for NZ and ANZ extending well into the visible region. Also, the  $E_b$  decreased in the order  $ZC > AZ > NZ > ANZ$ .

### X-Ray Diffraction measurement

The XRD characterization was performed to show the crystalline structure of the ZnO photocatalysts as well as to obtain an estimate of the grain size distribution. The X-ray diffraction pattern of the photocatalysts ZC, AZ, NZ, ANZ are shown. The peaks at  $2\theta$  values of  $24.09^\circ$ ,  $24.39^\circ$ ,  $27.64^\circ$ ,  $27.76^\circ$ ,  $64.31^\circ$ ,  $37^\circ$ ,  $35.44^\circ$ ,  $49.27^\circ$ ,  $49.46^\circ$ ,  $52.26^\circ$ ,  $59^\circ$  and  $38^\circ$  observed in the XRD spectra of ANZ are indicative of the typical hexagonal wurtzite structure of ZnO. An XRD spectrum of silver-doped zinc oxide (AZ) is the exact reproduction of the spectra of calcined zinc oxide (ZC). This similarity suggest 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 have narrow and sharp diffraction peaks. The difference in the XRD spectra of nitrogen-doped zinc oxide may be attributed to the difference in their calcination periods and the doping nature. The former (NZ) sample was calcined for only 4 hrs 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 size of ZnO nanoparticles is calculated by using the Scherrer's formula as stated in equation [3]:

$$D = 0.9\lambda / \beta \cos\theta \quad [3]$$

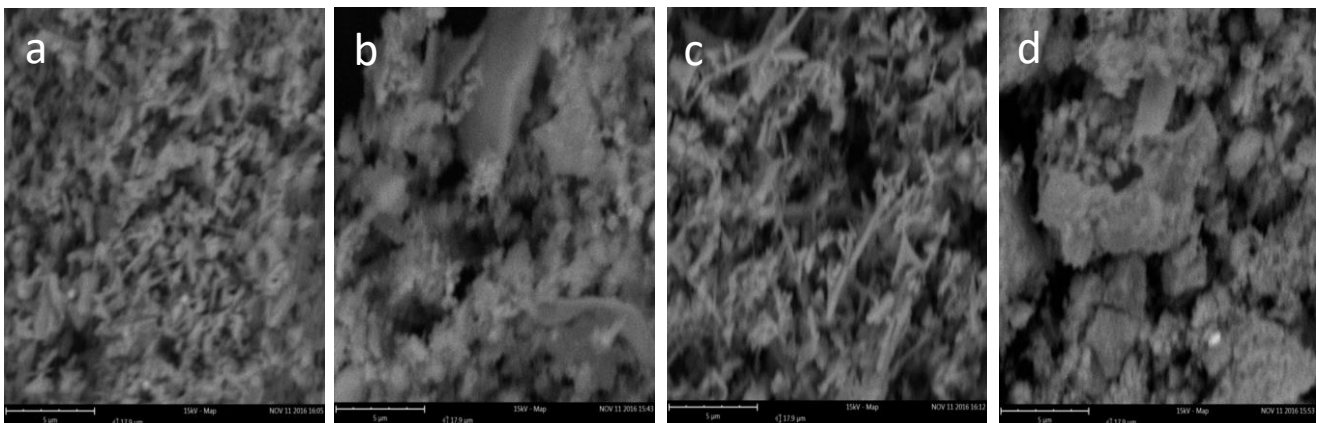
where  $K = \text{constant (0.9)}$ ,  $\lambda = \text{Radiation wavelength}$ ,  $HM$  (Full width to half wave maximum),  $\theta = \text{Bragg angle (in degree)}$  and  $D = \text{Particle}$ .

**Table 2.** Parameters derived from XRD Plots

Nano particles	2Theta ( $^\circ$ )	Beta value (nm)	Diameter (nm)
ZC	25.4362	0.20800	20.0
NZ	47.5644	0.13530	11.4
AZ	47.5726	1.90987	10.16
ANZ	49.2781	1.84764	10.71

### Scanning Electron Microscopy

SEM imaging was carried out to show the surface morphology of ZnO photocatalyst. The SEM investigations revealed that the synthesized particles were of nanometer size in all of the samples, in agreement with the XRD results. ZnO image indicates that the highly dispersed nano materials while the nitrogen doped ZnO exhibits hexagonal shaped nanoparticles and are highly aggregated. Such



**Figure 3.** SEM images of (a) Calcined Zinc Oxide (b) Nitrogen Doped Zinc Oxide (c) Silver Doped Zinc Oxide (d) Silver-Nitrogen Doped Zinc Oxide.

agglomeration makes it difficult to evaluate the grain size from SEM images. In the case of AZ and ANZ, the hexagonal shaped nano materials grew in high density

**Photodegradation results**

The photocatalytic degradation of Congo red dye was evaluated in the presence of the as- prepared photocatalysts (ZC, ANZ, AZ, and NZ) under UV irradiations, solar irradiation and in the dark. The characteristic peak of Congo red dye ( $\lambda = 490 \text{ nm}$ ) was taken as a standard for absorbance measurements for evaluation of photocatalytic activity.

**Effects of operating parameters**

**Effects of catalyst dosage.** The highest percentage degradation of Congo red shown in Figure 5 was achieved at 0.2 g (ZC 70%, ANZ 99.7%, AZ 92.5%, NZ 85.8%) of photocatalyst under UV irradiation at 120 min and pH 8. While under solar radiation and also the absence of irradiation at 0.2 g, the percentage degradations were found to be 40%, 84.3%, 76.1%, 65.7% and 19.2%, 9.3%, 9.5%, 11.4% for ZC, ANZ, NZ, AZ, respectively. Table 4 gives a summary of the percentage degradation of each catalyst ranging from 0.1 - 0.4 g.

The effect of catalyst loading on the degradation of Congo red can be explained as the amount of catalyst increased, from 0.1-0.2 g, more catalyst active sites and higher adsorption area were available for the generation of active radicals to degrade the dye (Ahmed *et al.*, 2010). Further increase in catalyst loading from 0.2-0.4 g led to the decrease in photo degradation. This could be due to light scattering effect and increase in the particle aggregation (LamLek, 2016). Arabpour and Nezamzadeh-Ejehieh (2015) reported that the excess of catalyst led to an increase in the turbidity of the suspension and consequently increased the light scattering effect. Thus, the light penetration decreased which resulted in lower degradation efficiency.

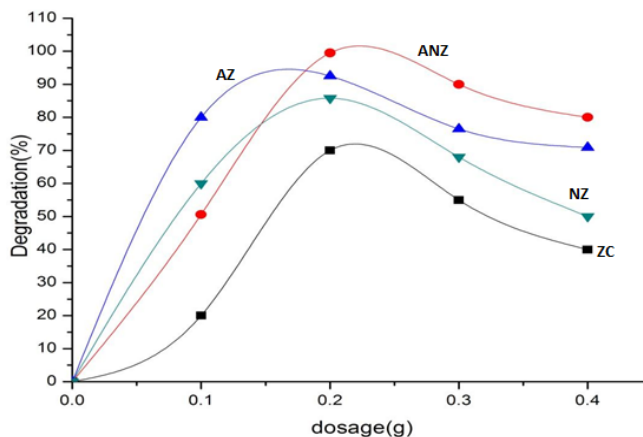


Figure 4. Plot of percentage degradation versus dosage of Congo red under UV

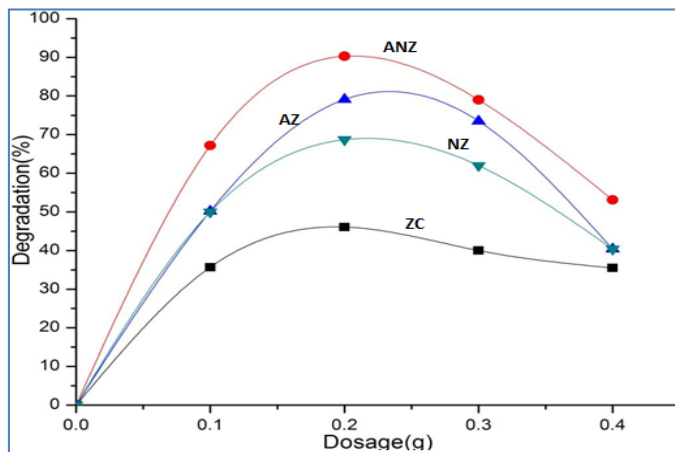


Figure 5. Percentage degradation versus dosage of Congo red under solar

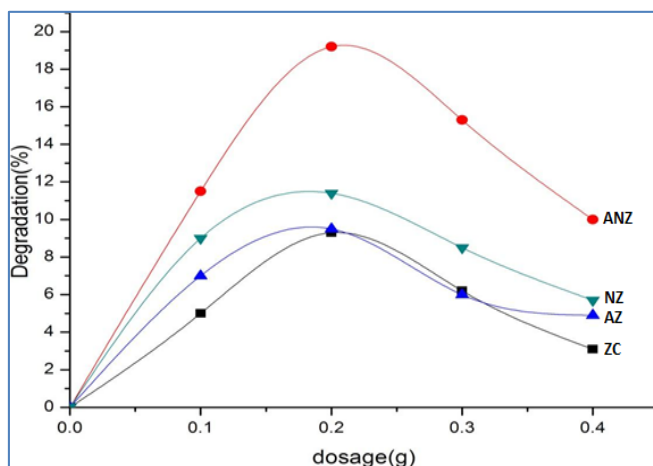


Figure 6 Percentage degradation versus dosage of Congo red in dark

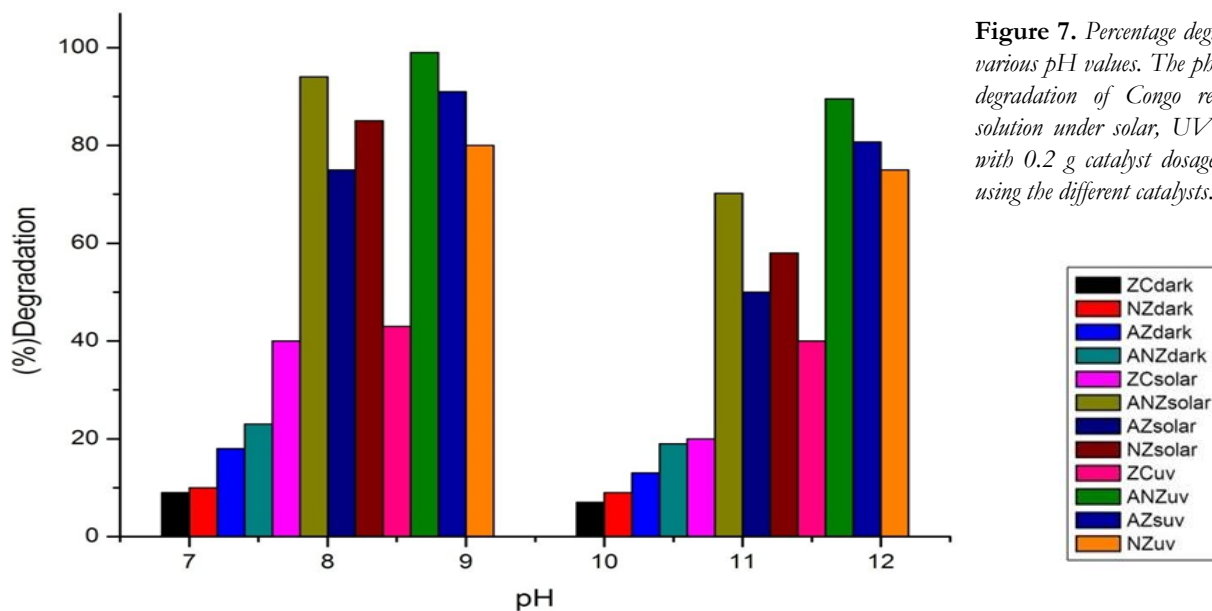
Nanoparticles	Time (min)	Dosage	% Degradation (UV)	% Degradation (solar)	% Degradation (dark)
ZC	120	0.1	35.2	45.3	7.5
ANZ			80	80.2	11.5
NZ			55.3	69	8
AZ			60.5	60	9
ZC	120	0.2	70	40	19.2
ANZ			99.5	84	9.3
NZ			85.8	76.1	9.5
AZ			92.5	65.7	11.4
ZC	120	0.3	45.2	25.1	7.5
ANZ			90	70.5	15.5
NZ			68.3	45.5	8
AZ			70.5	40.2	11.1
ZC	120	0.4	40	30.1	7
ANZ			85	65.3	13.5
NZ			45	45.7	9
AZ			65	35.9	11

**Table 3.** Summary of Catalyst dosage and percentage degradation of each nanoparticles from 0.1, 0.2, 0.3 and 0.4 g at 120 minutes irradiation time

**Effect of pH**

The initial pH of Congo red was varied by using 0.1 M NaOH solutions (to obtain pH of 8 and 11). The initial pH of Congo red in distilled water without using pH adjustors was 8. All the experiments were carried out with initial Congo red concentration of 10 mg/L. From the result, the photocatalytic experiment at pH 8 exhibited the highest percentage degradation and complete degradation was achieved after 120 min of irradiation. Slightly lower degradation efficiency was observed at pH 11(90.3 %) at 0.2 g catalyst loading. The degradation efficiency was related to the properties of the dye molecules and

catalyst. On the other hand, the degradation efficiency decreased as the pH was increased from 8 to 11 as depicted in Figure 7. From Figure 11, the zinc oxide under UV irradiation shows more photocatalytic activity than ZC under solar and in dark. This observation may be due to illumination effect. It was also observed from Figures 10 and 11 that under solar irradiations, the percentage degradation of CR is higher for NZ than AZ while the reverse is the case under UV irradiations. This observation could be attributed to nonmetals such as nitrogen incorporated in zinc oxide which modifies the electronic levels of zinc oxide resulting in its



**Figure 7.** Percentage degradation at various pH values. The photocatalytic degradation of Congo red aqueous solution under solar, UV and dark with 0.2 g catalyst dosage at pH 8 using the different catalysts.

band gap narrowing, thus, rendering it more responsive to sunlight (Zheng *et al.*, 2009). While AZ under UV irradiations can trap the photo-generated electrons, the recombination of electron hole pair is inhibited and thus enhancing its photocatalytic activity (Zhang *et al.*, 2007). However, in the 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 (Tesfay, 2012). The photocatalytic activity of ANZ is highest among all the studied photocatalysts under both solar as well as UV irradiations. This result may be due to the synergetic cumulative effect of silver and nitrogen co-doping that enhances the photocatalytic activity.

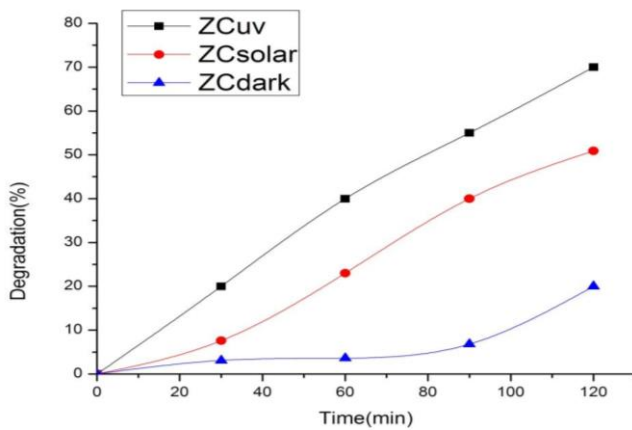


Figure 8. Comparative plot of ZC under solar, UV and dark at various irradiation times

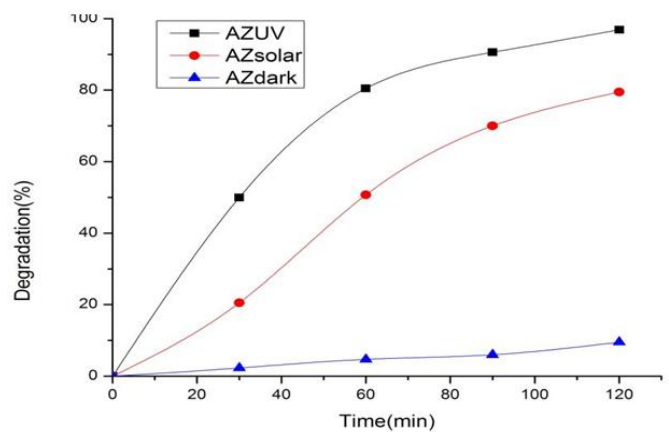


Figure 10. Comparative plot of AZ under solar, UV and dark at various irradiation time

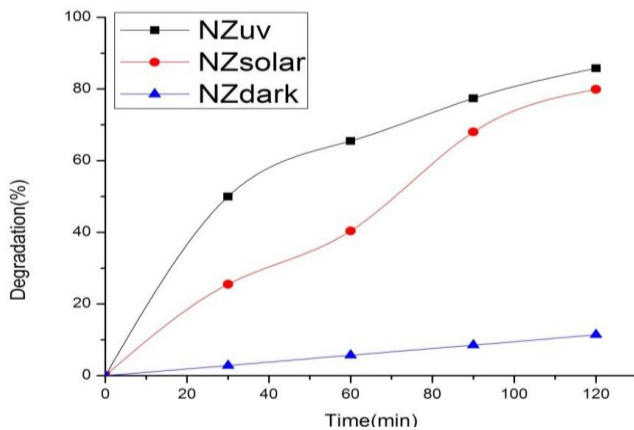


Figure 9. Comparative plot of NZ under Solar, UV and dark at different irradiation times

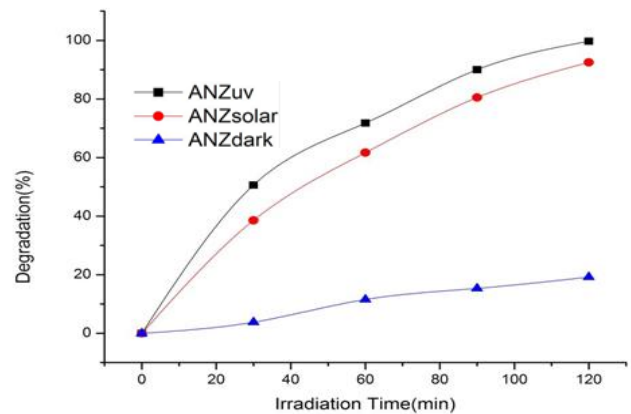


Figure 11. Comparative plot of ANZ under solar, UV and dark at various irradiation times

### Conclusions

An efficient method for synthesis of Zinc oxide, Nitrogen doped and Ag doped ZnO using one step liquid impregnation approach has been established. The characterization of the photocatalyst was also established using Scanning Electron Microscopy

(SEM), X-Ray Diffraction (XRD) and UV-Visible Spectrophotometer. The photocatalytic results for Congo red degradation show that the ANZ exhibited the highest photodegradation efficiency among the catalysts studied (ZC, NZ, ANZ and AZ) under UV irradiation.



The implication of this result is that doping of zinc oxide with silver and nitrogen enhanced the photodegradation efficiency of ANZ by trapping electron holes and thus by reducing electron-hole recombination and by shifting or modifying the band gap of zinc oxide. The operating parameters studied shows that the optimum ZnO concentration and pH of the reaction were 0.2 g/L and 8.0, respectively. Therefore, it could be concluded that the hazardous dye such as CR can be effectively degraded by using thermally heated ZnO photocatalyst under UV and solar light irradiation.

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